# 645. *The Oxidation of Some Higher Aromatic Hydrocarbons with Perbenzoic Acid.*

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Perbenzoic acid oxidation of anthracene, benzanthracene, naphthacene, 1 : 2 : 5 : 6-dibenzanthracene, and similar compounds in chloroform solution at 0° has been examined. In each case oxidation occurs in the *meso*-positions and not at potential ethylenic double bonds. The results accord with the view that perbenzoic acid is an electrophilic agent of a quite normal type.

Recent work (cf. Robertson and Waters, *J.*, 1948, 1578) has indicated that alkyl hydroperoxides may in part break down to free hydroxyl radicals which, as work in this laboratory has shown (Merz and Waters, this vol., pp. 2427, S 15), are able to oxidise benzene and other aromatic substances. It therefore seemed possible that analogous reactions might occur with acyl peroxides such as perbenzoic acid, $C_6H_5$·CO·O·OH. In this connection the brief report of Eckhardt (*Ber.*, 1940, **73**, 13) that of polynuclear aromatic hydrocarbons only the carcinogenic compounds were significantly attacked by perbenzoic acid in cold chloroform aroused interest, particularly since perbenzoic acid, like osmium tetroxide [which Cook and Schoental (*J.*, 1948, 170) and Badger (this vol., p. 456) have shown to attack polycyclic aromatic hydrocarbons in an unexpected manner] is widely used as a specific oxidiser of olefinic double bonds.

We have therefore examined the action of perbenzoic acid in chloroform solution at 0° on a number of hydrocarbons. We have isolated characteristic reaction products from the majority of them. In general our results accord with those of Eckhardt, but we have found that, given sufficient time, perbenzoic acid does appreciably attack many non-carcinogenic aromatic hydrocarbons, as the following table shows.

| | Atoms of oxygen taken up per mol. of hydrocarbon. | | |
|---|---|---|---|
| Hydrocarbon. | 1 Day. | 3 Days. | 5 Days. |
| Diphenylmethane | 0·28 | 0·33 | 0·35 |
| Triphenylmethane | 0·12 | 0·26 | 0·28 |
| Fluorene | 0·06 | 0·14 | 0·18 |
| Indane | 0·1 | 0·18 | 0·23 |
| Tetralin | 0·1 | 0·14 | 0·24 |
| Mesitylene | 0·6 | 1·1 | 1·7 |
| Acenaphthene | 2·0 | 3·1 | 3·3 |
| Anthracene | 1·5 | 1·8 | 1·9 |
| 1 : 2-Benzanthracene | 1·6 | 1·9 | 2·1 |
| 1 : 2 : 5 : 6-Dibenzanthracene | 1·6 | 3·0 | 3·7 |
| 9-Methylanthracene | 1·5 | 1·8 | 1·9 |

Few of these oxidations appear to proceed to completion: many virtually stop after about a week, even when the reaction mixture still contains both titratable peroxide and unchanged hydrocarbon, and a complicated sequence of consecutive reactions is evidently involved. Thus, as in the case of lead tetra-acetate oxidation (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 1893, 2542; Fieser and Putnam, *ibid.*, 1947, **69**, 1038), simple connections between structure, rates of oxidation, and carcinogenic properties cannot clearly be traced.

Whilst the kinetics of the oxidations are complex, so too are the mixtures of oxidation products which are formed. Anthracene was oxidised in part to anthraquinone and in part to a phenol, possibly anthraquinol, which was readily autoxidised in alkaline solution to yield a further quantity of anthraquinone; anthrone however could not be detected. Anthraquinone was also isolated from 9-methylanthracene. Both 1 : 2-benzanthracene and 1 : 2 : 5 : 6-dibenzanthracene were oxidised, in part, to their *meso*(9 : 10)-quinones, and there was no evidence of oxidation in the "K" or "phenanthrene positions" 3 and 4 which are prone to attack by osmium tetroxide. Similarly naphthacene was oxidised to naphthanthraquinone. Traces of benzophenone were formed from diphenylmethane, and traces of α-tetralone from tetralin.

Thus the action of perbenzoic acid on polycyclic aromatic hydrocarbons is not directly related to the "double-bond characters" of particular parts of these molecules, but seems to follow the same course as the oxidations which can be effected by chromium trioxide and lead tetra-acetate. Again, all these oxidations are very much slower than is the normal Prileschajew reaction between perbenzoic acid and an olefin.

Free-radical theories of oxidation by perbenzoic acid are to be discounted because those hydrocarbons which are easily autoxidised, *e.g.*, tetralin and indane, are amongst the least prone to attack. In contrast, oxidation seems to set in at the expected reactive centres of aromatic nuclei rather than at attached methylene groups, and this is in full accord with Swern's view (*J. Amer. Chem. Soc.*, 1947, **69**, 1692) that the per-acids are electrophilic reagents which tend to provide electropositively-polarised hydroxyl groups rather than neutral hydroxyl radicals.

Finally we examined very briefly the action of ozone on anthracene, since this did not appear to be fully known, and found that here again anthraquinone was an eventual reaction product. In view of the recent work of Cavill, Robertson, and Whalley (this vol., p. 1567) on the oxidations of some of the hydrocarbons which have been referred to above, this is but to have been expected.

## EXPERIMENTAL.

*Oxidation of Anthracene.*—Anthracene (4 g.), purified by distillation with ethylene glycol (Fieser, "Experiments in Organic Chemistry," 1941, p. 345, footnote), was dissolved in dry, freshly purified, alcohol-free chloroform (260 ml.) containing perbenzoic acid [3·6 g. recently made in N/10-solution in chloroform (Vogel, " Practical Organic Chemistry," p. 766)] and kept in a refrigerator for 6 days. After the chloroform solution had been shaken with sodium hydrogen carbonate solution to remove benzoic acid, phenols were separated by extraction under nitrogen with 7% sodium hydroxide solution, and the remaining liquid was evaporated to dryness. From the brownish solid some unchanged anthracene (m. p. 196°) was separated by fractional crystallisation from alcohol. The remainder of the product was dissolved in benzene and passed down a column of activated alumina. In this way anthracene and anthraquinone (m. p. and mixed m. p. 273°, after recrystallisation from benzene) were successively eluted and separated, leaving only a small amount of dark, strongly adsorbed residue.

The sodium hydroxide solution was deep red. A portion which had been exposed to the air for 3 days was found to have deposited a brownish solid which after purification proved to be anthraquinone. Acidification of the phenolic fraction gave a gum from which attempts were made, without success, to separate anthrone. On oxidation with chromic acid this crude material gave pure anthraquinone.

*Oxidation of* 9-*Methylanthracene*.—0·5 G. of this hydrocarbon (Sieglitz and Marz, *Ber.*, 1923, **56**, 162) was dissolved in a chloroform solution of perbenzoic acid (1·0 g.). The solution became deep-yellow. After storage in a refrigerator for several days it was shaken with dilute sodium hydroxide solution, dried, and evaporated, whereupon long needles of anthraquinone separated (m. p. and mixed m. p. 274°, from benzene); a further quantity of this was obtained from the mother-liquors by chromatographic separation on alumina.

*Oxidation of* 1 : 2-*Benzanthracene*.—Benzanthracene (0·5 g.) (Fieser, " Organic Reactions," Vol. I, p. 139), which had been purified chromatographically, was dissolved in a N/10-solution of perbenzoic acid (3·0 g.) in chloroform and stored in a refrigerator. The solution became yellow and then orange, and finally reverted to yellow. After 6 days it was washed twice with 5% sodium hydroxide solution and then with water, dried, and evaporated. The residual reddish resin was dissolved in benzene and passed through an alumina column. After a small quantity of unchanged hydrocarbon had been eluted, a lemon-yellow band followed, and this fraction on evaporation gave an orange-yellow solid which sublimed at its m. p. (144°). Two recrystallisations from methanol gave yellow needles of *meso*benzanthraquinone, m. p. 166° (0·12 g.); this m. p. was unchanged after admixture with an authentic specimen prepared by oxidising benzanthracene with chromic acid. The residue from the column was a red amorphous material which failed to sublime *in vacuo* or to crystallise.

*Oxidation of* 1 : 2 : 5 : 6-*Dibenzanthracene*.—Dibenzanthracene (0·5 g.) was dissolved in 7 equivalents of a N/10-solution of perbenzoic acid in chloroform and stored in a refrigerator. After small portions had been removed for analyses during a week, the remainder of the solution was worked up as described above. Chromatographic fractionation on alumina separated first some unchanged hydrocarbon, and then *meso*dibenzanthraquinone, which crystallised excellently, in long orange-yellow needles from a mixture of chloroform and ethyl alcohol and had m. p. 250° (Cook, *J.*, 1932, 1477, gives the m. p. as 248—250°). It gave a red solution with alkaline sodium dithionite.

*Oxidation of Naphthacene*.—The hydrocarbon (0·3 g.) was suspended in purified chloroform containing perbenzoic acid (1·5 g.). After 5-days' storage in the refrigerator, all the hydrocarbon having then dissolved, the liquid was shaken with sodium hydroxide solution and then water. After evaporation, the residue was dissolved in benzene and passed through an alumina column. The first band to be eluted was red and consisted of unchanged naphthacene, but the next band was orange-yellow and after evaporation and recrystallisation yielded naphthacenequinone, m. p. 294°.

Oxidation of fluorene, diphenylmethane, and tetralin was carried out in a similar way, though with all of these very little reaction occurred. Small amounts of the 2 : 4-dinitrophenylhydrazones of the corresponding ketones were obtained from each and were identified by mixed m. p.s.

*Ozonolysis of Anthracene*.—Ozonised oxygen was passed for 5 hours through a solution of purified anthracene (4 g.) in acetic anhydride (350 ml.) at 0°. The resulting yellow solution was carefully poured on ice–water and set aside overnight. The yellow solid which separated was collected, dissolved in benzene, and passed down an alumina column. The first band to be eluted contained anthracene, and the second anthraquinone (m. p. and mixed m. p. 273°).

*Relative Speeds of Oxidation*.—The hydrocarbons listed in the table were each dissolved in a chloroform solution of perbenzoic acid to give initial mixtures containing 4 mols. of perbenzoic acid per mol. of hydrocarbon. They were stored just below 0° in a refrigerator in glass-stoppered vessels, and samples were taken at daily intervals for titration with sodium thiosulphate after addition of potassium iodide and acetic acid. With each set of experiments there was also stored a comparison batch of perbenzoic acid in the same sample of chloroform. When due care was observed in preparing the solutions, the drop in titre of this blank reagent was quite small and decidedly less than that of any of the reacting mixtures. Reactions were often continued for 10—14 days, but, though oxidation frequently ceased after 5—7 days, in few of the mixtures was all the perbenzoic acid consumed. The data summarised in the table indicate only the significant trends of the oxidation curves for each hydrocarbon and have been computed by subtracting the drop in titre of the blank reagent.

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