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Oxidation of Polycyclic, Aromatic Hydrocarbons

A Review of the Literature

U.S. DEPARTMENT OF COMMERCE

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R. Stuart Tipson

Institute of Materials Research
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Oxidation of Polycyclic, Aromatic Hydrocarbons[1]

A Review of the Literature

R. Stuart Tipson

A survey has been made of the literature on the oxidation of polycyclic, aromatic hydrocarbons. Information has been assembled on (1) the oxidants effective in the oxidation of such hydrocarbons, (2) the relative reactivity of the hydrocarbons, (3) the conditions under which oxidation proceeds, (4) the chemical mechanisms involved when such oxidations occur, and (5) the products formed.

1. Introduction

Pyrolysis or incomplete combustion of carbon-containing materials at high temperatures gives rise to polycyclic, aromatic compounds. Consequently, many compounds of this nature have been detected as pollutants in the air of large cities, particularly where dispersal is retarded.

Such air pollutants include many polycyclic, aromatic hydrocarbons and certain of their oxidation products. The majority of the hydrocarbons of this kind that have thus far been found in polluted air are listed in table 1, in the order of increasing size of the molecule, together with the corresponding Ring Index number (RRI No.) [1].[2] Some of these hydrocarbons are carcinogenic to animals (see table 1) and, possibly, to man. Eleven carcinogenic hydrocarbons have thus far been detected in automobile exhaust fumes; five are also present in practically all airborne particles (such as dust and soot) [2].

From particulate matter, obtained from polluted air, quinones of such hydrocarbons as pyrene (5262),[3] benzo[*a*]pyrene (6399), and dibenzo[*def,mno*]chrysene (7033), as well as other oxidized organic compounds (largely unidentified as yet), have been isolated and identified [3].

This suggests that, after release of reactive hydrocarbons into the atmosphere, some oxidation may normally occur in the air. Indeed, thirty years ago, it was discovered [4] that, on exposure to air containing ozone, the carcinogenic benzo[*a*]pyrene (6399) is transformed into less carcinogenic or noncarcinogenic material. Such oxidation is to be expected, as polluted air contains a number of oxidants: the nitrogen oxides, oxygen, and ozone of unpolluted air, together with such compounds as sulfur dioxide, produced by combustion.

The oxidation of polycyclic, aromatic hydrocarbons is also of interest because, in evolving ways for reducing air pollution, attention is currently being given to the development of chemical devices for oxidizing atmospheric pollutants produced by incomplete combustion and pyrolysis in automobile and Diesel exhaust fumes.

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[1] This Monograph was prepared as part of a study of the oxidation of polycyclic, aromatic hydrocarbons being conducted in the Organic Chemistry Section under the direction of Horace S. Isbell and the author. The work was partly supported by the Division of Air Pollution, Public Health Service, U.S. Department of Health, Education, and Welfare.

[2] Figures in brackets indicate the literature references at the end of this Monograph. The references for tables are given at the end of the respective tables.

[3] The number in parentheses, following the name of a hydrocarbon, is the RRI No. for that hydrocarbon, as given in [1]. This number is definitive; it is used because of the multiplicity of names often found in the literature for the same hydrocarbon, but may be omitted when the structure is depicted.

TABLE 1. *Some polycyclic, aromatic hydrocarbons found in polluted air, automobile exhaust, and Diesel exhaust*

RRI No.	Hydrocarbon	Source[a]	References
1754	Naphthalene	A	1
1754[b]	2-methyl-	A	1
3127	Fluorene	A	1,2
3133	Acenaphthylene	A	1
3133[b]	Acenaphthene	A	1
3618	Anthracene	A	1,2
3619	Phenanthrene	A	1,2
4773	11*H*-Benzo[*b*]fluorene	A	2
4778	11*H*-Benzo[*a*]fluorene	A	2
4780	7*H*-Benzo[*c*]fluorene	A	2
4799	Fluoranthene	A	1
5253	Benz[*a*]anthracene[c]	A,B,C	1,3
5254	Chrysene[c]	A,B,C	1,3,4
5262	Pyrene	A,C,D	1,4
5262[b]	1-methyl-	A	1
5262[b]	2,7-dimethyl-	A	1
6070	Benz[*e*]acephenanthrylene[c]	A,C,D	3,5,6
6075	Benzo[*k*]fluoranthene	A,C,D	5,6
6078	Benzo[*j*]fluoranthene[c]	C	3
6092	Benzo[*ghi*]fluoranthene	A	5
6383	Dibenz[*a*,*h*]anthracene[c]	C	3
6399	Benzo[*a*]pyrene[c]	A,B,C,D	1,3,4,7
6400	Benzo[*e*]pyrene[c]	A,B,C	1,3,4
6401	Perylene	A	1
9508	Indeno[1,2,3-*cd*]pyrene[c]	C	3
7001	Dibenzo[*a*,*l*]naphthacene	A,C,D	1,6
7026	Naphtho[1,2,3,4-*def*]chrysene[c]	C	3
7030	Dibenzo[*def*,*p*]chrysene[c]	C	3
7033	Dibenzo[*def*,*mno*]chrysene	A,C,D	1,7,8
7036	Benzo[*ghi*]perylene[c]	A,B,C,D	1–5,8
7392	Coronene	A	1,2,5

[a] Key: A, air; B, practically all airborne, particulate samples; C, automobile exhaust; D, Diesel exhaust.

[b] Derivative.

[c] Reported to be carcinogenic to experimental animals.

References for table 1

1. E. Kennaway and A. J. Lindsey, Brit. Med. Bull. 14, 124 (1958).
2. E. Sawicki, T. R. Hauser, W. C. Elbert, F. T. Fox, and J. E. Meeker, Am. Ind. Hyg. Assoc. J. 23, 137 (1962).
3. E. Sawicki, Chemist-Analyst 53 (No. 1), 24 (1964).
4. P. Kotin, H. L. Falk, P. Mader, and M. Thomas, A.M.A. Arch. Ind. Hyg. Occ. Med. 9, 153 (1954).
5. P. Kotin and H. L. Falk, Cancer 12, 147 (Jan.-Feb. 1959).
6. T. W. Stanley, Chemist-Analyst 49, 47 (June 1960).
7. P. Kotin, H. L. Falk, and M. Thomas, A.M.A. Arch. Ind. Hyg. Occ. Med. 9, 164 (1954).
8. P. Kotin, H. L. Falk, and M. Thomas, A.M.A. Arch. Ind. Health 11, 113 (1955).

In considering the fate of these hydrocarbons and methods for minimizing their effects as air pollutants, it thus became of interest to assemble all of the available information on (1) the oxidants effective in the oxidation of polycyclic, aromatic hydrocarbons, (2) the relative reactivity of the hydrocarbons, (3) the conditions under which oxidation proceeds, (4) the chemical mechanisms involved when such oxidations occur, and (5) the products formed. The present Monograph is a review of the oxidation of selected representatives of the group of polycyclic, aromatic hydrocarbons *by oxidant systems containing oxygen.* All of the principal methods which have been investigated will be discussed, but the treatment is not intended to be exhaustive. Biological oxidation will not be considered.

2. Oxidants for Polycyclic, Aromatic Hydrocarbons

The action of many different oxidants on a variety of polycyclic, aromatic hydrocarbons has been rather perfunctorily studied during the past hundred years, and the results are widely scattered through the literature. In only a few instances have systematic investigations been undertaken.

Listed alphabetically in tables 2 and 3 are those oxidants whose action on such hydrocarbons has been the most systematically examined; the effect of each of these six oxidants on eight different hydrocarbons is summarized in table 3. Oxidants that have received less attention in this field are listed alphabetically in table 4.

For only one oxidant studied to date, namely osmium tetroxide–pyridine, has the action of the oxidant (both as regards positions of attack and kind of product) been found to be invariant (see table 3), regardless of the structure of the hydrocarbon oxidized. In all other instances, the kind of oxidation effected by any one oxidant depends on the character of the hydrocarbon being oxidized. Furthermore, for some oxidants, the oxidizing action of the oxidant depends on the conditions under which the oxidation is performed. Consequently, references are provided in tables 2 and 4 to the sections of this article wherein the particular oxidizing action is described.

Table 2. *Principal oxidants for polycyclic, aromatic hydrocarbons*

	Oxidant	Action described in sections
1	Benzoyl peroxide	8.2.1; 9.1.1
2	Chromium trioxide (or sodium dichromate)	8.1.1; 9.1.2; 9.2.2.(1); 9.2.3.(1); 10.1
3	Hydrogen peroxide plus osmium tetroxide	8.2.2; 9.1.3; 9.2.1.(1); 9.2.3.(2)
4	Osmium tetroxide plus pyridine (and hydrolysis)	9.2.1.(2)
5	Ozone (with subsequent treatment)	8.1.5; 9.1.13; 9.2.2.(5)
6	Peroxyacetic acid	9.1.8; 9.2.2.(3); 9.2.3.(5)

3. Kinds of Oxidation of Polycyclic, Aromatic Hydrocarbons

As may be seen from table 3, the kind of oxidation caused by an oxidant acting on any one hydrocarbon embraces two features: (a) the class of product, and (b) the positions of attack.

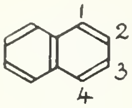
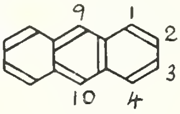
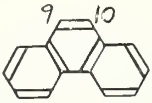
3.1. Classes of Products

The various kinds of oxidation product are discussed in detail in sections 8 to 10. As may be seen from table 3, those often encountered include acyloxy derivatives, diols, or *o*- or *p*-diones. Other possible products are epoxides, hydroperoxides, and peroxides. If a bond is ruptured, the product may be a dialdehyde, an aldehydic acid, or a dicarboxylic acid.

3.2. Positions of Attack

In some instances, *one-center attack* (resulting in substitution) may occur, as in the oxidation of benzo[*a*]pyrene with benzoyl peroxide (see table 3) to give a benzoyloxy derivative. A similar effect is caused by lead tetraacetate (see pp. 27 and 29), although two-center addition followed by elimination may be involved. One-center attack is also encountered in hydrogen abstraction at a reactive center by an oxidant, to give a free radical, followed, for example, by combination of two such radicals to afford a dimer.

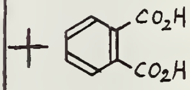
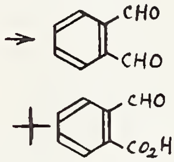
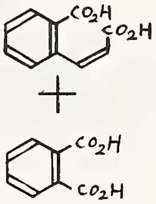
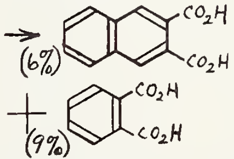
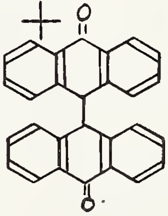
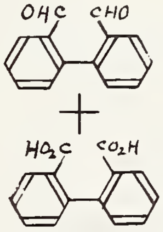
TABLE 3. *Products from the oxidation of some polycyclic, aromatic hydrocarbons*

RRI No.	Hydrocarbon	Oxidants			
		$(C_6H_5CO)_2O_2$	References	CrO_3	References
1754	 Naphthalene	1-ol benzoate + 2-ol benzoate + 1-phenylnaphthalene + 2-phenylnaphthalene + binaphthyls (1,1'-,1,2'-, and 2,2'-)	1,2	(<u>para</u>) 1,4-dione	3
3618	 Anthracene	9-ol benzoate + (<u>para</u>) 9,10-dione	14	(<u>para</u>) 9,10-dione	15
3619	 Phenanthrene	"No reaction"	14	(<u>ortho</u>) 9,10-dione + diphenic acid	20

References for table 3

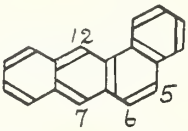
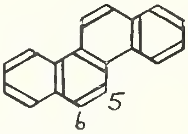
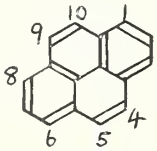
1. A. Perret and R. Perrot, Helv. Chim. Acta 28, 558 (1945).
2. D. I. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc. 1958, 1878.
3. C. E. Groves, J. Chem. Soc. 26, 209 (1873). N. H. J. Miller, J. Russ, Phys. Chem. Soc. 16, 414 (1884). F. R. Japp and N. H. J. Miller, J. Chem. Soc. 39, 220 (1881). E. A. Braude and J. S. Fawcett, Org. Syntheses 33, 50 (1953).
4. N. A. Milas, U. S. Pat. 2,395,638 (1946).
5. J. W. Cook and R. Schoental, J. Chem. Soc. 1950, 47.
6. J. W. Cook and R. Schoental, J. Chem. Soc. 1948, 170; Nature 161, 237 (1948).

and oxidation products

H_2O_2—OsO_4	References	OsO_4—C_5H_5N	References	O_3	References	CH_3CO-OOH	References
1-ol + (p) 1,4-dione (o) + 1,2-dione 	4,5	Reacts	6	(o) attacks C1-C2 	7	(p) 1,4-dione + (o) 	8-13
(p) 9,10-dione	4,5	(o) 1,2,3,4-tetra-hydro-1,2,3,4-tetrol	6	(p) attacks C-9 and C-10 → 9,10-dione (62%) (o) attacks C1-C2 	16-18	(p) 9,10-dione 	8, 9, 11, 19, 19a
9-ol + (o) 9,10-dihydro-9,10-diol + 9,10-dione + diphenic acid	5	(o) 9,10-dihydro-9,10-diol	21	(o) attacks C9-C10  + diphenic acid	17,18, 22,23	(o) 9,10-dione + diphenic acid	8, 9, 11, 24

7. C. Harris and V. Weiss, Ann. 343, 369 (1905). L.Seekles, Chem. Weekblad 20, 261 (1923); Rec. Trav. Chim. 42, 706 (1923). L. W. F. Kampschmidt and J. P. Wibaut, Rec. Trav. Chim. 73, 431 (1954). P. S. Bailey and F. J. Garcia-Sharp, J. Org. Chem. 22, 1008 (1957). P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, J. Org. Chem. 29, 697 (1964). C. D. Johnson and P. S. Bailey, J. Org. Chem. 29, 703 (1964).
8. G. G. Henderson and R. Boyd, J. Chem. Soc. 97, 1659 (1910).
9. G. Charrier and A. Moggi, Gazz. Chim. Ital. 57, 736 (1927).
10. J. Böeseken and G. Slooff, Rec. Trav. Chim. 49, 100 (1930).
11. R. T. Arnold and R. Larson, J. Org. Chem. 5, 250 (1940).
12. E. Ibuki, J. Chem. Soc. Japan, Pure Chem. Sect. 70, 286 (1949).
13. Y. Odaira, S. Takigawa, and S. Tsutsumi, Kogyo Kagaku Zasshi 62, 89 (1959).
14. I. M. Roitt and W. A. Waters, J. Chem. Soc. 1952, 2695.

Table 3. *Products from the oxidation of some polycyclic, aromatic hydrocarbons*—Cont.

RRI No.	Hydrocarbon	Oxidants			
		$(C_6H_5CO)_2O_2$	References	CrO_3	References
5253	 Benz[a]anthracene	7-ol benzoate	14	(p) 7,12-dione	25
5254	 Chrysene	"No reaction"	14	(o) 5,6-dione	28
5262	 Pyrene			1,6-dione (1/3) + 1,8-dione (2/3)	29,30

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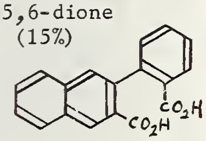
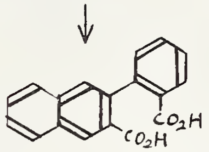
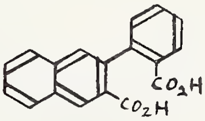
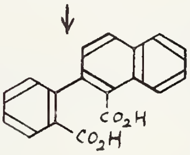
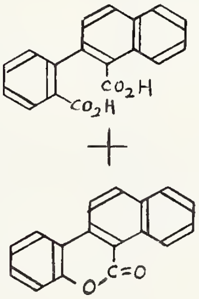
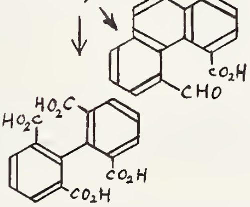
15. J. Fritzsche, J. Prakt. Chem. [1] 106, 274 (1869). C. Graebe and C. Liebermann, Ann. (Suppl.) 7, 257 (1870). W. H. Beisler and L. W. Jones, J. Am. Chem. Soc. 44, 2296 (1922).
16. Heinemann, British Pat. 5514 (1915). I. M. Roitt and W. A. Waters, J. Chem. Soc. 1949, 3060. P. S. Bailey and J. B. Ashton, J. Org. Chem. 22, 98 (1957). P. S. Bailey, Chem. Ind. (London) 1957, 1148. P. G. Copeland, R. E. Dean, and D. McNeil, J. Chem. Soc. 1961, 3858. F. Dobinson and P. S. Bailey, Chem. Ind. (London) 1961, 632.
17. P. G. Copeland, R. E. Dean, and D. McNeil, Chem. Ind. (London), 1959, 329.
18. P. G. Copeland, R. E. Dean, and D. McNeil, Chem. Ind. (London), 1960, 98.
19. G. Charrier and G. B. Crippa, Gazz. Chim. Ital. 57, 741 (1927).
19a. A. R. Leeds, Ber. 14, 1382 (1881).

and oxidation products

H_2O_2—OsO_4	References	OsO_4—C_5H_5N	References	O_3	References	CH_3CO-OOH	References
(p) 7,12-dione (20%) (o) + 5,6-dihydro-5,6-diol + 5,6-dione (15%) + 	5	(o) 5,6-dihydro-5,6-diol	6,26	(o) attacks C5-C6 	17, 18, 22, 27	(p) 7,12-dione + (o) 	11, 22
(o) 5,6-dione	5	(o) 5,6-dihydro-5,6-diol	6	(o) attacks C5-C6 	17, 22	(o) 	22
(in *tert*-BuOH) 1,6-dione + 1,8-dione (o) (in Me$_2$CO) 4,5-dione	5 31	(o) 4,5-dihydro-4,5-diol	6	(o) attacks C4-C5 (and C9-C10) 	18, 30, 32	1,6-dione + 1,8-dione	11

20. R. Fittig and E. Ostermayer, Ann. 166, 361 (1873). C. Graebe, Ann. 167, 131 (1873). R. Anschuetz and G. Schultz, Ann. 196, 32 (1879). L. Oyster and H. Adkins, J. Am. Chem. Soc. 43, 208 (1921). F. Bischoff and H. Adkins, J. Am. Chem. Soc. 45, 1030 (1923). H. W. Underwood, Jr., and E. L. Kochmann, J. Am. Chem. Soc. 46, 2069 (1924). F. J. Moore and E. H. Huntress, J. Am. Chem. Soc. 49, 1324 (1927).
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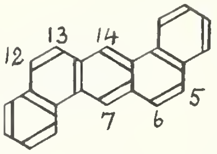
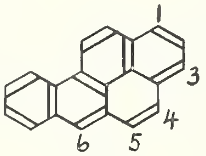
TABLE 3. *Products from the oxidation of some polycyclic, aromatic hydrocarbons*—Cont.

RRI No.	Hydrocarbon	Oxidants $(C_6H_5CO)_2O_2$	References	CrO$_3$	References
6383	 Dibenz[*a*,*h*]-anthracene	(1) Oxygen present (*p*) 7,14-dione (2) Oxygen absent no reaction	14	(*p*) 7,14-dione (major) + (*o*) 5,6-dione (minor)	33
6399	 Benzo[*a*]pyrene	6-ol benzoate	14	1,6-dione + 3,6-dione	30,36

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24. W. F. O'Connor and E. J. Moriconi, J. Am. Chem. Soc. 73, 4044 (1951); Ind. Eng. Chem. 45, 277 (1953). W. F. O'Connor, F. T. Wallenberger, and E. J. Moriconi, Brennstoff-Chem. 38, 170 (1957). S. Havel and J. A. Weigner, Chem. Prumysl 10, 10 (1960). Ruetgerswerke A.-G., Brit. Pat. 853,369 (1960).
25. C. Graebe, Ann. 340, 249 (1905). K. Dziewonski and E. Ritt, Bull. Intern. Acad. Polonaise, 1927A, 181.
26. G. M. Badger, J. Chem. Soc. 1949, 456.
27. E. J. Moriconi, W. F. O'Connor, and F. T. Wallenberger, Chem. Ind. (London) 1959, 22; J. Am. Chem. Soc. 81, 6466 (1959).
28. C. Liebermann, Ann. 158, 299 (1871). E. Bamberger and C. Burgdorf, Ber. 23, 2433 (1890). C. Graebe and F. Hoenigsberger, Ann. 311, 257 (1900).
29. C. Graebe, Ann. 158, 285 (1871). G. Goldschmiedt, Monatsh, 4, 309 (1883). E. Bamberger and M. Philip, Ann. 240, 147 (1887).
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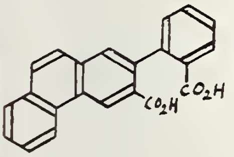
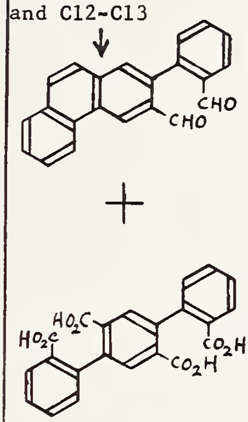
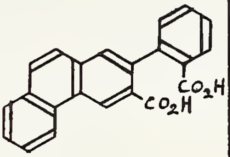
and oxidation products

H_2O_2—OsO_4	References	OsO_4—C_5H_5N	References	O_3	References	CH_3CO-OOH	References
(p) 7,14-dione + (o) 5,6-dione + (35%) 	5	(o) 5,6,12,13-tetrahydro-5,6,12,13-tetrol	6	(o) attacks C5-C6 and C12-C13 	34	(p) 7,14-dione + (o) 5,6-dione +  (60-80%)	35
1,6-dione + 3,6-dione + (o) 4,5-dione	5	(o) 4,5-dihydro-4,5-diol	6	1,6-dione (75%) + 3,6-dione (25%) (o) + 4,5-dione (trace)	37		

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31. F. G. Oberender and J. A. Dixon, J. Org. Chem. 24, 1226 (1959).
32. L. F. Fieser and F. C. Novello, J. Am. Chem. Soc. 62, 1855 (1940). M. S. Newman and H. S. Whitehouse, J. Am. Chem. Soc. 71, 3664 (1949). G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, J. Chem. Soc. 1950, 2326. C. Danheux, L. Hanoteau, R. H. Martin, and G. Van Binst, Bull. Soc. Chim. Belge 72, 289 (1963).
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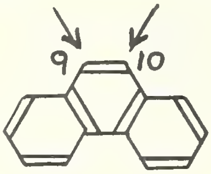
34. E. J. Moriconi, G. W. Cogswell, W. J. Schmitt, and W. F. O'Connor, Chem. Ind. (London) 1958, 1591. E. J. Moriconi, W. F. O'Connor, W. J. Schmitt, G. W. Cogswell, and B. P. Fuerer, J. Am. Chem. Soc. 82, 3441 (1960).
35. B. L. Van Duuren, I. Bekersky, and M. Lefar, J. Org. Chem. 29, 686 (1964).
36. J. W. Cook, R. S. Ludwiczak, and R. Schoental, J. Chem. Soc. 1950, 1112.
37. E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, J. Am. Chem. Soc. 83, 4618 (1961).

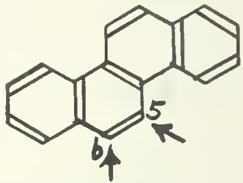
Table 4. *Some oxidants for polycyclic, aromatic hydrocarbons*

Oxidant	Action described in sections
Lead tetraacetate	8.1.2; 8.2.3; 9.1.4
Nitric acid, nitrates, nitrites	9.1.5; 9.2.2.(2); 10.2
Nitrogen oxides	9.1.6; 9.1.7
Osmium tetroxide plus sodium periodate	9.2.3.(4)
Oxygen	8.1.3; 9.1.9; 9.2.1.(3)
Oxygen plus ultraviolet light	8.1.4; 8.2.4; 9.1.10; 9.1.11
Oxygen plus vanadium pentoxide	9.1.12; 9.2.2.(4)
Oxygen plus various catalysts	9.1.12
Potassium permanganate	9.2.2.(6); 9.2.3.(6); 10.3
Ruthenium dioxide plus sodium periodate	9.2.3.(7)
Selenium dioxide	8.1.6; 9.1.14; 9.2.3.(8)
Miscellaneous oxidants	8.2.5; 9.1.15; 9.2.1.(4); 9.2.3.(3)

On the other hand, many oxidants effect *two-center attack*, either stepwise or simultaneous. For some polycyclic, aromatic hydrocarbons (for example, phenanthrene and chrysene), the *positions* of attack are invariant (see table 3), regardless of the oxidant employed. However, the *kind of product* depends on the oxidant employed. Thus, whereas osmium tetroxide–pyridine causes hydroxylation of phenanthrene to the 9,10-diol, ozone ruptures the bond at C9–C10, and chromium trioxide gives the 9,10-dione (together with some diphenic acid formed by rupture of the bond at C9–C10).



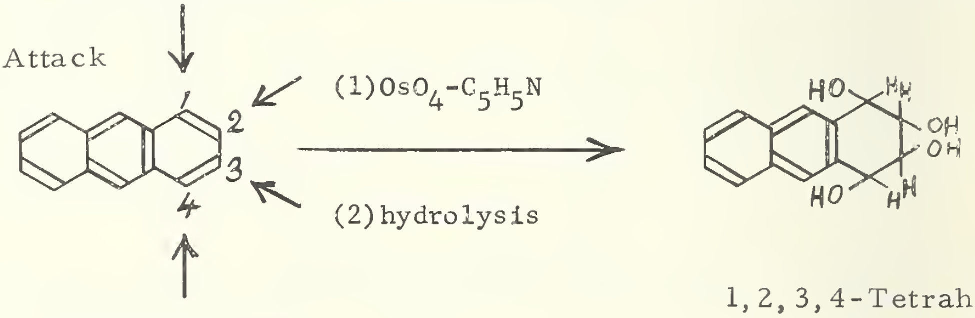
Phenanthrene (3619)



Chrysene (5254)

In other instances, the positions of attack on the *same* hydrocarbon are different for different oxidants. Thus, whereas osmium tetroxide–pyridine attacks the *ortho* positions at C1–C2 and C3–C4 of anthracene [5], chromium trioxide attacks the *para* positions at C–9 and C–10 of this hydrocarbon [6].

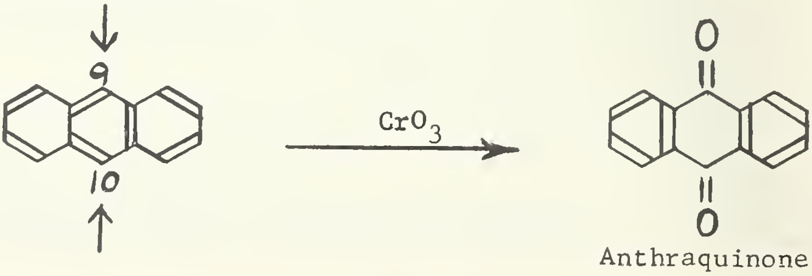
ortho Attack



Anthracene (3618)

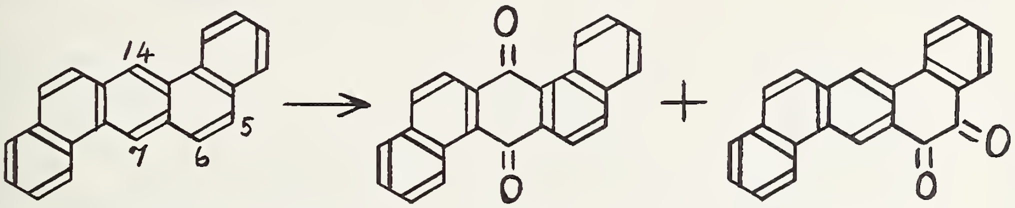
1,2,3,4-Tetrahydro-1,2,3,4-anthratetrol

para Attack



Anthraquinone

Again, in some instances, a single oxidant acting on a single hydrocarbon may simultaneously attack different molecules of that hydrocarbon either *ortho* or *para*. For example, chromic acid oxidizes dibenz[*a,h*]anthracene to a mixture containing (mainly) the *p*-dione with some *o*-dione.



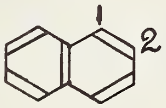
Dibenz[a,h]anthracene (6383) 7,14-Dione (major) 5,6-Dione (minor)

The two kinds of oxidation mentioned for anthracene are prototypes of the positions of attack generally encountered in two-center attack on polycyclic, aromatic hydrocarbons, namely, *ortho* and *para*. In the former (*ortho* attack), reaction occurs at a reactive bond, and leads either to formation of the *o*-diol or *o*-dione or to rupture of this bond. The latter (*para* attack) is exemplified by transannular addition and by the formation of *p*-diones. It is probable that oxidation to a *p*-dione actually involves two separate one-center attacks, the first occurring at the reactive center having the lowest localization energy. This stepwise attack may account also for the fact that such hydrocarbons as pyrene (5262) and benzo[*a*]pyrene (6399), which have no reactive *para* centers, undergo "pseudo-*para*" attack.

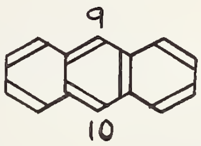
Finally, if the hydrocarbon has an alkyl side-chain, the side chain may undergo oxidative degradation; and if the hydrocarbon has one or more reactive methylene groups in one or more of the rings, these may be the sites of attack.

4. Reactive Centers

For benzene, all of the carbon atoms are equally reactive; but, in the polycyclic, aromatic hydrocarbons, some carbon atoms may be more reactive than others. Thus, experience has shown that, in naphthalene, C–1 is more reactive than C–2, and that, in anthracene, C–9 (≡ C–10) is much more reactive than the other carbon atoms present.



Naphthalene (1754)



Anthracene (3618)

Mathematical evaluations of the reactive centers of conjugated hydrocarbons, made by the valence-bond method and by the molecular-orbital method, have been summarized by the Pullmans [7]. In the following brief discussion, some predictions obtained by the molecular-orbital method are indicated.

4.1. The Most Reactive Center

For an electrophilic or nucleophilic attack, or a radical substitution, to proceed at a given carbon atom of a conjugated hydrocarbon, the electronic structure of the hydrocarbon has to be disturbed in such a way that the appropriate number of electrons become localized at the carbon atom attacked. The amount of energy needed for producing this

TABLE 5. *Localization energies of the various centers of some polycyclic, aromatic hydrocarbons*[a]

RRI No.	Carbon atom number[b]													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1754......	**1.81**	*2.12*	......	**1.81**										
3618......	*1.57*	1.89	......	......	......	......	......	......	**1.26**	**1.26**				
5252......	*1.42*	1.69	......	......	**1.13**	......	......	......	......	......	......	**1.13**		
6376......	1.32	1.54	......	......	*0.89*	**0.80**	......	......	......	......	......	......	**0.80**	
5253......	1.98	1.96	2.13	1.84	1.66	1.66	**1.35**	1.63	1.98	1.92	1.86	*1.44*		
6377......	1.93	1.89	2.07	1.80	1.53	1.58	1.13	**1.09**	1.46	1.77	1.75	1.48	*1.12*	1.20
6378......	1.68	1.92	1.99	1.64	**1.36**	1.58	......	**1.36**	......	......	......	......	*1.47*	*1.47*
6381......	2.00	2.08	2.08	2.00	......	......	......	......	**1.50**	*1.70*	......	2.00	......	**1.50**
6382......	1.95	1.99	2.13	1.85	1.71	1.70	**1.44**	......	......	......	......	......	......	*1.60*
6383......	1.97	1.97	2.16	1.83	*1.66*	1.71	**1.51**	......	......	......	......	......	......	**1.51**
3619......	*1.86*	2.18	2.04	1.96	......	......	......	......	**1.79**	**1.79**				
5254......	*1.80*	2.16	2.02	1.90	......	**1.67**	......	......	......	......	1.90			
5255......	1.86	1.85	2.10	*1.83*	**1.79**	1.86								
6384......	1.92	2.01	2.17	1.81	**1.67**	1.86	......	......	......	......	......	......	*1.78*	*1.78*
5256......	**2.02**	*2.12*	......	2.02										
5262......	**1.51**	2.31	**1.51**	*1.68*	*1.68*	**1.51**	......	**1.51**	*1.68*	*1.68*				
6399......	*1.38*	2.27	1.41	1.55	1.55	**1.15**	1.55	2.12	1.73	1.81	1.81	1.50		
6400......	*1.68*	2.25	**1.63**	1.73										
6401......	*1.44*	2.12	**1.33**	......	......	......	......	......	......	......	2.08	1.98		

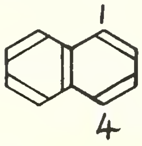
[a] Calculated, in arbitrary units, by M. J. S. Dewar, J. Am. Chem. Soc. 74, 3357 (1952).

[b] Boldface numbers indicate the most reactive centers, and italic numbers indicate the next most reactive centers.

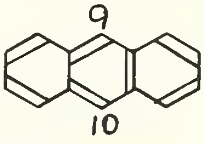
localization is called the *localization energy* of this carbon atom. Obviously, the higher its localization energy, the lower is the reactivity of the center; the lower the localization energy, the higher the reactivity.

Dewar [8] has calculated the localization energies of the various positions in the molecule for a number of alternant hydrocarbons. The results are collected in table 5, with the RRI numbers for the respective hydrocarbons; the names of the hydrocarbons are omitted from table 5, but are given in table 6.

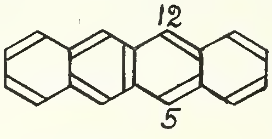
The most reactive centers, together with the *next* most reactive centers, are given in table 6, from which it may be seen that, for *the linear hydrocarbons,* the most reactive center predicted corresponds to that in naphthalene (1 ≡ 4) or anthracene (9 ≡ 10). For *angular hydrocarbons* containing an anthracene moiety in which the carbon atoms corresponding to the anthracenic C–9 and C–10 are free, these were predicted to be the reactive centers, even though a phenanthrene moiety in which the phenanthrenic C–9 and C–10 are free should be present.



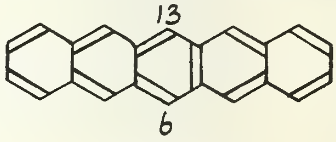
Naphthalene



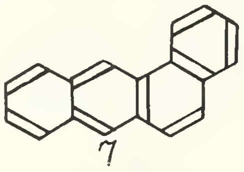
Anthracene



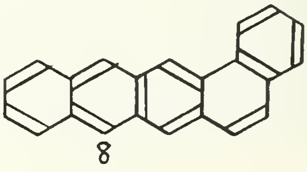
Naphthacene



Pentacene



Benz[a]anthracene



Benzo[a]naphthacene

TABLE 6. *The most reactive and next most reactive centers (predicted) for some polycyclic, aromatic hydrocarbons*[a]

RRI No.	Hydrocarbon	Most reactive center[b]	Next most reactive center
	Linear		
1754	Naphthalene	°1*(=4*=5=8)	°2(=3=6=7)
3618	Anthracene	9*(=10*)	[c]1(=4=5=8)
5252	Naphthacene	5*(=6=11=12*)	[c]1(=4=7=10)
6376	Pentacene	6*(=13*)	5(=7=12=14)
	Angular		
	(a) **Reactive anthracene moiety**		
5253	Benz[*a*]anthracene	7*	12*
6377	Benzo[*a*]naphthacene	8*	13*
6378	Pentaphene	5*(=8)	13(=14*)
6381	Dibenz[*a,c*]anthracene	9*(=14*)	[d]10(=13)
6382	Dibenz[*a,j*]anthracene	7*	14*
6383	Dibenz[*a,h*]anthracene	7*(=14*)	[e]5(=12)
	(b) **Reactive phenanthrene moiety**		
3619	Phenanthrene	°9(=°10)	[f]1(=8)
5254	Chrysene	[g]6(=12)	[f]1(=7)
5255	Benzo[*c*]phenanthrene	[e]5(=8)	[h]4(=9)
6384	Picene	[e]5(=8)	13(=14)
	Condensed ring systems		
5256	Triphenylene	°1*(=4*=5=8=9=12)	°2(=3=6=7=10=11)
5262	Pyrene	1(=3=6=8)	°4(=°5=9=10)
6399	Benzo[*a*]pyrene	6	1
6400	Benzo[*e*]pyrene	3(=6)	1(=8)
6401	Perylene	3(=4=9=10)	1(=6=7=12)

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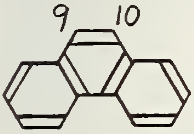
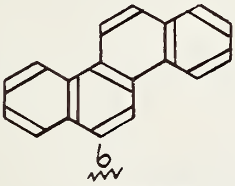
[a] From M. J. S. Dewar, J. Am. Chem. Soc. 74, 3357 (1952).
[b] The asterisks indicate a *para* pair, and the ° superscripts indicate an *ortho* pair of reactive centers.
[c] The *ortho* position is C–2.
[d] The *ortho* position is C–11.
[e] The *ortho* position is C–6.
[f] The *para* position is C–4.
[g] The *ortho* position is C–5.
[h] The *para* position is C–1.

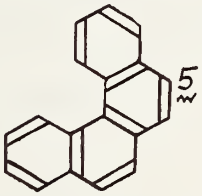
In angular hydrocarbons that contain no such anthracene moiety but which have a phenanthrene moiety in which C–9 and C–10 are not fused to another ring, it was predicted that one of *these* atoms would be the most reactive.



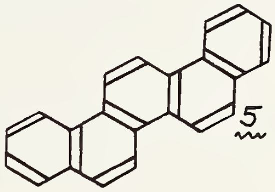
Phenanthrene



Chrysene

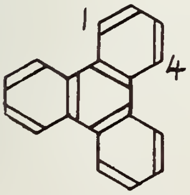


Benzo[c]phenanthrene

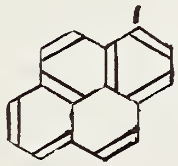


Picene

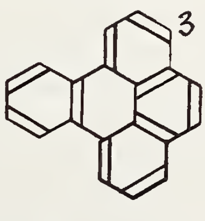
For hydrocarbons having *more-condensed ring-systems,* the most reactive position pre-



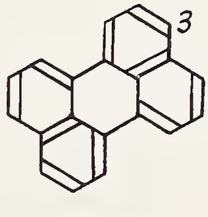
Triphenylene



Pyrene



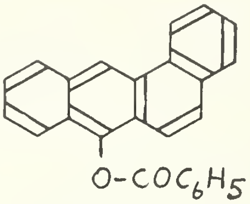
Benzo[e]pyrene



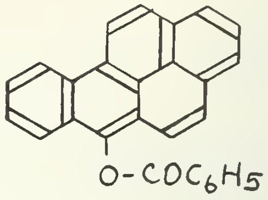
Perylene

dicted is adjacent to a point of ring fusion and may be regarded as that of a naphthalene moiety.

In practically all cases that have been studied experimentally, the positions predicted for one-center attack are those actually found. Thus, benzoyl peroxide attacks the most reactive center of benz[*a*]anthracene and benzo[*a*]pyrene:



Benz[a]anthracen-7-ol benzoate



Benzo[a]pyren-6-ol benzoate

The reactivity of the reactive center of the linear hydrocarbons progressively increases [9] ; that is, addition of each ring causes an increase in reactivity at the reactive center, in the order naphthalene$<$anthracene$<$naphthacene$<$pentacene, and, as may be seen from table 5, the localization energy of the most reactive center progressively decreases.

4.2. *para* Reactive Centers

In reactions involving two-center attack in which the two centers are *para* to each other, use is made of the *para*-localization energy, that is, the energy required for simultaneously localizing an electron at each of the two positions considered. The *para*-localization energies for the various possible positions in some alternant hydrocarbons have been calculated by Brown [10] and Dewar [8]. The *para* positions predicted to be the most reactive are listed in table 7, from which it may be seen that they are thóse to be expected from the predictions given in table 6.

For the linear hydrocarbons, the reactivity of *para* centers increases as the middle of the molecule is approached. Also, the localization energy for the most reactive pair of *para* centers decreases with increasing size of the molecule; that is, the relative reactivity increases. The reactivity of the *para* centers in nonlinear hydrocarbons is always lower than that of the corresponding linear hydrocarbons.

In all cases that have been studied, these predictions of *para* reactive centers agree with those actually found.

4.3. *ortho* Reactive Centers

Although the structural formula of a polycyclic, aromatic hydrocarbon is normally written with single and double bonds, pure single bonds and pure double bonds are actually not present in the compound. The structural formula depicts an extreme resonance form, and is not an accurate representation of the electronic configuration of the molecule; each carbon–carbon bond possesses some degree of double-bond character. Thus, in the same molecule, two "double bonds," usually depicted as alike, may differ in reactivity. Furthermore, a "double bond" situated at a superficially similar position in two different hydrocarbons may have a different reactivity in each.

In considering reactions involving two-center attack at adjacent carbon atoms, use has been made of the *ortho*-localization energy, that is, the energy required for localizing

Table 7. *The most reactive* para *positions (predicted) for some alternant hydrocarbons*

RRI No.	Hydrocarbon	Most reactive *para* positions predicted[a]
	Linear	
1754	Naphthalene	1,4[b]
3618	Anthracene	9,10[b]
5252	Naphthacene	5,12[b]
6376	Pentacene	6,13[b]
6996	Hexacene	6,15
	Angular	
	(a) **Reactive anthracene moiety**	
5253	Benz[*a*]anthracene	7,12[b]
6377	Benzo[*a*]naphthacene	8,13[b]
6378	Pentaphene	5,14[b]
6379	Benzo[*b*]chrysene	7,12
6381	Dibenz[*a*,*c*]anthracene	9,14[b]
6382	Dibenz[*a*,*j*]anthracene	7,14[b]
6383	Dibenz[*a*,*h*]anthracene	7,14[b]
	(b) **Nonreactive phenanthrene moiety**	
3619	Phenanthrene	[1,4][b, c]
5254	Chrysene	[1,4][c]
5255	Benzo[c]phenanthrene	[1,4][c]
6384	Picene	[1,4][c]
	Condensed ring systems	
5256	Triphenylene	[1,4][c]
5262	Pyrene	–
6401	Perylene	–

[a] By R. D. Brown, J. Chem. Soc. 1950, 691.
[b] By M. J. S. Dewar, J. Am. Chem. Soc. 74, 3357 (1952).
[c] Not reactive.

an electron at each of the two carbon atoms involved. This energy might thus be regarded as the energy required for converting the conjugated, aromatic bond into a pure double bond. Alternatively, it is the energy needed for localizing a pure double bond between the two carbon atoms; indeed, it is often referred to as the "bond-localization energy." The *ortho*-localization energy can be estimated from the difference between the resonance energy of the hydrocarbon and that of the residue which would be left on removal of the two *ortho* carbon atoms under consideration. The smaller the *ortho*-localization energy, the more reactive is the bond.

By application of these principles, Brown [11] has calculated the reactivities of the carbon–carbon bonds in each of a number of alternant hydrocarbons, and thence has predicted the most reactive bond in each. The results are given in table 8, together with predictions made by Dewar [8] by the molecular-orbital method, from which it may be seen that, for all of the hydrocarbons having a phenanthrene moiety whose C–9 and C–10 atoms are *not* fused to another ring, these two atoms were predicted to be the most reactive *ortho* pair. For the other hydrocarbons, a bond corresponding to the 1,2-bond of naphthalene was predicted to be the most reactive.

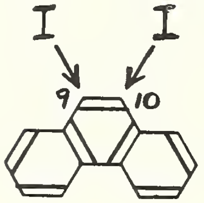
Because of the difference in the electronic configurations necessary for reactions involving (a) one-center attack and (b) two-center, *ortho* attack, the *ortho* positions listed in table 8 as the most reactive do not necessarily include the most reactive centers or even the next most reactive centers (given in table 6), although a reactive center is often one of the atoms involved with a reactive bond. Thus, if the most reactive center is indicated by I, and the next most reactive center by II, the hydrocarbons can be classified in six groups as regards the adjacent carbon atoms predicted to be those subject to *ortho* attack.

TABLE 8. *The most reactive* ortho *positions (predicted) for some alternant hydrocarbons*

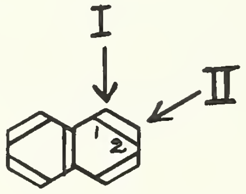
RRI No.	Hydrocarbon	Most reactive *ortho* positions predicted[b]
	Linear	
1754	Naphthalene	1,2[b]
3618	Anthracene	1,2[b]
5252	Naphthacene	1,2
6376	Pentacene	1,2
	Nonlinear	
	(a) **Naphthalene moiety**	
5256	Triphenylene	1,2[b]
6381	Dibenz[*a*,*c*]anthracene	10,11[b]
	(b) **Phenanthrene moiety**	
3619	Phenanthrene	9,10[b]
5253	Benz[*a*]anthracene	5,6[b]
5254	Chrysene	5,6[b]
5255	Benzo[*c*]phenanthrene	5,6[b]
5262	Pyrene	4,5[b]
6377	Benzo[*a*]naphthacene	5,6[b]
6378	Pentaphene	6,7[b]
6379	Benzo[*b*]chrysene	5,6
6380	Dibenzo[*b*,*g*]phenanthrene	7,8
6382	Dibenz[*a*,*j*]anthracene	5,6[b]
6383	Dibenz[*a*,*h*]anthracene	5,6[b]
6384	Picene	5,6
6385	Benzo[*g*]chrysene	9,10
6386	Benzo[*c*]chrysene	7,8
6387	Dibenzo[*c*,*g*]phenanthrene	1,2
6399	Benzo[*a*]pyrene	4,5
6400	Benzo[*e*]pyrene	4,5[b]

[a] By R. D. Brown, J. Chem. Soc. **1950**, 3249.
[b] By M. J. S. Dewar, J. Am. Chem. Soc. 74, 3357 (1952).

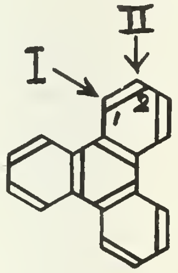
These groups are those hydrocarbons involving (1) two I, as for phenanthrene; (2) I and II, as for naphthalene and triphenylene; (3) II and II, as for pyrene; (4) I and the position *ortho* to it, as for chrysene, benzo[*c*]phenanthrene, and picene; (5) II and the position *ortho* to it (because a double bond including position I would obviously not be susceptible



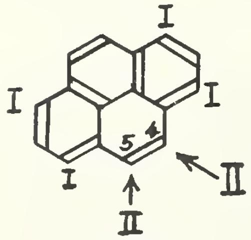
Phenanthrene



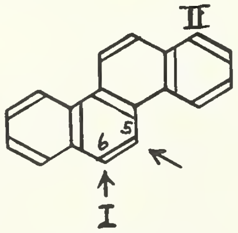
Naphthalene



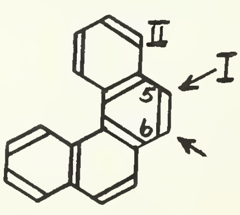
Triphenylene



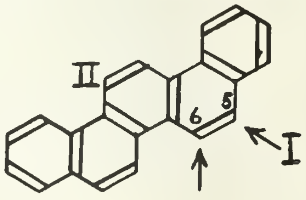
Pyrene



Chrysene

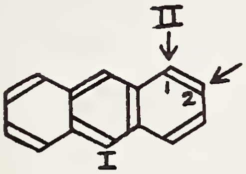


Benzo[c]phenanthrene

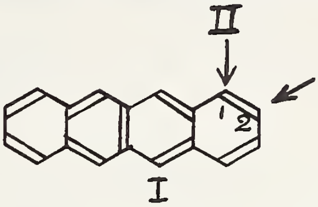


Picene

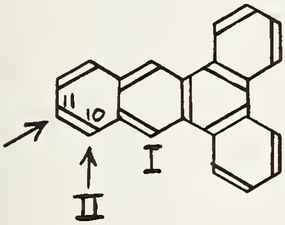
to *ortho* attack), as for anthracene, naphthacene, dibenz[*a,c*]anthracene, and dibenz[*a,h*]-



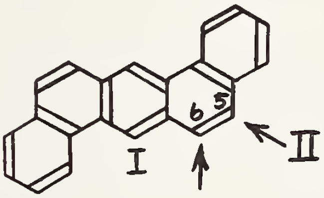
Anthracene



Naphthacene

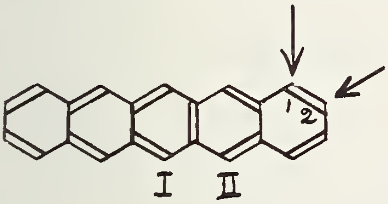


Dibenz[*a*,*c*]anthracene

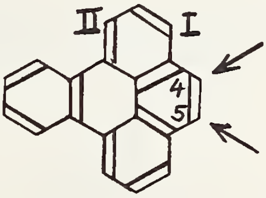


Dibenz[*a*,*h*]anthracene

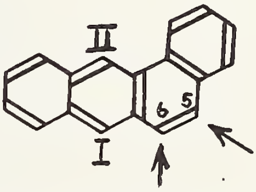
anthracene; and (6) *neither I nor II*, as for pentacene, benzo[*e*]pyrene, benz[*a*]anthracene, benzo[*a*]naphthacene, pentaphene, and dibenz[*a,j*]anthracene.



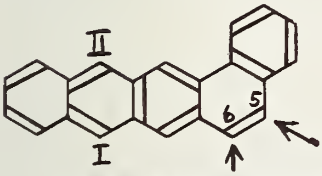
Pentacene



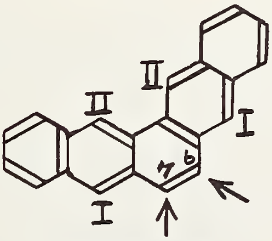
Benzo[*e*]pyrene



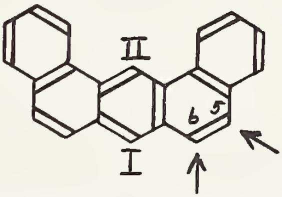
Benz[*a*]anthracene



Benzo[*a*]naphthacene



Pentaphene



Dibenz[*a*,*j*]anthracene

For all cases that have been studied, the positions predicted for *ortho* attack agree with those found experimentally.

Brown [11] also calculated the reactivity of the most reactive bond in each of these hydrocarbons, relative to that of the 9,10-bond of phenanthrene (which was arbitrarily assigned the value of unity). The results are given in table 9, the hydrocarbons being listed in order of increasing reactivity of the most reactive bond.

The most reactive bond predicted for naphthalene is at C1–C2 [12], and this has been confirmed experimentally [13,14]. However, the relative reactivity for the C1–C2 bond of

TABLE 9. *Most reactive bond (predicted) and calculated relative reactivity thereof, for some polycyclic, aromatic hydrocarbons*[a]

RRI No.	Hydrocarbon	Most reactive bond (predicted)		Relative reactivity (calcd)	
			No.	of most reactive bond	Total
5256	Triphenylene	1,2	6	1×10^{-7}	–
6381	Dibenz[*a*,*c*]anthracene	10,11	2	0.0002_5	0.0005
3618	Anthracene	1,2	4	0.001_8	0.007
5252	Naphthacene	1,2	4	0.0044	0.02
6376	Pentacene	1,2	4	0.005_5	0.02
6385	Benzo[*g*]chrysene	9,10	1	0.008_5	0.009
5254	Chrysene	5,6	2	0.04_3	0.09
6384	Picene	5,6	2	0.09	0.2
5255	Benzo[*c*]phenanthrene	5,6	2	0.10	0.2
6387	Dibenzo[*c*,*g*]phenanthrene	1,2	2	0.2	0.4
6386	Benzo[*c*]chrysene	7,8	1	0.22	0.4
6379	Benzo[*b*]chrysene	5,6	1	0.33	0.3
6380	Dibenzo[*b*,*g*]phenanthrene	7,8	1	0.72	0.8
6400	Benzo[*e*]pyrene	4,5	1	<1	<1
3619	Phenanthrene	9,10	1	**1.000**	**1**
5262	Pyrene	4,5	2	1.6	3
6383	Dibenz[*a*,*h*]anthracene	5,6	2	2.4	5
6382	Dibenz[*a*,*j*]anthracene	5,6	2	2.9	6
5253	Benz[*a*]anthracene	5,6	1	5.1	5
6377	Benzo[*a*]naphthacene	5,6	1	8.0	8
6399	Benzo[*a*]pyrene	4,5	1	12	12
6378	Pentaphene	6,7	1	18	18

[a] From R. D. Brown, J. Chem. Soc. **1950**, 3249.

TABLE 10. *Predicted,*[a] *and observed, relative rate constants*[b] *for the addition of osmium tetroxide–pyridine to some polycyclic, aromatic hydrocarbons*

RRI No.	Hydrocarbon	Relative reactivity of reactive bond	Total relative reactivity	Relative rate constant	
				Predicted	Observed
6386	Benzo[*c*]chrysene	0.22	0.4	0.06	slow
3619	Phenanthrene	1.00	1	0.2	0.1
5253	Benz[*a*]anthracene	5.1	5	1	1
6383	Dibenz[*a*,*h*]anthracene	2.4	5	1	1.3
6399	Benzo[*a*]pyrene	12	12	2	2.0

[a] R. D. Brown, J. Chem. Soc. **1950**, 3249.
[b] G. M. Badger, J. Chem. Soc. **1949**, 456; G. M. Badger and R. I. Reed, Nature **161**, 238 (1948).

naphthalene is less than for anthracene; consequently, in hydroxylation with osmium tetroxide–pyridine, a concentrated solution of this reagent was used (in order to provide forcing conditions). Because addition to the C1–C2 bond gives a derivative that has, in the nonbenzenoid ring, a double bond having a very small bond-localization energy, a second equivalent of osmium tetroxide reacts with this bond, affording a diadduct.

Similarly, addition of this reagent to the C1–C2 bond of anthracene would give a product, related to 2-vinylnaphthalene, having an exocyclic bond of very low bond-localization energy, and it was to be expected that this bond would react with a second equivalent of the reagent, affording a diadduct. This has been found experimentally [5].

For phenanthrene, the relative reactivity of the 9,10-bond is much higher than that of the 1,2-bond of naphthalene and anthracene; this greater reactivity has been confirmed experimentally [5,15,16].

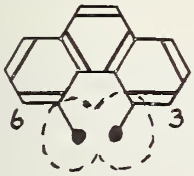
Now, the rate of reaction found experimentally corresponds to the sum of the reactivity for *all* of the bonds in the hydrocarbon. For instance, the most reactive bond occurs four times in anthracene, naphthacene, and pentacene; this number is given in column 4 of table 9. By multiplying the relative reactivity of the most reactive bond by this factor, an estimate of the *total* relative reactivity was obtained (see column 6 of table 9).

In table 10, five hydrocarbons are listed in their order of increasing (predicted) total reactivity (relative to that of phenanthrene, arbitrarily assigned a value of unity), together with the predicted rate constants (relative to benz[*a*]anthracene as unity) and those actually observed for the addition of osmium tetroxide–pyridine (in chloroform at 20° C). As may be seen from table 10, the agreement between the predicted values and those found experimentally was excellent.

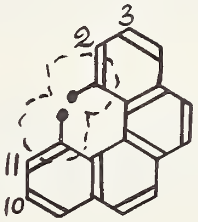
4.4. Effect of Conformation of the Hydrocarbon

Until fairly recently, it had been assumed that all polycyclic, aromatic hydrocarbons have a *planar* conformation. In some of the studies on the oxidation of such hydrocarbons, workers encountered certain supposed "anomalies" which are now explicable by taking the correct conformation of the molecule into account.

It is now known that nonbonded carbon atoms do not generally approach closer than 3.0 Å, and that normal H–H distances are 2.4 to 2.5 Å. For some polycyclic, aromatic hydrocarbons, adoption of a planar conformation would necessitate compression of nonbonded atoms to well within this forbidden range. For example, it is seen that the protons at C–4 and C–5 of phenanthrene, and those at C–1 and C–12 of benzo[*c*]phenanthrene [17], interfere with each other if the hydrocarbon has a planar conformation. This phenomenon has been referred to as "molecular overcrowding."

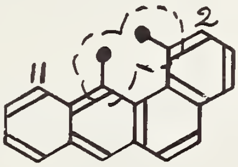


Phenanthrene



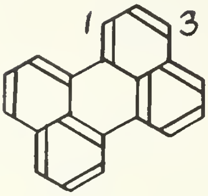
Benzo[c]phenanthrene

Similarly, in benz[*a*]anthracene, there is crowding at C–1 and C–12.



Benz[a]anthracene

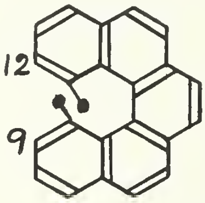
Relief of such a strain is, in some instances, obtained by adoption of a *nonplanar,* stable conformation. This results in assumption, by certain atoms and bonds, of positions in space that are different from those present in the planar conformation. As a consequence, the susceptibility of such atoms to oxidation may differ from that predicted by calculations that ignore conformational effects. For example, in perylene, by the localization theory, C–3 should have greater proton affinity than C–1. However, the two positions



Perylene

actually have almost identical affinities; this is presumably because of added ease of distortion in the region at C–1 as compared with C–3.

In dibenzo[*c,g*]phenanthrene, the region associated with C–10 and C–11 is very over-



Dibenzo[c,g]phenanthrene

crowded; this is relieved [18] by displacements of atoms in a direction perpendicular to the mean plane of the molecule. The atoms on one side of the molecule are displaced upwards, and those on the other side are displaced downwards. For some atoms, the displacement is as much as 1.7 Å.

4.5. Effect of Methyl Substituents

Methyl groups act as slight donors of electrons to aromatic compounds; this causes slight increases in the electron densities of the bonds and increases in bond orders, resulting in enhanced double-bond reactivity. The eects of methyl substituents on the reactivity of reactive centers, on *para*-localization energies, and on *ortho*-localization energies have been discussed [19].

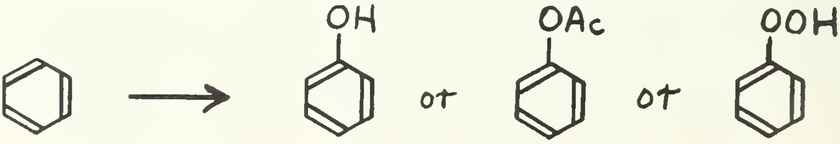
The rate of reaction of osmium tetroxide–pyridine with polycyclic, aromatic hydrocarbons and their methyl derivatives is an excellent measure of the reactivity of the double bonds [13]. It was found that the methyl groups greatly affect the rate of oxidation; moreover, the *position* of the methyl groups determines the magnitude of the effect.

For benz[*a*]anthracene and its methyl homologs, the relative rate of reactivity of the 5,6-bond agreed with calculations of the effect of methyl groups thereon [20].

5. One-Center Attack

5.1. Oxidation Resulting in Substitution

In oxidation by substitution, the aromatic character of the attacked ring is preserved. Substitution may be *direct,* as in the formation of phenols in some free-radical reactions



[21]. However, in some substitution reactions, the reaction proceeds by way of an intermediate *addition product* which has been isolated [16, 22]. In other oxidations resulting in substitution, the mechanism operating has not yet been determined.

Attack occurs chiefly at the most reactive center predicted (see table 6), although some molecules may be attacked only at the next most reactive center. For example, in reactions of naphthalene with free radicals, substitution occurs mainly at C–1 only (see table 11), but, simultaneously, some of the molecules are attacked at C–2 only.

Typical reagents are hydrogen peroxide in ultraviolet light, hydrogen peroxide catalyzed by ferrous sulfate (the Fenton reagent), benzoyl peroxide (see section 8.2.1), and lead tetraacetate (see section 8.2.3).

TABLE 11. *Proportions of 1-substitution and 2-substitution products from reaction of naphthalene with free-radical reagents*

Reagent	Entering radical	1-Isomer	2-Isomer	References
		Percent	*Percent*	
H_2O_2 (in U.V. light)	OH	76	24	1
H_2O_2–$FeSO_4$	OH	79	21	1
$(PhCO_2)_2$ at 80° C	$PhCO_2$	76	24	2
$(PhCO_2)_2$ at 85° C	$PhCO_2$	73	27	3
$(PhCO_2)_2$ at 100° C	$PhCO_2$	68	32	3
$(PhCO_2)_2$ at 100° C	$PhCO_2$	88	12	4

References for table 11

1. E. Boyland and P. Sims, J. Chem. Soc. 1953, 2966.
2. R. Huisgen and R. Grashey, Ann. 607, 46 (1957).
3. D. I. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc. 1958, 1878.
4. B. M. Lynch and K. H. Pausacker, Australian J. Chem. 10, 165 (1957).

5.1.1. Oxidative Coupling

In oxidative coupling, hydrogen abstraction from a reactive center affords a free radical which can then react with another such free radical to give a dimer. The dimer may now undergo hydrogen abstraction and coupling, and so on, resulting in the formation of a series of polymers.

In the first step, the hydrogen atom is removed directly, either by an oxy anion or by a free radical (such as OH or HO_2) produced by interaction of the oxidant with the solvent. Oxidative coupling is caused, for example, by benzoyl peroxide (see section 8.2.1).

6. Two-Center Attack

6.1. Addition to Two Reactive Centers

In this kind of oxidation, the net effect is attack at two carbon atoms which may be, but are not necessarily, *ortho* or *para* to each other. The positions at which attack occurs can depend on the reagent and experimental conditions employed, as well as on the structure of the hydrocarbon being oxidized. The localization-energy requirements for *ortho* as against *para* attack may not be directly comparable. Thus, according to the Pullmans [23], whereas in an addition reaction at a bond, the decisive factor is the stability of the *final* product, in addition reactions nonadjacent carbon atoms, the electronic characteristics of the *initial* state have a greater influence.

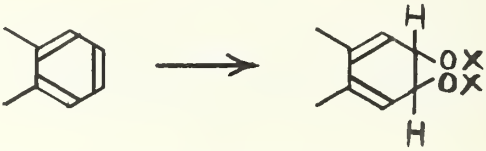
6.1.1. *para* Addition

Because of the increase in reactivity of the reactive centers of the linear benz-homologs as the series is ascended, there is a parallel increase in the ease of formation of addition compounds. Thus, anthracene reacts with nitrogen dioxide to give the 9,10-diadduct (see section 9.1.7) and with oxygen in the light to give the 9,10-peroxide (see section 9.1.10); and, as the series is ascended, the product is more readily formed and is increasingly more stable.

6.1.2. *ortho* Addition

In oxidation by addition to a "double" bond, transfer of oxygen atoms occurs, from an oxygen-containing oxidant to the two carbon atoms at the ends of the bond, and the aromatic character of the attacked ring is thereby removed.

In general terms, the reaction may be depicted as



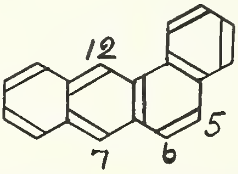
The hydrocarbon furnishes two of its π-electrons, to form two new σ-bonds between the reagent and the hydrocarbon. Examples are given in section 9.2.1.

Oxidants that may produce this result include the following: hydrogen peroxide plus a catalyst, osmium tetroxide plus pyridine, and (perhaps) ozone.

Because addition may be followed by elimination, a substitution product, such as might be obtained by a one-center attack, often results from *ortho* attack.

6.2. Oxidation to the Dione

If, in oxidation to a dione, the attack at the two carbon atoms were simultaneous, it should occur at the two atoms for which the combined localization energy is the minimum. Now, oxidation of benz[*a*]anthracene (for example, with chromium trioxide) gives the 7,12-dione, despite the fact that the *ortho*-localization energy calculated for C5–C6 is less



Benz[a]anthracene (5253)

Table 12. *Predicted diones, and those actually obtained by the oxidation of polycyclic hydrocarbons with chromium trioxide*

RRI No.	Hydrocarbon	Dione (predicted[a] and found)
		para
1754	Naphthalene	1,4–
3618	Anthracene	9,10–
5252	Naphthacene	5,12–
6376	Pentacene	6,13–
5253	Benz[*a*]anthracene	7,12–
6377	Benzo[*a*]naphthacene	8,13–
		pseudo-*para*
5262	Pyrene	1,6– plus 1,8–
		ortho
3619	Phenanthrene	9,10–
5254	Chrysene	5,6–

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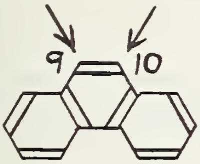
[a] By M. J. S. Dewar, J. Am. Chem. Soc. 74, 3357 (1952).

than the *para*-localization calculated for C7,C12 [8, 11]. This suggests that an electron-deficient cation *first attacks a single center*, namely, that having the lowest localization energy; then, attack occurs at that carbon atom which will afford *the most stable dione.*

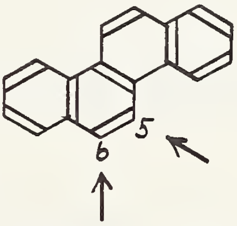
The *second* point of attack is a center of equal reactivity (if there is one) or the next most reactive center, although some oxidation may occur at the third most reactive center. The most reactive center and the next most reactive center for a number of hydrocarbons were listed in table 6. In all cases thus far examined, the positions predicted for two-center attack (see table 12) agree with those found experimentally.

Thus, for naphthalene, anthracene, naphthacene, and pentacene, oxidation occurs at two equally reactive centers, giving the *p*-dione. For benz[*a*]anthracene and benzo[*a*]-naphthacene, reaction at the most reactive center and then at the next most reactive center affords the *p*-dione indicated.

In phenanthrene, C–9 and C–10 are equally reactive centers; oxidation occurs at these to give the *o*-dione. Similarly, chrysene is oxidized at C–6, the most reactive center, and then at C–5, to give the stable *o*-dione.

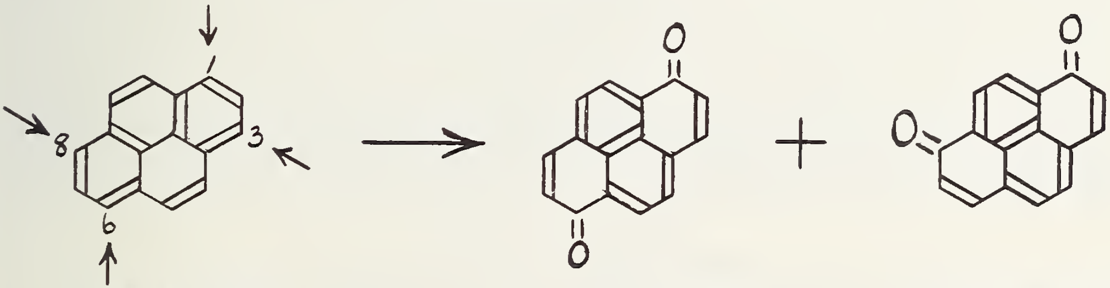


Phenanthrene (3619)



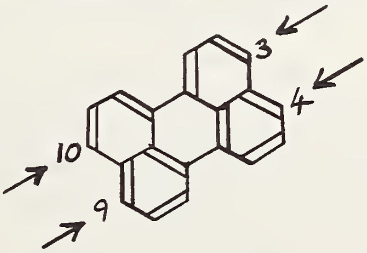
Chrysene (5254)

In pyrene, C–1, C–3, C–6, and C–8 are equally reactive centers, and a mixture of the 1,6- (≡ 3, 8-) and 1,8- (≡ 3, 6-) diones is formed on oxidation with, for example, chromium trioxide. No 1,3-dione would be expected, as it would be less stable than the other diones.



Pyrene (5262)   1,6-Pyrenedione   1,8-Pyrenedione

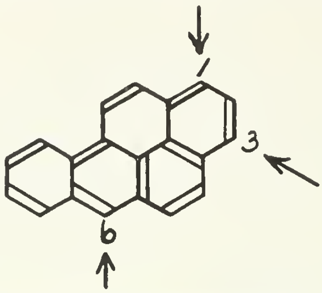
Perylene has four equivalent, reactive centers, at C–3, C–4, C–9, and C–10, and the



Perylene (6401)

expected 3,10-dione is formed with chromium trioxide [24].

Dewar's predictions [8] indicate that, in benzo[*a*]pyrene, the most reactive center is



Benzo[a]pyrene (6399)

at C–6, the next most reactive center is at C–1, and the third most reactive center is at C–3. This explains why, by the action of appropriate oxidants, benzo[*a*]pyrene gives a mixture of the 1,6-dione with the 3,6-dione.

7. Pre-oxidative Behavior

A knowledge of the behavior to be expected of polycyclic, aromatic hydrocarbons in certain environments *prior* to occurrence of oxidation is helpful in understanding the mechanisms involved when oxidation does take place.

7.1. With Oxygen

In 1937, Sklar [25] observed, in the ultraviolet absorption spectrum of benzene exposed to the air, certain bands which he ascribed to a singlet–triplet transition. These bands (at about 312, 321, 330, and 340 mμ) were also observed by subsequent workers [26]. However, it remained for Evans [27] to discover that these bands disappear when the dissolved oxygen is removed, but reappear (and are stronger) when the benezene is saturated with oxygen. The same phenomenon was observed with naphthalene and other polycyclic, aromatic hydrocarbons [28]. Nitric oxide (NO) has a similar effect, and it was pointed out that both oxygen and nitric oxide are both paramagnetic and electron-accepting. Evans concluded that the effect is largely due to the paramagnetic effect of the oxygen molecule, but that charge transfer might play some part. Other workers [29] have considered that the enhancement of the singlet–triplet absorption bands is due to charge transfer in which oxygen is the electron acceptor and the hydrocarbon (Z) is the

$$Z + O_2 \rightleftharpoons Z - O_2$$

electron donor; this explanation has now been accepted by Evans [30].

In related work, it has been found that oxygen quenches the fluorescence of many polycyclic, aromatic hydrocarbons [31–33], and this effect, also, has been attributed [32] to formation of a charge-transfer complex of the hydrocarbon with oxygen. Nitric oxide also quenches the fluorescence, and sulfur dioxide causes a decrease in intensity of the fluorescence.

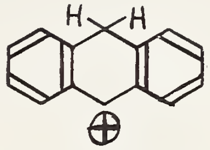
7.2. With Strong Acids

In 1940, Weiss [34] pointed out that any compound containing conjugated double bonds should be capable of forming ions, particularly *positive* ions; he described [35] the formation of salts of anthracene, benzo[*a*]pyrene, benzo[*a*]perylene, and coronene with perchloric acid, pyrophosphoric acid, and sulfuric acid; for example:

$$[C_{14}H_{10}]^+ \quad [C\ell O_4]^-$$

Anthracene perchlorate

Thus, the hydrocarbons behave as bases in strongly acidic solvents [36], giving a proton complex or carbonium ion, such as



It was found that a solution of perylene in concentrated sulfuric acid is paramagnetic [37], because of the formation of free radicals; the electron spin resonance spectrum [38] showed that singly charged, monopositive ions of perylene are formed. In *oxygen-free* hydrofluoric acid (or hydrofluoric acid–boron trifluoride), the perylene is present as a proton complex; however, when oxygen gas is introduced, part of the protonated species is converted into the monovalent, positive ion [39]. That is, in hydrofluoric acid, the aromatic hydrocarbons (Z) behave as bases; when the aromatic hydrocarbons are dissolved in strongly proton-active *and* oxidizing media, they give proton complexes *and* positive ions. Thus, solutions of anthracene in sulfuric acid [40], or in hydrofluoric acid plus oxygen, give both species [41].

$$Z + HF \rightleftharpoons ZH^{+} + F^{-}$$

$$Z + H_2SO_4 \rightleftharpoons ZH^{+} + HSO_4^{-}$$

From a study of the action of oxygen on perylene dissolved in trifluoroacetic acid [42], it was found that greater acidity of the solvent favors electron transfer, leading to the formation of a monopositive ion in the ion pair.

$$Z - O_2 \rightleftharpoons Z^{+} \cdot O_2^{-}$$

In addition, a solution of perylene in perchloric acid shows absorption bands (at 503 and 530 mμ), said to indicate the presence of a paramagnetic ion [43].

Such reactions are undoubtedly important in oxidations conducted in, or with, strong acids.

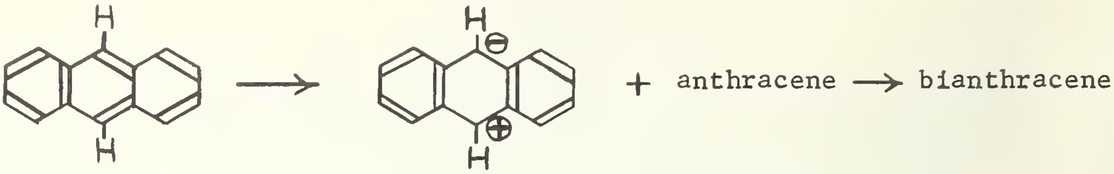
7.3. With Ultraviolet Light (Non-oxidative Dimerization)

Under the influence of ultraviolet light, dimerization can occur; although this is not oxidative, since hydrogen abstraction is not involved, it is mentioned, as it may be encountered in such studies.

Fritzsche [44] found that, if a cold, saturated solution of anthracene in benzene is kept in sunlight, dimerization occurs, to give 9,9′:10,10′-bianthracene [45,46]; this is sparingly soluble and crystallizes out. On being melted, it is depolymerized to anthracene.

Solutions of anthracene in xylene, anisole, or phenetole, when boiled in the light, give the dimer [45] ; but, if boiling is continued in the dark, the monomer is regenerated. Benz[*a*]-anthracene behaves similarly.

Chloroform and carbon disulfide inhibit this dimerization [47], but ether promotes it. The dimerization is attributed [48] to formation of excited diradicals of anthracene which



react with normal molecules of anthracene. To prevent formation of anthraquinone, oxygen must be excluded [49].

The self-quenching of fluorescence observed with irradiated solutions of polycyclic, aromatic hydrocarbons has been attributed [32] to reaction of excited molecules (Z^*) with unexcited molecules (Z) to give molecules of a transient dimer; this is reversed in the

$$Z^* + Z \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} Z^+Z^- \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} Z_2$$

dark. Ordinarily, these dimers have very short lives [50]. For naphthalene in benzene, the transient dimer is formed in 0.1 *M* naphthalene, but not below this concentration [33].

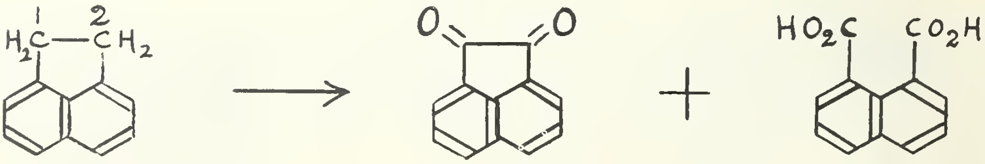
8. Agents Causing One-Center Attack

8.1. At an Active Methylene Group

8.1.1. Chromium Trioxide

Chromium trioxide in hot, glacial acetic acid (or sodium dichromate in aqueous sulfuric acid) oxidizes a reactive methylene group to a ketone group. For example,

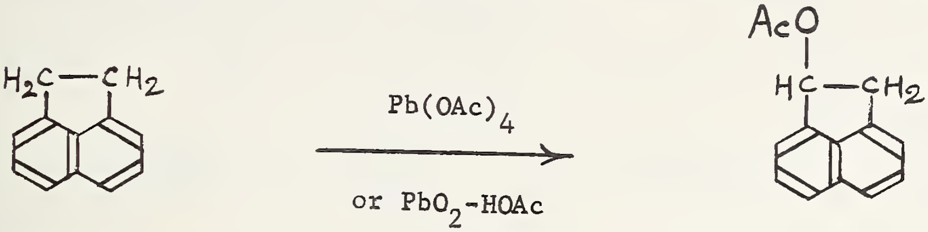
Fluorene (3127) Fluoren-9-one



Acenaphthene (3133) Acenaphthenequinone Naphthalic acid

8.1.2. Lead Tetraacetate

Lead tetraacetate, used in excess, oxidizes an active methylene group. For example,



Acenaphthene (3133)

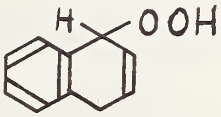
1-Acenaphthenol acetate

This reagent oxidizes fluorene to fluoren-9-one [51].

8.1.3. Oxygen

In pyridine, in the presence of benzyltrimethylammonium hydroxide, fluorene is oxidized by oxygen to fluorenone at room temperature [52] ; the reaction is not sensitive to light.

1,4-Dihydronaphthalene is oxidized by oxygen to the hydroperoxide [53] and other products.



1,4-Dihydro-1-naphthyl hydroperoxide

8.1.4. Oxygen and Ultraviolet Light

On treatment with oxygen and ultraviolet light for 30 hr at 70° C, fluorene in benzene gives the stable 9-fluorenyl hydroperoxide [54].

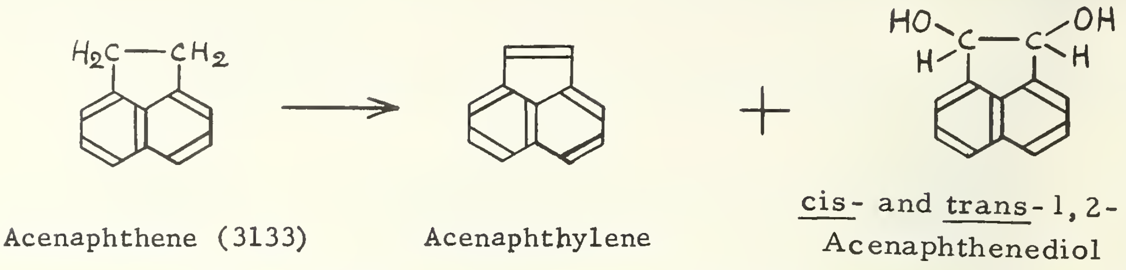
8.1.5. Ozone

Ozone oxidizes fluorene to fluoren-9-one [51].

8.1.6. Selenium Dioxide

Selenium dioxide in hot acetic acid or acetic anhydride may oxidize an active methylene group to a carbonyl group. For example, fluorene gives fluoren-9-one [55] in 65 percent yield.

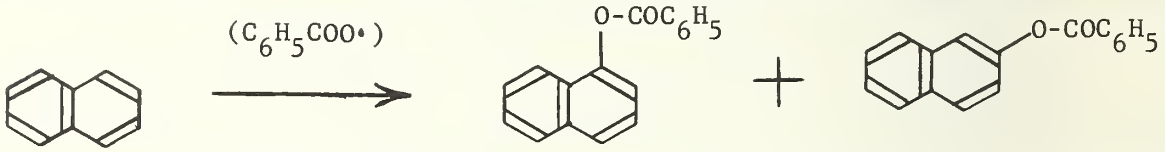
Acenaphthene, in the absence of solvent, gives [56] a mixture of acenaphthylene and the *cis*- and *trans*-1,2-acenaphthenediols. With acetic acid as the solvent, it gives, in addition to these products, a polyacenaphthylene and a binaphthylenecyclobutane [57].



8.2. Oxidation of One Reactive Methylidyne (Methine) Grouping

8.2.1. Benzoyl Peroxide

(a) *Substitution.* On treatment of naphthalene with benzoyl peroxide at 85° C, the principal reaction is nuclear benzoyloxylation [58] at C–1 and, separately, at C–2 by benzoyloxy radicals, giving naphthyl 1- and 2-benzoates in the ratio 73:27 (see table 11).



The substitution consists of addition of the benzoyloxy radical, followed by elimination of a hydrogen atom. (Side reactions leading to phenylation and to oxidative coupling are discussed in section 8.2.1b.)

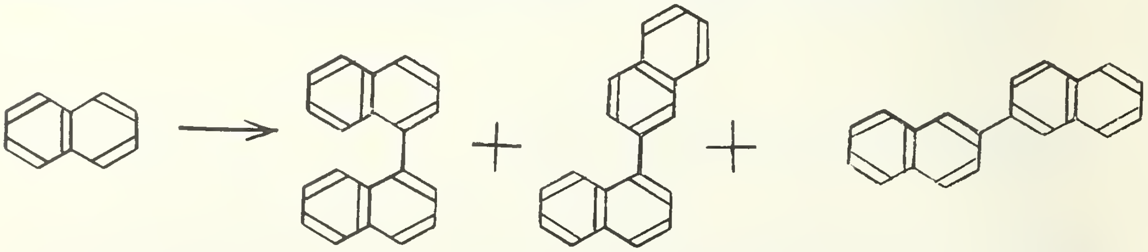
The relative reactivity of C–2 is raised [58] by increasing the reaction temperature to 100° C; simultaneously, the main reaction (benzoyloxylation) decreases, and phenylation increases.

(b) *Oxidative coupling.* Benzoyl peroxide gives rise to benzoyloxy radicals [59] and to phenyl radicals.

$$\mathrm{PhCO\text{-}O\text{-}O\text{-}COPh} \rightleftharpoons 2\ \mathrm{PhCO\text{-}O}\bullet$$

$$\mathrm{PhCO\text{-}O}\bullet \rightleftharpoons \mathrm{Ph}\bullet + \mathrm{CO_2}$$

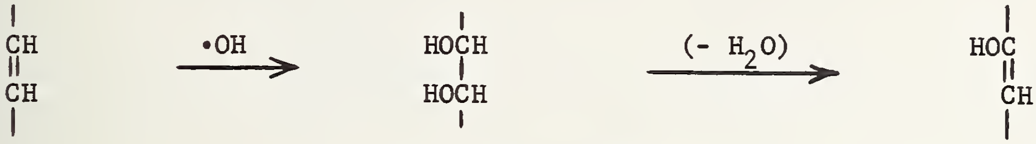
In the reaction of benzoyl peroxide with naphthalene [58], the benzoyloxy radicals act in two ways: (a) by direct substitution to give naphthyl 1- and 2-benzoates (see section 8.2.1a), and (b) by hydrogen abstraction, followed by dimerization, to give binaphthyls in the ratio of 54:42:4 for the 1,1′-, 1,2′-, and 2,2′-isomers.



The free phenyl radicals cause nuclear phenylation at C–1 and C–2 (giving an 82:18 mixture of 1- and 2-phenylnaphthalenes).

8.2.2. Hydrogen Peroxide Catalyzed by Osmium Tetroxide

This reagent oxidizes naphthalene to give, in part, 1-naphthol (see table 3). Similarly, phenanthrene gives, in part, 9-phenanthrol. It is probable that the diol is first formed (see section 9.2.1 (1)), and that this undergoes dehydration.

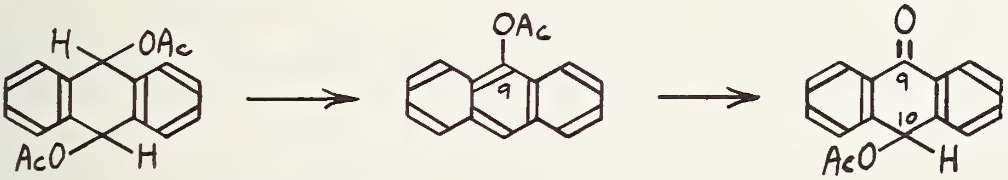


$$\begin{matrix} | \\ \mathrm{CH} \\ \| \\ \mathrm{CH} \\ | \end{matrix} \xrightarrow{\bullet\mathrm{OH}} \begin{matrix} | \\ \mathrm{HOCH} \\ | \\ \mathrm{HOCH} \\ | \end{matrix} \xrightarrow{(-\ H_2O)} \begin{matrix} | \\ \mathrm{HOC} \\ \| \\ \mathrm{CH} \\ | \end{matrix}$$

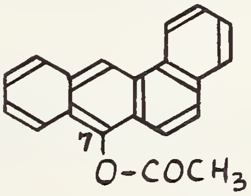
8.2.3. Lead Tetraacetate

In the reaction of lead tetraacetate with anthracene in benzene at 35 to 55° C, a mixture of the *cis* and *trans* diadducts is formed [60].

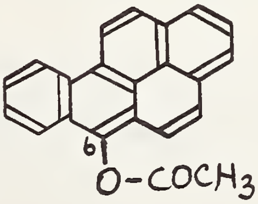
Used hot, this reagent causes acetoxylation of some aromatic hydrocarbons. Thus, with anthracene, the acetate of 9-anthrol and that of 10-hydroxyanthrone are formed [60], the mechanism probably involving addition of an acetoxyl group to each reactive center, followed by elimination, as shown. Similarly [61], but not necessarily by the same mechanism,



benz[a]anthracene →



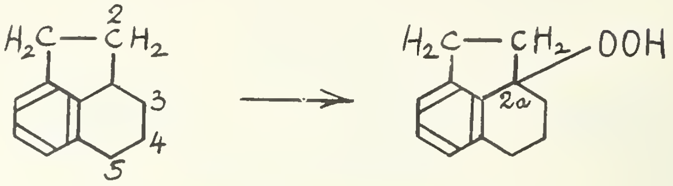
and benzo[a]pyrene →



Instead of lead tetraacetate, red lead oxide plus glacial acetic acid was originally used. A similar mixture of acetates was produced from anthracene by the action of ceric acetate, manganese dioxide, stannic oxide, or vanadium pentoxide in glacial acetic acid [60,62].

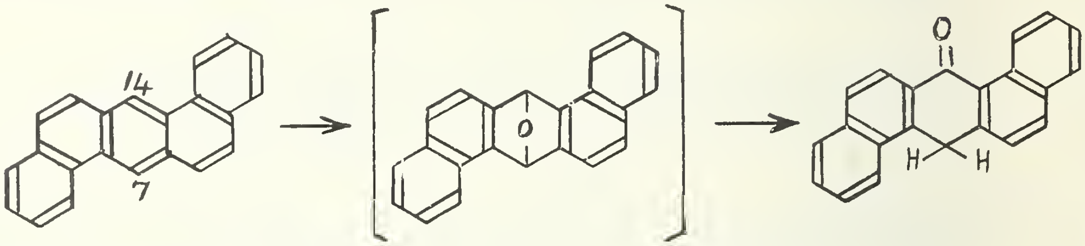
8.2.4. Oxygen and Ultraviolet Light

Treatment of 2a,3,4,5-tetrahydroacenaphthene with oxygen and light for 150 hours at room temperature gives the hydroperoxide [63].



8.2.5. Peroxybenzoic Acid

On oxidation of dibenz[*a*,*h*]anthracene with peroxybenzoic acid [64], a 7.3-percent yield of 7,14-dihydrodibenz[*a*,*h*]anthracen-7-one is obtained, presumably via intermediate formation of the 7,14-epoxide.



Dibenz[a,h]anthracene (6383)

7,14-Dihydro-dibenz[a,h]anthracen-7-one

Pyrene gives a mixture [65] of 1- and 4-pyrenols, as well as other products (see sections 9.1.8 and 9.2.1 (4)).

9. Agents Causing Two-Center Attack

9.1. At Two, Nonadjacent, Methylidyne (Methine) Groupings

9.1.1. Benzoyl Peroxide

Benzoyl peroxide attacks anthracene to give anthraquinone. Similarly, dibenz[*a*,*h*]-anthracene gives the 7,14-dione (see table 3).

9.1.2. Chromium Trioxide

On oxidation with chromium trioxide in glacial acetic acid (or dichromate in sulfuric acid), two nonadjacent methine groups may give the corresponding dione (see table 3). For some of the hydrocarbons (e.g., naphthalene, anthracene, benz[*a*]anthracene, and dibenz-[*a*,*h*]anthracene), this product is the *p*-dione. However, for benzo[*a*]pyrene, which lacks any *para* pair of reactive centers, a mixture of the 1,6-dione and 1,8-dione is formed.

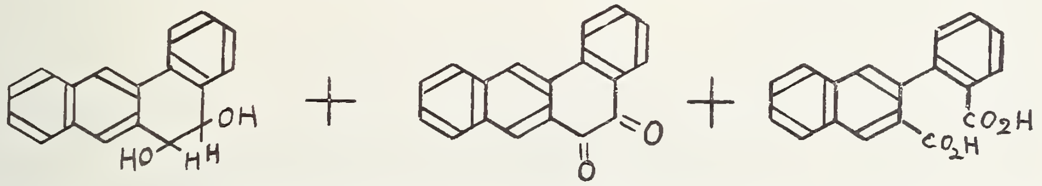
9.1.3. Hydrogen Peroxide Catalyzed by Osmium Tetroxide

By use of the Milas reagent (see section 9.2.1 (1)), two nonadjacent methine groups may be oxidized to the corresponding dione. Thus, anthracene is attacked exclusively at C–9 and C–10, the reactive centers, to give anthraquinone (see table 3).

In some instances (see table 3), this reagent affords two series of products [65a]; one results from attack at nonadjacent centers, and the other from addition to a reactive bond (see sections 9.1.3 and 9.2.1 (1)). The two attacks appear to be simultaneous, but the relative proportions of the products depend on the relative reactivities of these two sites of attack.

By comparison of the respective behavior of anthracene, benz[*a*]anthracene, and dibenz[*a,h*]anthracene, the effect (on these reactivities) of nonlinear addition of a benzene ring was ascertained. Whereas anthracene reacts solely at the reactive *para* centers, benz[*a*]anthracene reacts in *both* ways; it gives the 7,12-dione by attack at the nonadjacent, reactive centers, but it also gives the 5,6-diol (see section 9.2.1 (1)), a smaller proportion of the 5,6-dione (see section 9.2.3 (2)), a small proportion of 3-(*o*-carboxyphenyl)-2-naphthoic acid (from ring-scission of the 5,6-dione), and some phthalic acid.

Benz[a]anthracene Benz[a]anthracene-7,12-dione



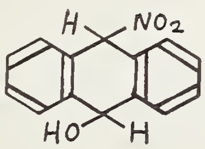
In contrast, dibenz[*a,h*]anthracene gives mainly the 5,6-dione, by reaction at the 5,6-bond (see table 3). Thus, addition of *one* benzene ring to anthracene raises the reactivity of the reactive bond and lowers the reactivity of the nonadjacent reactive centers; and addition of a *second* ring enhances these two effects even more, so that the 5,6-bond becomes the most reactive part of the molecule.

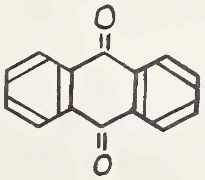
9.1.4. Lead Tetraacetate

With 2 molar proportions of lead oxide in hot glacial acetic acid, anthracene is oxidized to 10-hydroxyanthrone acetate [60,62].

9.1.5. Nitric Acid

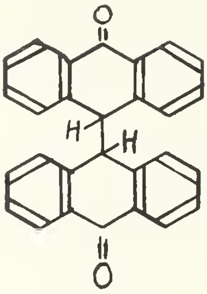
Whereas dilute nitric acid adds to C–9 and C–10 of anthracene [66], concentrated





nitric acid gives anthraquinone [67]. Nitrates, oxides of nitrogen, and nitrites have also been used, under a variety of conditions, for oxidation of anthracene to anthraquinone (see table 13).

In hot, glacial acetic acid, nitric acid acting on anthracene causes both (a) dimerization, and (b) oxidation to the ketone [68].



10,10'-Bianthrone

Table 13. *Oxidation of anthracene to anthraquinone by action of nitric acid, nitrates, oxides of nitrogen, or nitrites*[a]

Reactant and conditions	References
Liquid nitrogen dioxide	1
Nitrogen dioxide in acetic acid	2
Nitrogen oxides in water or ethanol	3
Nitrogen dioxide in benzene	4
Nitrogen oxides in nitrobenzene	5
Nitrogen dioxide in presence of mercuric nitrate, in nitrobenzene at 100–110° C	6
Nitrogen dioxide and air, at 200° C	7
Nitrogen dioxide and air, or nitric oxide and air, at 200° C	8
Ditto (in presence of zinc dust or lead oxide, to neutralize nitric acid)	9
Air and ZnO or CuO treated with NO_2, at 250–300° C	10
Nitrogen dioxide and air, anthracene mixed with pumice or asbestos (to minimize nitration)	8,10
Nitrogen oxide in presence of Zn compounds or Cu oxides	11
Oxygen plus small proportion of nitrogen oxides or fuming HNO_3, in presence of cobalt nitrate in acetic acid or other solvent, at 80–90° C.	12
Nitric acid in nitrobenzene–acetic acid, in presence of mercuric nitrate	13
Oxygen, catalyzed by nitric acid, oxides of nitrogen, or nitrites (liquid phase)	14
Sodium nitrate plus $MgCl_2 \cdot 6H_2O$ at 210° C	15
Sodium nitrite in acetic acid–acetic anhydride, with oxygen under pressure at 90° C	16

[a] Only references to early work are given.

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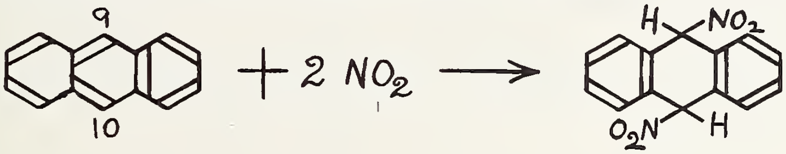
9.1.6. Nitric Oxide and Ultraviolet Light

When a solution of naphthalene, irradiated with ultraviolet light, is exposed to nitric oxide, the hydrocarbon is excited to the triplet state, and the diradical reacts with the nitric oxide [69].

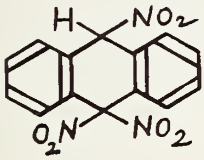
9.1.7. Nitrogen Dioxide (Addition)

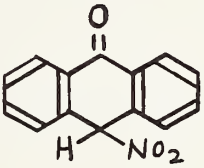
Anthracene reacts with nitrogen dioxide to give 9,10-dihydro-9,10-dinitroanthracene.



Anthracene

By further action (or with nitric acid), two other products are formed.





9.1.8. Organic Peroxy Acids

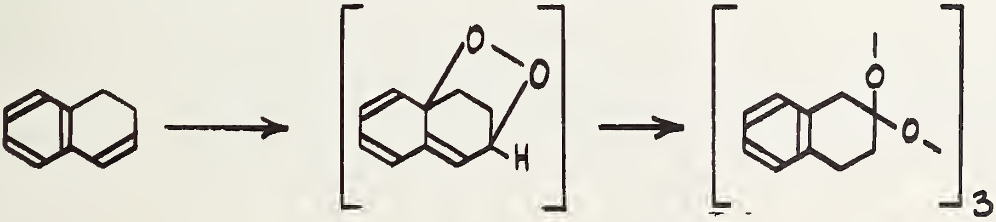
Peroxyacetic acid (or hydrogen peroxide in acetic acid) may attack nonadjacent methine groupings, as for naphthalene, anthracene benz[*a*]anthracene, and pyrene (see table 3), to give the corresponding dione. Thus, with peroxyacetic acid, anthracene gives anthraquinone [70]. Similarly, with this reagent, benz[*a*]anthracene gave [71] the 7,12-dione as the sole product. The same dione was obtained by use of peroxybenzoic acid [72]. Under more drastic conditions, peroxyacetic acid gave [73], in addition to the 7,12-dione, some 3-(*o*-carboxyphenyl)-2-naphthoic acid.

Pyrene, oxidized with peroxybenzoic acid, gives a mixture [65] of the 1,6- and 1,8-diones, as well as other products (see sections 8.2.5 and 9.2.1 (4)).

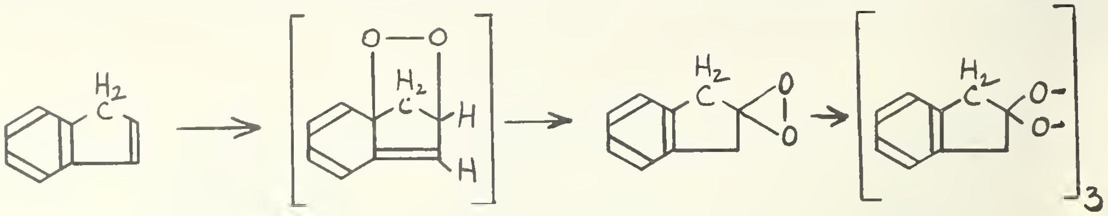
9.1.9. Oxygen

Fritzsche [6] found that, when solutions of anthracene are kept for a long time in flasks open to the air, anthraquinone crystallizes out. The same reaction proceeds more rapidly [74] with oxygen under pressure at 210–260° C.

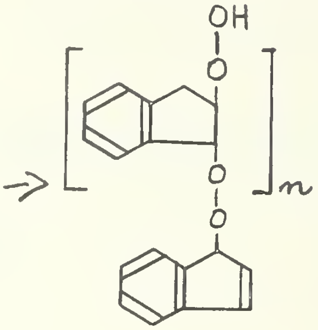
On treatment with oxygen for 430 hr at 18° C, 1,2-dihydronaphthalene gives the unstable *para* transannular peroxide [75], among other products (see section 9.2.1 (3)). This peroxide rearranges to a trimer.



Indene, treated with oxygen for 100 hr at 25° C, allegedly gives, among other products, an unstable, *meta* transannular peroxide [54,76] which rearranges to a trimer.



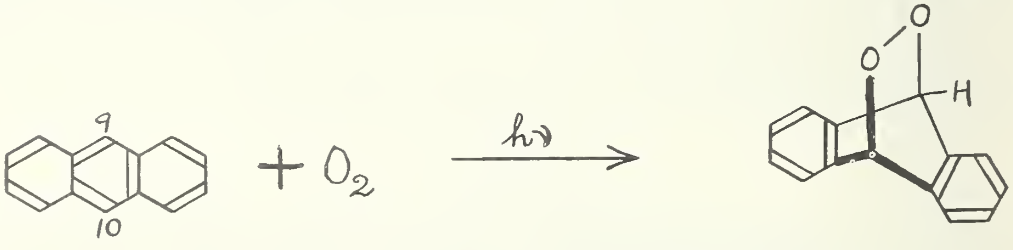
However, according to Russell [77], the structure of the polymeric peroxide is



9.1.10. Oxygen and Ultraviolet Light (Transannular Addition)

On treatment with oxygen while being irradiated with sunlight or ultraviolet light, anthracene gives a photo-oxide [78] if the solvent is carbon disulfide; but, if the solvent is benzene, bianthracene is formed [44] (see section 7.3).

In 1930, it was shown [79] that, for pentacene, the photo-oxide has a transannular structure, and it has since been found that this is the general structure for such photo-oxides. Thus, for anthracene, a molecule of oxygen is added [78,80], across the central



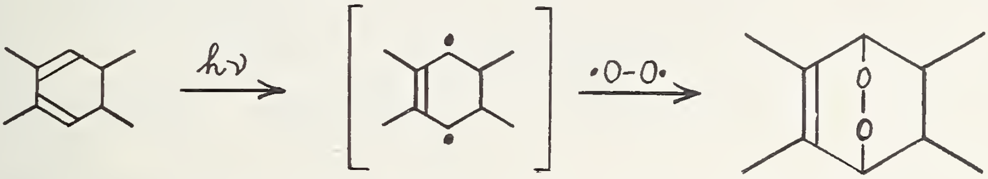
Anthracene (3618) 9,10-Dihydro-9,10-epidioxyanthracene

ring (from C–9 to C–10), to give the 9,10-peroxide. Naphthacene [81] and pentacene are photo-oxidized more readily, and the reaction occurs so readily with hexacene [82] and heptacene that solutions of these hydrocarbons, exposed to air and light, are almost instantaneously photo-oxidized. The ease of formation of the photo-oxide is related to the triplet-energy level of the excited species. The nonlinear hydrocarbons react, with oxygen, less readily than the linear polyacenes, or not at all.

The oxygen molecule has two unpaired electrons and is a diradical. Under the action

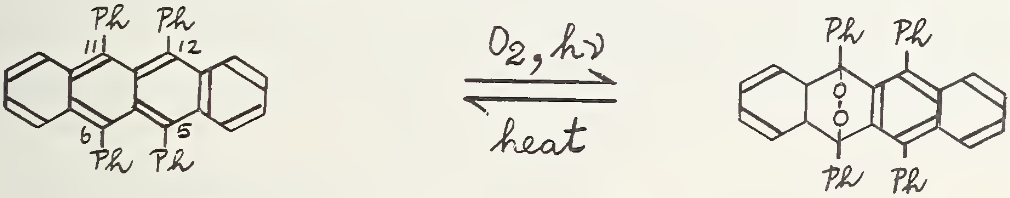
$:\mathrm{O}\overset{\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot}{—}}\mathrm{O}:$ or $\cdot\mathrm{O}\text{-}\mathrm{O}\cdot$

of ultraviolet light, transannular addition of oxygen occurs at the most reactive centers of linear aromatic hydrocarbons having two reactive centers that are *para* to each other, as in the anthracenoid hydrocarbons, giving transannular peroxides. Electronically excited molecules of the hydrocarbon take part in the addition, and the triplet state is involved. It seems probable that the absorbed light excites the dienoid structure to a diradical which then rapidly reacts with the oxygen diradical. The overall process involves consumption of diradicals with no regeneration; hence, these are not chain reactions.



The transannular addition of oxygen is facilitated by the presence of electron-donating substituents (e.g., methyl or phenyl) at the reactive centers; thus, 9,10-dimethoxyanthracene is readily photo-oxidized [83]. Addition is retarded by such electron-attracting groups as carboxyl and cyano at these centers.

Many of the photo-oxides dissociate on heating, with liberation of oxygen; the extent of the dissociation depends on the nature of the substituents. Thus, the photo-oxide of 5,6,11,12-tetraphenylnaphthacene (rubrene) [84] and those of the 9,10-diarylanthracenes readily dissociate on heating, to give the original hydrocarbon plus free oxygen [78,85]; the photo-oxides of the 10-aryl-9-methylanthracenes liberate less than 50% of their oxygen on being heated; and the 9-alkyl- and 9,10-dialkyl-anthracene photo-oxides *do not liberate oxygen.*



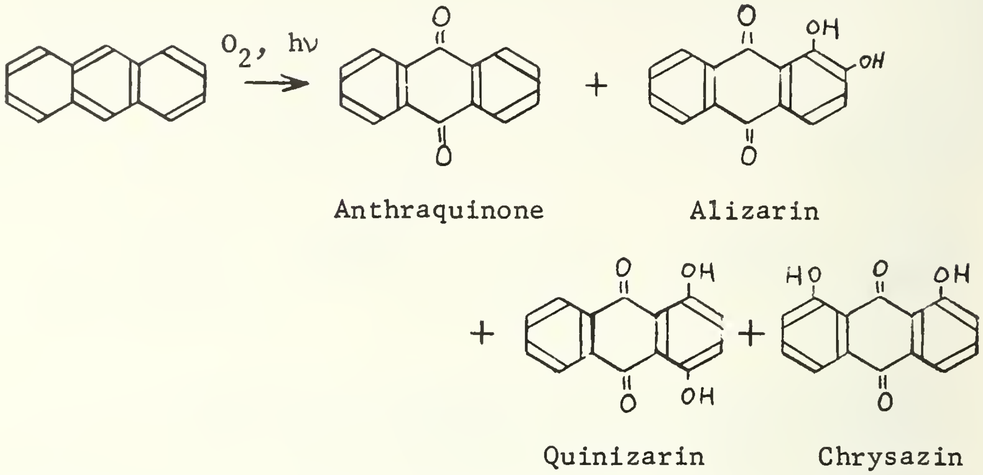
Rubrene

If a sublimed film of anthracene is treated with *dry* oxygen and ultraviolet light (3650 Å), it is unchanged. However, if the sublimation is conducted in dry oxygen, under the same irradiation, onto a plate at —180° C, there occur slight, temperature-dependent, spectral changes which were attributed [86] to formation of a loose adduct of anthracene with oxygen. On the other hand, if the latter sublimation is performed in *moist* oxygen, the irradiated anthracene reacts immediately to give a product, having the spectrum of a cyclic photo-oxide, which is changed to a more stable form by warming to —150° C and recooling to —180° C [87]. This stable form is also obtained by sublimation, *in the dark,* of anthracene onto a plate at —180° C, in moist oxygen. Tetracene and benz[*a*]anthracene do not exhibit this behavior.

9.1.11. Oxygen and Ultraviolet Light, with Catalysts

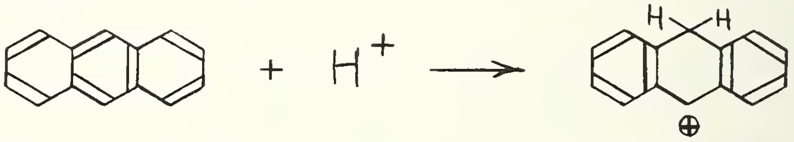
During the chromatography of benzene solutions of anthracene on columns of alumina, oxidation of part of the hydrocarbon to anthraquinone was observed [88]; the oxidation was attributed to oxygen adsorbed on the surface of the alumina [89]. However, it was pointed out [90] that the oxidation does not occur in the dark, and so photo-oxidation is involved.

If anthracene adsorbed on alumina is exposed to ultraviolet light, anthraquinone is formed, together with alizarin (1,2-dihydroxyanthraquinone), quinizarin (1,4-dihydroxyanthraquinone), and chrysazin (1,8-dihydroxyanthraquinone) [91].



The relative proportions of the products depend to a large extent on the pretreatment given the adsorbent. Naphthalene on alumina gives 1,2-naphthoquinone only. Oxidation was also observed on other adsorbents. On zinc oxide, only anthraquinone was obtained from anthracene. Silica gel was found to be particularly effective [92], giving a 50 percent yield of anthraquinone from anthracene after 1 hr of ultraviolet irradiation; oxidation was much slower on magnesium oxide or potassium chloride, and 10 hr of irradiation on alumina gave a 10 percent yield of quinizarin.

It was supposed [93] that, in the *absence* of oxygen, a carbonium ion is formed by transfer of a proton from silica–alumina to C–9 of the anthracene; when oxygen is *present,*



this ion is oxidized. Hence, the role of the silica-alumina is that of a catalyst. Other studies [94] have shown that interaction of the hydrocarbon with protonic acid sites on the catalyst give a hydrocarbon–proton complex; electron transfer from this complex to oxygen affords a positive radical-ion of the hydrocarbon. However, in the *absence* of oxygen, anhydrous silica–alumina or zeolites give a positive radical-ion of the hydrocarbon on the catalyst by transfer of a single electron from the hydrocarbon to an acid site on the catalyst [38b,c,95]. Stable carbonium ions of polycyclic, aromatic hydrocarbons are obtained [96] by irradiating a mixture with silica gel (or silica–alumina) at —78° C with cobalt-60 γ-radiation for 1 hr.

9.1.12. Oxygen with Various Catalysts

With air over vanadium pentoxide at 300 to 500° C, two nonadjacent methine groups may afford the corresponding dione; thus, anthracene gives anthraquinone (see table 14). Similarly, pyrene [97] gives a mixture of the 1,6-dione and the 1,8-dione.

According to Senseman and Nelson [98], the vanadium pentoxide is reduced to a lower oxide of vanadium, and this is then re-oxidized to the pentoxide by oxygen.

Various catalysts used for liquid-phase or vapor-phase oxidation, with air or oxygen, of anthracene to anthraquinone, are given in table 14.

Because of the alternate reduction and oxidation of the oxide, only oxide catalysts consisting of oxides of metals having more than one degree of oxidation, and capable of ready reduction to a lower oxide and reoxidation to a higher oxide, are effective.

TABLE 14. *Oxidation of anthracene to anthraquinone, in the liquid or vapor phase, with air or oxygen plus a catalyst*[a]

Conditions	References
Liquid phase	
Vanadium compounds are more active than chromium compounds, in liquid suspension	1
Suspension in aqueous $FeSO_4$ solution	2
In acetic acid, plus osmium tetroxide, at 10 atm at 50–100° C	3
In pyridine, or dispersed in aqueous alkali, in presence of Cu, Co, Ni, or Pb compounds as catalysts.	4
In pyridine or aqueous ammonia, with or without CuO or $CuSO_4 \cdot 5H_2O$, at 170° C	4
In acetic acid, under pressure, in presence of copper vanadate or ammonium vanadate at 100–120° C or 160° C.	5
Vapor phase	
(a) **Over vanadium pentoxide**	
Oxides of metals of the 5th and 6th group of the Periodic Table, particularly vanadium pentoxide	6
Vanadium oxides, or vanadate, on pumice	7
Ditto, mixed with moist carbon dioxide gas	8
Vanadium oxides plus oxides of other metals, on pumice or asbestos	9
Vanadium oxides plus molybdenum oxides	10
(b) **Over other catalysts**	
Coal or peat	11
Oxides of chromium, molybdenum, tungsten, or uranium, at 500° C	12
A contact mass containing boric acid, at 400–430° C	13
Crushed firebrick mixed with phosphoric acid, at 380–400° C	14
Zeolites containing combined vanadium	15
Arsenates, chromates, molybdates, stannates, uranates, or vanadates of cerium, cobalt, copper, lead, nickel, silver, or thorium.	16
Titanium oxide (on pumice) pretreated with 2% (by volume) of nitrogen oxides, at 400–500° C	17

[a] Only references to early work are given.

References for table 14

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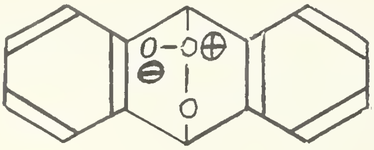
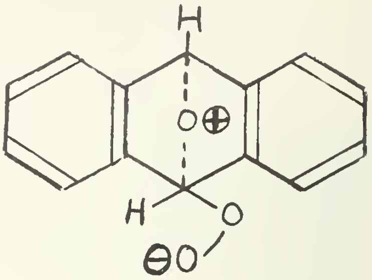
Anthraquinone was also prepared by passing a stream of air through an intimate mixture of powdered anthracene and alumina for 48 hr at 120° C [99]; fluorene gave fluoren-9-one. By use of alumina pretreated with sodium methoxide, less drastic conditions (24 hr at 55° C) were effective.

9.1.13. Ozone

Ozone attacks anthracene predominantly by *para* addition to the reactive centers at C–9 and C–10 [72,100]. With acetic acid as the solvent, a 70 to 75 percent yield of anthraquinone is obtained. Three equivalents of ozone are absorbed, and the initial product may result from transannular addition, as in formation of the photo-oxide, to give I; alternately, the first product may be the π-complex, II.

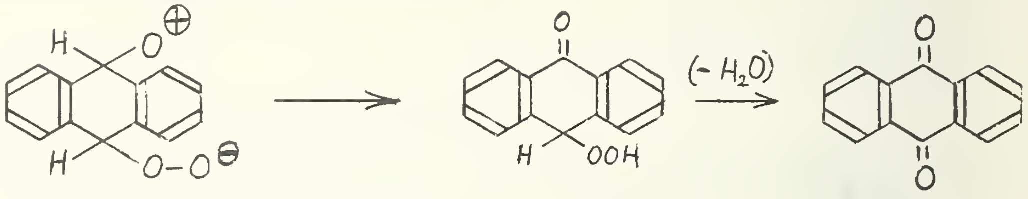


I



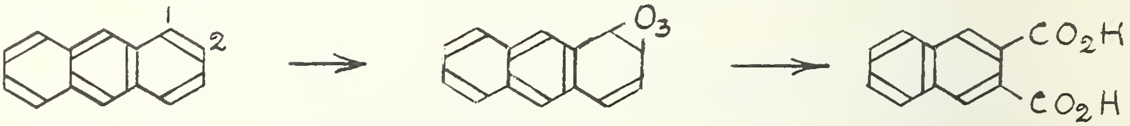
II

Either I or II could now give rise to III.



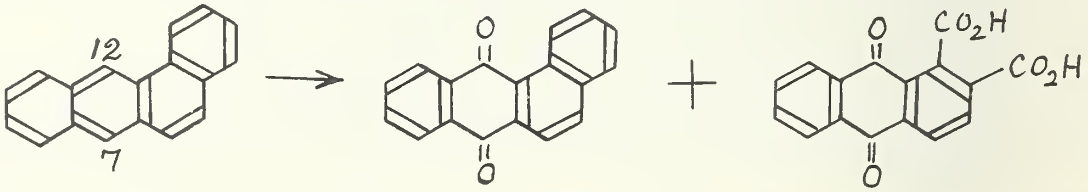
III

However, this does not account for the absorption of three molar proportions of ozone; a small proportion of 2,3-naphthalenedicarboxylic acid is also formed [101], showing that there is a much slower *ortho* attack at the reactive C1–C2 bond.



Naphthacene behaves similarly [101,102].

Ozone, likewise, reacts with benz[*a*]anthracene by both *ortho* and *para* addition. By treatment with one molar proportion of ozone [103], the main product was the 7,12-dione,

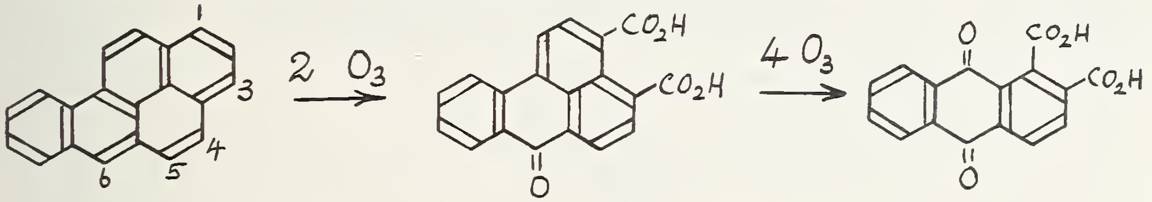


and a small proportion of 1,2-anthraquinonedicarboxylic acid was also formed. However, by using different conditions [73,101,104], a 13 percent yield of the 7,12-dione and 11 percent of 3-(*o*-carboxyphenyl)-2-naphthoic acid was obtained. Use of 2 molecular propor-

tions of ozone gave 17 percent of each of these. This indicates attack at the 5,6-bond, as well as at the 7,12-positions.

Whereas anthracene and naphthacene react mainly by *para* addition, naphthalene, phenanthrene, chrysene, pyrene, and triphenylene react by *ortho* addition (see section 9.2.2(5)). From a consideration of the resonance energies and redox potentials in relation to the observed course of ozonization, it has been concluded [105] that ozone reacts preferentially at the positions which give the most stable *ortho* or *para* adduct as the intermediate.

However, the behavior of benzo[*a*]pyrene with ozone fits into neither category, as this hydrocarbon lacks any *para* pair of reactive centers. With one molar proportion of ozone, a 3:1 mixture of the 1,6-dione and the 3,6-dione is formed, together with a trace of the 4,5-dione [106]. With larger proportions of ozone, rupture of rings occurs.



9.1.14. Selenium Dioxide

Selenium dioxide, in the absence of solvent, oxidizes anthracene to anthraquinone in 76 percent yield [55a]; with nitrobenzene as solvent, the yield is 73 percent [107].

9.1.15. Miscellaneous Reagents

A great variety of different oxidants have been used during the past hundred years for the oxidation of certain of the polycyclic, aromatic hydrocarbons. Some of those used for the oxidation of anthracene to anthraquinone are listed in table 15.

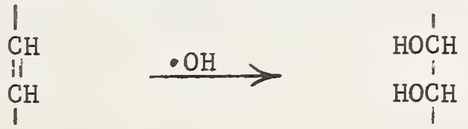
9.2. At a "Double" Bond

9.2.1. Addition to a "Double" Bond

(1) *Hydrogen peroxide, catalyzed by osmium tetroxide.* In a study of oxidation effected by hydrogen peroxide, Milas [108] examined the effect of a number of catalysts, including osmium tetroxide, vanadium pentoxide, and chromium trioxide. He found that a good solvent for the reaction is *tert*-butyl alcohol.

Mugdan and Young [109] evaluated the various methods for hydroxylation with hydrogen peroxide in the presence of catalysts, and decided that anhydrous hydrogen peroxide catalyzed by osmium tetroxide, in *tert*-butyl alcohol, is probably the best. This "Milas reagent" probably contains *tert*-butyl hydroperoxide, $Me_3C\text{-}O\text{-}OH$, which can, indeed, be used instead of the Milas reagent.

The active agent is the free hydroxyl radical, •OH, and this reacts with a reactive bond of some aromatic hydrocarbons to give a diol. For example, phenanthrene gives



$$\begin{array}{c} | \\ CH \\ \| \\ CH \\ | \end{array} \xrightarrow{\cdot OH} \begin{array}{c} | \\ HOCH \\ | \\ HOCH \\ | \end{array}$$

9,10-dihydro-9,10-phenanthrenediol and benz[*a*]anthracene affords the 5,6-diol (see table 3) together with other products. In other instances, although the reaction undoubtedly proceeds via a diol, no diol is actually isolated, as it is oxidized further, to the *ortho*-dione (see section 9.2.3 (2)).

Mugdan and Young [109] also found that *pertungstic* acid is an efficient catalyst; however, it is less reactive than osmium tetroxide and so was used at 60 to 70° C. In contrast to osmium tetroxide, it is nontoxic; also, it is cheaper. This reagent does not appear to have been applied to polycyclic, aromatic hydrocarbons.

TABLE 15. *Miscellaneous oxidants used for the oxidation of anthracene to anthraquinone*[a]

Oxidant and conditions	References
Bismuth nitrate (and heating)	1
Cerium sulfate in 20% sulfuric acid	2
Chromic chlorate, aqueous solution (and heating)	3
Ferric chlorate, aqueous solution (and heating)	3
Iodic acid in boiling acetic acid	4
Iodine and concentrated nitric acid, in chloroform	5
Manganese dioxide, in ethanol–toluene	6
Manganese dioxide plus oxides of molybdenum or vanadium, in boiling sulfuric acid	7
Manganese salts	8
Potassium bromate in boiling acetic acid	4
Potassium chlorate in concentrated formic acid	9
Potassium chlorate plus sodium nitrate plus magnesium chloride.$6H_2O$ at 130–150°	10
Sodium chlorate in concentrated formic acid	9
Sodium chlorate plus magnesium chloride	10
Sodium chlorate plus osmium tetroxide in 50% acetic acid	11
Sodium chlorate plus vanadium pentoxide, plus 2% sulfuric acid in acetic acid	12
Sodium chlorite plus an osmium salt, at room temperature	13,14
Sodium hypochlorite	13
Electrochemical oxidation in the presence of	
Cerium compounds	15,16
Lead dioxide, as oxygen carrier	17
Oxygen carriers	16,18
Vanadium compounds	19
Vanadium pentoxide in 20% sulfuric acid, at 80°	20

[a] Only references to early work are given.

References for table 15

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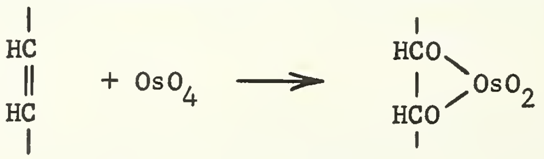
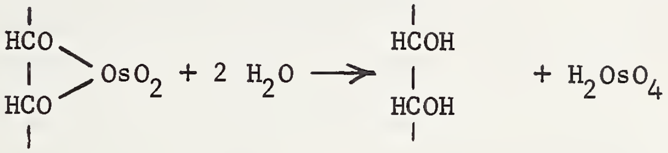
19. Farbw. vorm. Meister Lucius and Bruening, Ger. Pat. 172,654 (1903); Chem. Abstr. 1, 132.
20. Brit. Pat. 19,178 (1902); French Pat. 345,701 (1904); U. S. Pat. 823,435 (1906).

(2) *Osmium tetroxide–pyridine.* Criegee [110] discovered that osmium tetroxide is an excellent hydroxylating agent. Treatment of an olefin with an equivalent of the reagent in cold dry ether, benzene [22], cyclohexane [22], or dioxane [110,111] slowly gives an

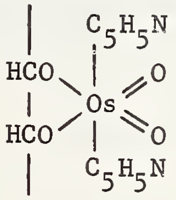


addition compound, which usually is precipitated from the solution, in almost quantitative yield, in less than 4 days. The product, an ester of osmic acid, may be hydrolyzed to the *cis*-diol.



$$\begin{array}{c}|\\ \mathrm{HCO}\\ |\\ \mathrm{HCO}\\ |\end{array}\!>\mathrm{OsO_2} + 2\ \mathrm{H_2O} \longrightarrow \begin{array}{c}|\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\end{array} + \mathrm{H_2OsO_4}$$

Criegee and coworkers also discovered that, if a tertiary base is added to the reaction mixture, the initial addition of osmium tetroxide is accelerated; *pyridine* is particularly effective [22]. A bright-colored compound having the character of an osmic ester and containing two molecules of the tertiary base per molecule is precipitated in almost quantitative yield.



This ester may then be hydrolyzed to the diol. Various reagents have been used for hydrolysis, including (a) acidic solutions of potassium or sodium chlorate, (b) hydrogen sulfide, (c) sodium sulfite in aqueous ethanol, or (d) potassium hydroxide in the presence of L-ascorbic acid, formaldehyde, or D-mannitol; of these, sodium sulfite and D-mannitol, respectively, have been the most widely used. Criegee found that *cis*-olefins give *erythro*-diols, and *trans*-olefins give *threo*-diols.

By use of this reagent under anhydrous conditions, with subsequent hydrolysis, Criegee and coworkers [22] hydroxylated phenanthrene to 9,10-dihydro-9,10-phenanthrenediol.

Phenanthrene

A systematic study revealed that the reagent attacks *ortho* reactive centers exclusively [5,16,112]. This behavior contrasts with the attack by a variety of other oxidants at the most reactive *para* (or pseudo-*para*) centers in the molecule. The reagent is, therefore, especially useful for determining the most reactive *ortho* centers in polycyclic, aromatic hydrocarbons which also contain very reactive *para* or pseudo-*para* centers. For example, for those hydrocarbons which contain a phenanthrene moiety having C–9 and C–10 nonfused, a quantitative estimation of the relative reactivity at the 9,10-positions of the phenanthrene moiety may be made.

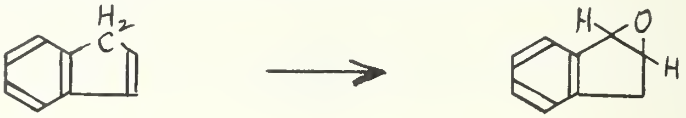
On treating anthracene with the reagent, and hydrolyzing, 1,2,3,4,tetrahydro-1,2,3,4-anthratetrol is obtained. It is supposed that the *initial* addition is at the 1,2-bond; the product contains a true ethylenic bond at C–3 to C–4, which readily reacts with a second molecule of the reagent. The positions of addition for other polycyclic, aromatic hydrocarbons are given in table 3.

Anthracene

The reaction is simple and affords high yields. However, osmium tetroxide has the following *disadvantages:* (1) it has a high equivalent weight, (2) it is very expensive, (3) it is fairly volatile, and (4) *its vapors are very poisonous and severely injure the eyes.*

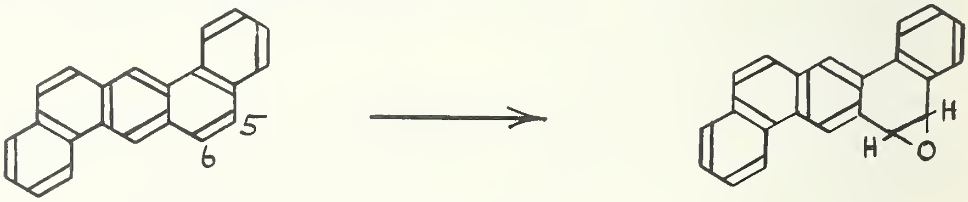
(3) *Oxygen.* In autoxidation, oxygen can add to a very reactive bond. Thus, on treating 1,2-dihydronaphthalene with oxygen for 430 hr at 18° C, 1,2-epoxy-1,2,3,4-tetrahydronaphthalene is formed [75], together with 3,4-dihydro-2(1*H*)-naphthalenone, *trans*-1,2,3,4-tetrahydro-1,2-naphthalenediol, and other products (see section 9.1.9).

(4) *Peroxybenzoic acid.* With peroxybenzoic acid, an atom of oxygen may be added to a "double" bond to give the epoxide, as with indene [113].



1, 2-Epoxyindan

On oxidation of dibenz[*a,h*]anthracene with peroxybenzoic acid [64], an 0.04-percent yield of the 5,6-epoxide is obtained.



Dibenz[a,h]anthracene (6383)

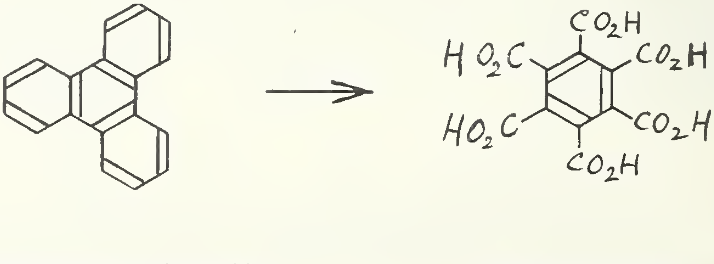
5, 6-Epoxy-5, 6-dihydrodibenz[**a,h**]anthracene

Pyrene gives the 4,5-dihydro-4,5-diol [65], presumably via the 4,5-epoxide, together with other products (see sections 8.2.5 and 9.1.8).

9.2.2. Addition to, and Rupture of, a "Double" Bond

(1) *Chromium trioxide.* Chromium trioxide in hot acetic acid, or sodium dichromate in aqueous sulfuric acid, can rupture a bond, presumably *via* the *o*-dione. It is likely that a cyclic addition product of the chromium trioxide at the "double" bond is first formed. An example is the oxidation of phenanthrene to diphenic acid (see table 3).

(2) *Nitric acid.* Rupture of "double" bonds can be caused by nitric acid, or by nitric acid followed by permanganate. Thus, with fuming nitric acid, triphenylene gives [114] mellitic acid.



Triphenylene (5256)

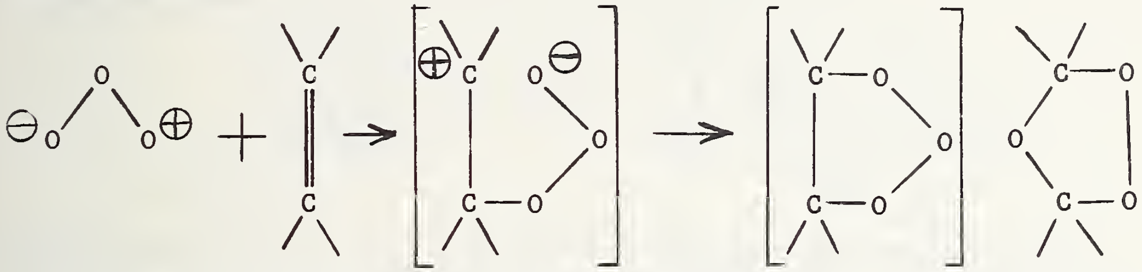
Mellitic acid

(3) *Organic peroxy acids.* Hydrogen peroxide in acetic acid attacks the most reactive "double" bonds of some polycyclic, aromatic hydrocarbons; in some instances, subsequent rupture of the "double" bond occurs (see table 3).

(4) *Oxygen, catalyzed by vanadium pentoxide.* Vapor-phase oxidation of chrysene with air over vanadium pentoxide gives phthalic anhydride [97].

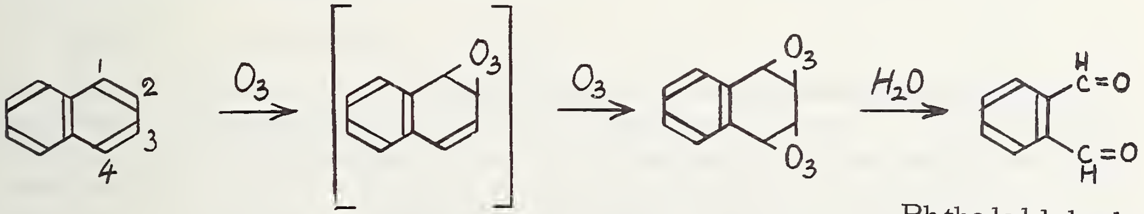
(5) *Ozone.*

(a) *In a nonparticipating solvent.* For many of the polycyclic, aromatic hydrocarbons, dissolved in an ice-cold, stable, nonparticipating solvent, one molecule of ozone adds to a reactive "double" bond, to give an ozonide which rearranges with rupture of the bond, possibly as follows.

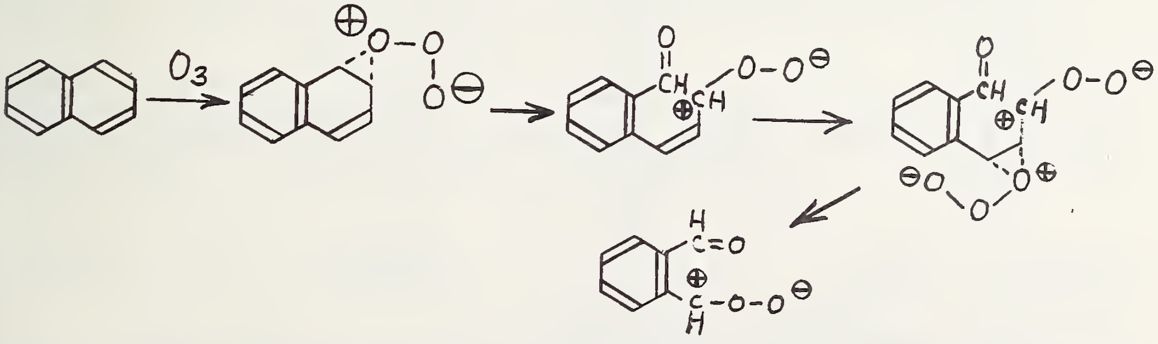


Ozonides are unstable; and so, products are isolated either by (a) reducing the ozonide and then hydrolyzing, or (b) oxidizing further with hydrogen peroxide. The ring fission occurs at the positions originally occupied by the most reactive bond (or bonds).

Naphthalene readily reacts with two equivalents of ozone, to give a "diozonide" [115,116]; slow absorption of ozone then continues until five equivalents have been taken up. In naphthalene, the 1,2-bond has the lowest bond-localization energy [8,11]. This bond presumably reacts first, to give a mono-ozonide which has an *olefinic* 3,4-bond that is rapidly attacked. Treatment of this product with water gives phthalaldehyde. The reaction was originally considered to proceed as follows,

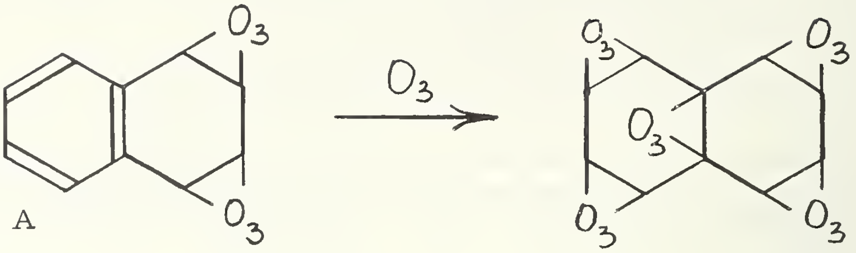


via the 1,2:3,4-diozonide. However, according to Bailey [116], the reaction does not involve formation of a diozonide, but of a polymer of the intermediate ion I.

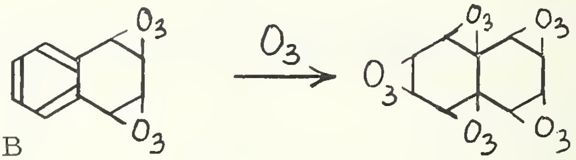


I

Nevertheless, *for approximate depictions*, the attack of ozone is more conveniently shown as $\rangle O_3$. The absorption of five equivalents of ozone was originally explained as involving formation of the penta-ozonide from the diozonide (A or B).

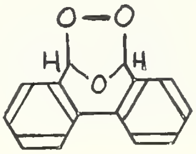


A

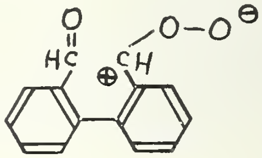


B

For naphthalene and phenanthrene, the attack of ozone can be explained as attack at the *bond* of lowest bond-localization energy *or* at the *centers* of lowest atom-localization energy. Ozone reacts with *phenanthrene* at the 9,10-bond exclusively and one equivalent of ozone is absorbed. The product was originally considered to be the monomeric ozonide I, but later work [117,118] has shown that it is a polymer of II.



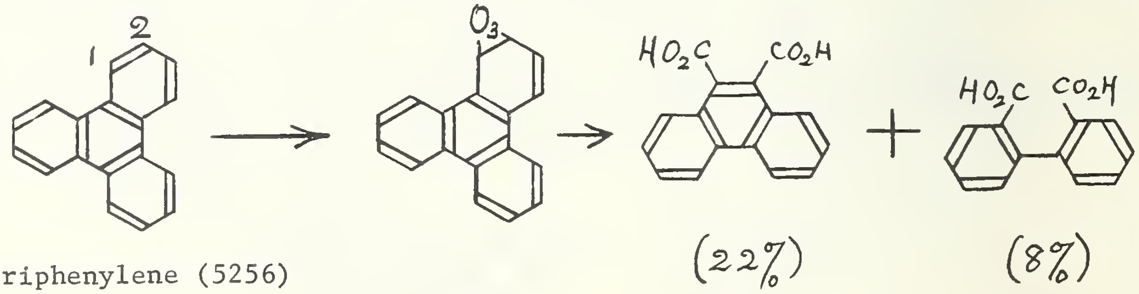
I



II

Ozonolysis of a number of nonlinear, polycyclic hydrocarbons in inert solvents has been studied [73]. Criegee and coworkers [119] had suggested that, under these conditions, intermediate ions are formed and that these interact to give polymeric ozonides. Wibaut and deBoer [120] ozonized phenanthrene and isolated a trimer. Bailey and Mainthia [121] decided that a mixture of polymers is formed; and Copeland and coworkers [73] confirmed this conclusion.

Triphenylene is attacked [73] at the 1,2-bond.



Triphenylene (5256)

In *picene,* the 5,6- and 7,8-bonds have the lowest bond-localization energies. Picene readily absorbs two equivalents of ozone; on oxidative decomposition of the product, a

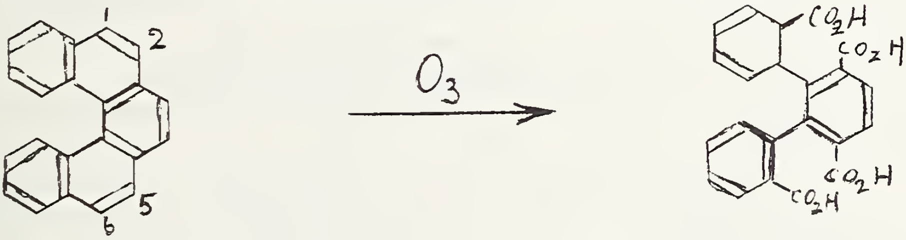
35 percent yield of an anhydride is obtained [73].

Picene (6384)

Similarly benzo[*g*]chrysene is attacked at the 9,10-bond [73].

Benzo[g]chrysene (6385) (69%)

Dibenzo[*c,g*]phenanthrene is attacked at the 1,2- and 5,6-bonds [73].

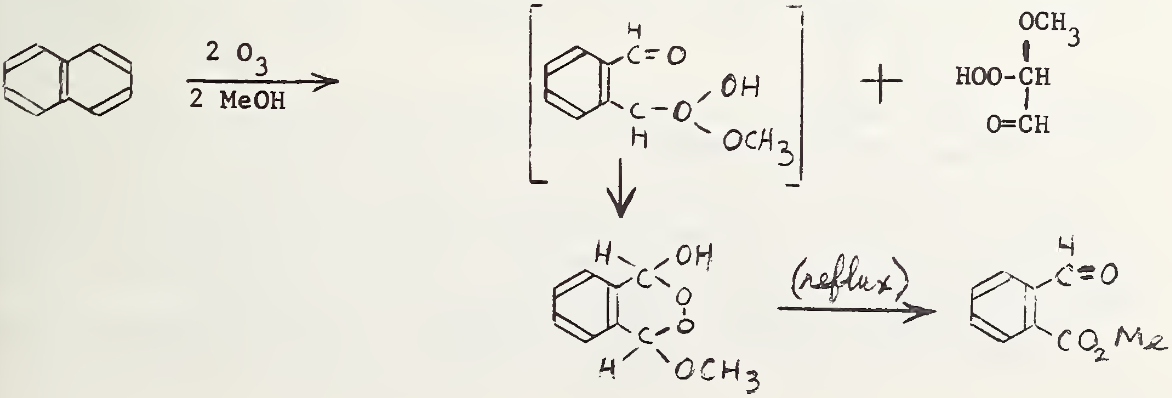


Dibenzo[c,g]phenanthrene (6387) (65%)

Other examples of attack by ozone at the bond (or bonds) of lowest bond-localization energy are given in table 3.

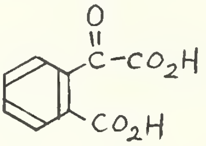
Examples involving attack by ozone at *para* or pseudo-*para* reactive centers, instead of (or as well as) at *ortho* reactive centers, are discussed in section 9.1.13.

(b) *In a participating solvent.* If ozonolysis is conducted in the presence of a participating solvent, such as methanol, the solvent combines with the ozonolysis product [116]. For example, ozonolysis of naphthalene in methanol gives 4-methoxy-2,3-benzodioxan-1-ol [122], which, on refluxing in methanol, gives methyl phthalaldehydate.

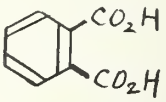


(6) *Potassium permanganate.* As discussed later (section 9.2.3 (6)), potassium permanganate probably gives a cyclic, manganate ester at the most reactive bond; in water, this presumed ester hydrolyzes immediately to the glycol. With some polycyclic, aromatic hydrocarbons, this glycol is now oxidized by the permanganate, with oxidative cleavage of the C–C bond of the glycol, affording aldehyde groups which are, in turn, oxidized to carboxyl groups.

The effect may differ, according as the solution is acid or alkaline. Thus, in alkaline solution, naphthalene is oxidized by permanganate to phthalonic acid [123,124], but in acid solution, the oxidation proceeds a stage further, giving phthalic acid [124]. Similarly, triphenylene is oxidized [114b] to mellitic acid.



Phthalonic acid

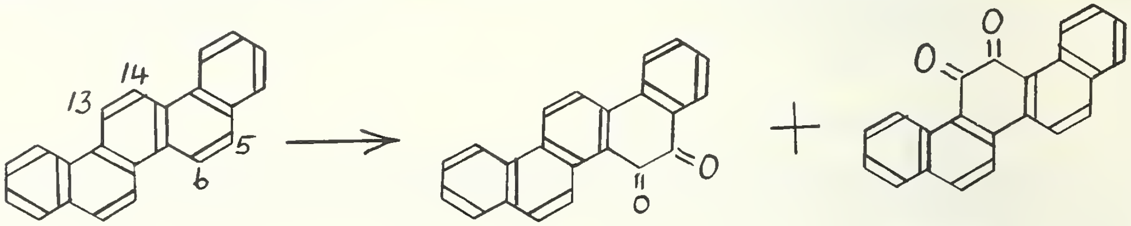


Phthalic acid

9.2.3. Oxidation of *ortho*-Methine Groupings

(1) *Chromium trioxide.* Chromium trioxide in glacial acetic acid, or sodium dichromate in sulfuric acid, may oxidize two adjacent methine groupings to the corresponding *ortho*-dione (see table 3). It has been suggested that a chromate ester is formed as the intermediate, as with ester formation by osmium tetroxide.

Oxidation of picene gives a mixture [125] of the 5,6-dione and the 13,14-dione, in the ratio of 3.6 to 1.

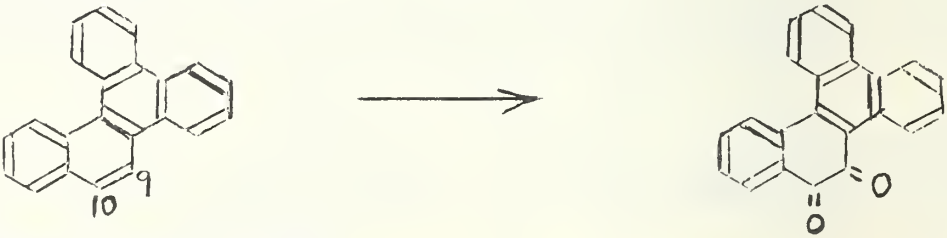


Picene (6384)

5,6-Picenedione

13,14-Picenedione

Similarly, benzo[*g*]chrysene gives the 9,10-dione [126].



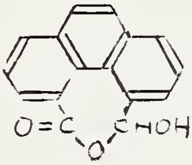
Benzo[g]chrysene (6385)

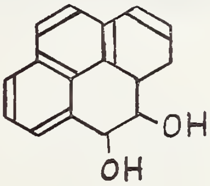
(2) *Hydrogen peroxide, catalyzed by osmium tetroxide.* The *o*-dione may be obtained by oxidation of two adjacent methine groups with hydrogen peroxide catalyzed by osmium tetroxide. The bond that, from calculations of bond order and localization energy, is the most reactive is the one attacked (see table 3).

Cook and Schoental [65a] stated that, on oxidation of pyrene with this reagent in *tert*-butyl alcohol, a mixture of 1,6-pyrenedione and 1,8-pyrenedione was formed. However, using the same reagent in *acetone,* Oberender and Dixon [127] obtained 4,5-pyrenedione. The 4,5-bond has the lowest bond-localization energy, and the 1,6- and 1,8-diones were not detected.

(3) *Iodic acid.* Iodic acid in glacial acetic acid, at the boiling point, oxidizes phenanthrene to phenanthrenequinone [128].

(4) *Osmium tetroxide and sodium periodate.* With this reagent, pyrene is oxidized exclusively at the 4,5-bond, giving [127] a 23 percent yield of 4,5-pyrenedione and a 24 percent yield of the lactol of 5-formyl-4-phenanthrenecarboxylic acid. Presumably, *the osmium tetroxide reacts first,* to give the 4,5-diol, and this is then oxidized to the 4,5-dione by the periodate.

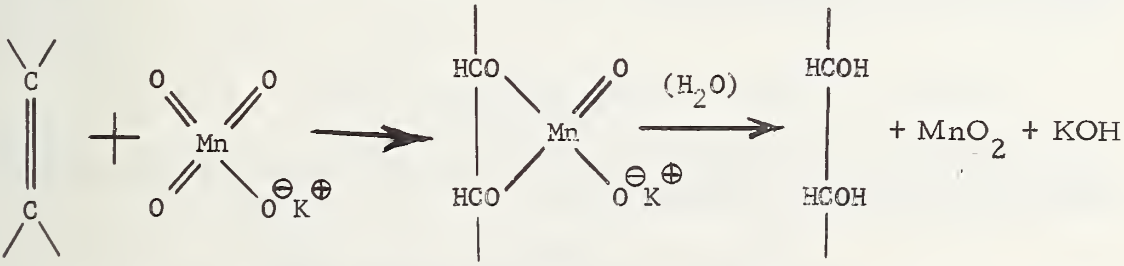




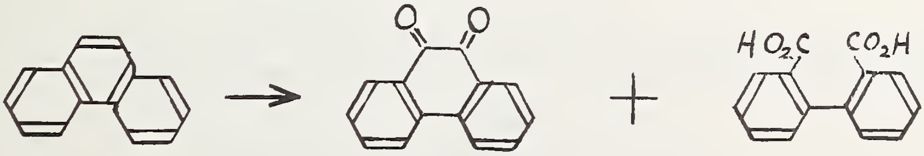
4,5-Dihydro-4,5-pyrenediol

(5) *Peroxyacetic acid.* This reagent may attack a reactive double bond, as for naphthalene, phenanthrene, benz[*a*]anthracene, and chrysene (see table 3).

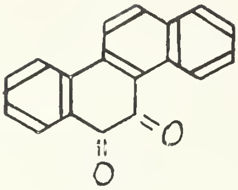
(6) *Potassium permanganate.* Potassium permanganate is capable of hydroxylating a double bond to give a glycol, isolation of which is difficult or impossible because *the glycol itself* is then subject to oxidation. However, where the glycol has been isolated and *cis-* or *trans-*diols *could* be formed (e.g., from cyclohexene), the product is exclusively the *cis-*(*erythro*)-diol, indicating that the addition involves formation of the cyclic, manganate ester.



With some hydrocarbons, oxidation then proceeds, to give the *o*-dione. Thus, phenanthrene gives [73,129] a 51 percent yield of phenanthrenequinone, together with less than 5 percent of diphenic acid.



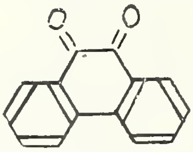
Similarly, chrysene gives the 5,6-dione [73].



5,6-Chrysenedione

(7) *Ruthenium dioxide and sodium periodate.* This reagent reacts with pyrene [127] at the 4,5-bond and also at the carbon atoms of greatest electron density, giving 11 percent of 4,5-pyrenedione, 2 percent of 1,6-pyrenedione, and 1 percent of the lactol of 4-formyl-5-phenanthrenecarboxylic acid, together with 10 percent of an unidentified aldehyde.

(8) *Selenium dioxide.* In the absence of a solvent, selenium dioxide has practically no action on phenanthrene; a 3 percent yield of the quinone is obtained [55a]. In suspension in water or dissolved in nitrobenzene, no quinone is formed [107a,b].



Phenanthrenequinone

10. Oxidative Degradation of an Alkyl Side-Chain

For polycyclic, aromatic hydrocarbons bearing an alphatic side-chain, some oxidants oxidize the side chain more readily than they attack the nucleus.

10.1. Chromium Trioxide

Used below 40° C, chromium trioxide (or chromic acid) in acetic anhydride oxidizes a methyl group to an aldehyde group.

$$\text{aryl—CH}_3 \xrightarrow{\text{CrO}_3} \text{aryl—CH(OAc)}_2 \xrightarrow{\text{CrO}_3} \text{aryl—CHO}$$

Hot chromium trioxide in acetic acid (or chromic acid in aqueous sulfuric acid) oxidizes an alkyl side-chain to a carboxyl group.

$$\text{aryl—(CH}_2)_{\underline{n}}\text{—CH}_3 \xrightarrow{\text{CrO}_3} \text{aryl—CO}_2\text{H}$$

10.2. Nitric Acid

For use as an oxidant, the nitric acid should be diluted; conditions for nitration should be avoided. A methyl group is then oxidized to a carboxyl group.

$$\text{aryl—CH}_3 \xrightarrow{\text{HNO}_3} \text{aryl—CO}_2\text{H}$$

10.3. Potassium Permanganate

An excess of potassium permanganate, in acid or alkali, oxidizes an alkyl side-chain to a carboxyl group.

$$\text{aryl}-(\text{CH}_2)_{\underline{n}}-\text{CH}_3 \xrightarrow{\text{KMnO}_4} \text{aryl}-\text{CO}_2\text{H}$$

11. Summary of Action of Various Oxidants

The various kinds of oxidation may be grouped in four main categories, according to the type of reaction involved. These are (1) one-center attack, (2) addition to a double bond, (3) addition at *para* centers, (4) formation of *o*-, pseudo-*p*-, or *p*-diones. Table 16 summarizes the kinds of action of the various oxidants under these four categories.

TABLE 16. *Action of various oxidants*

Oxidant	Kind of action[a]
Benzoyl peroxide	1,4
Chromium trioxide (or sodium dichromate)	1,2,4
Hydrogen peroxide plus osmium tetroxide	1,2,4
Iodic acid	4
Lead tetraacetate	1,3
Nitric acid, nitrates, nitrites	2,3,4
Nitrogen oxides	3,4
Osmium tetroxide plus pyridine (and hydrolysis)	2
Osmium tetroxide plus sodium periodate	4
Oxygen	1,2,3,4
Oxygen plus ultraviolet light	1,3
Oxygen plus vanadium pentoxide	2,4
Oxygen plus various catalysts	4
Ozone (with subsequent treatment)	1,2,3,4
Peroxyacetic acid	2,4
Peroxybenzoic acid	1,2
Potassium chlorate plus osmium tetroxide	4
Potassium permanganate	2,4
Ruthenium dioxide plus sodium periodate	4
Selenium dioxide	1,4

[a] Key: 1, one-center attack; 2, addition to a double bond; 3, addition at *para* centers; 4, formation of *o*-, pseudo-*p*-, or *p*-dione.

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