649. *The Ozonolysis of Polynuclear Aromatic Hydrocarbons. Part I.*

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The reaction of ozone with both fluorene and benzo[*b*]fluorene has been shown to occur at the aromatic portion of the molecule and only to a very limited extent at the methylene bridge. From fluorene, homophthalic acid was the main product accompanied by a small amount of fluorenone. Benzo[*b*]fluorene gave equal amounts of homophthalic and phthalic acid and rather less fluorene-2,3-dicarboxylic acid.

The ozonolysis of fluorenone yielded phthalic acid. This was also a product from benzo[*b*]fluorenone, with a similar quantity of fluorenone-2,3-dicarboxylic acid.

Stepwise degradation of solvent fractions of coal tar pitch may offer a possible method for the more precise designation of the structure of the aromatic nuclei they contain. To provide data for such a study the ozonolysis of selected polynuclear hydrocarbons has been studied. Part of this work has already been summarised.[1]

This paper describes the ozonolysis of fluorene, benzo[*b*]fluorene, and the derived fluorenones. The usual oxidising agents attack fluorene at the reactive methylene group, giving fluorenone as the main product.[2] Similarly, with ozone, Cavill *et al.*[3] have reported that compounds containing reactive methylene groups are converted mainly into the ketones with occasionally some intermediate alcohol formation; fluorene, for example, is stated to give 24% of fluorenone.

This tendency is not apparent from the results of the present work. When fluorene reacted with two mols. of ozone in chloroform or *sym*-tetrachloroethane and the product was decomposed with alkaline peroxide, only 6% of fluorenone was obtained, the major product (64%) being homophthalic acid; some unchanged fluorene (13·8%) was recovered. When a three-molar proportion of ozone was used all the fluorene reacted, the yields of homophthalic acid and fluorenone remaining almost unaltered.

Fluorenone reacted only very slowly with ozone, giving 73% of phthalic acid. The absence of this acid from the products of the fluorene ozonolysis confirms the finding that the ketone is not formed in any appreciable quantity even as an intermediate product.

Benzo[*b*]fluorene is oxidised by chromic acid to the ketone.[4] With a two-molar proportion of ozone in chloroform solution it gives homophthalic (29%), phthalic (30%), and fluorene-2,3-dicarboxylic acid (19%). No benzo[*b*]fluorenone was detected although it might have been present since from the esterification product of the crude fluorene-2,3-dicarboxylic acid was separated a small amount of the dimethyl ester of the corresponding fluorenone diacid which was shown to be an ozonolysis product of the ketone; alternatively this acid could have been an oxidation product of the fluorene diacid.

It is concluded that, under the conditions used, the reactive methylene group in fluorene and benzo[*b*]fluorene is only slightly attacked by ozone.

Badger has classified ozone with osmium tetroxide and diazoacetic ester as double-bond reagents;[5] with aromatic molecules the attack occurs at the most reactive double bonds. Wibaut, on the other hand, suggests that ozone behaves as an electrophilic reagent attacking the positions of highest electron-density.[6] The most reactive carbon atom in the fluorene molecule, as indicated by nitration, halogenation, etc., is that at the 2-position.

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[1] Copeland, Dean, and McNeil, *Chem. and Ind.*, 1959, 329; 1960, 98.

[2] Fittig and Schmitz, *Annalen*, 1878, **193**, 141; Graebe and Rateanu, *ibid.*, 1894, **279**, 258; Randall, Benger, and Groocock, *Proc. Roy. Soc.*, 1938, *A*, **175**, 432.

[3] Cavill, Robertson, and Whalley, *J.*, 1949, 1567.

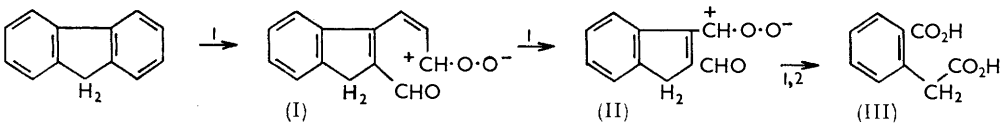
[4] Koelsch, *J. Amer. Chem. Soc.*, 1933, **55**, 3885.

[5] Badger, *Quart. Rev.*, 1951, **5**, 155.

[6] Wibaut, *J. Chim. Phys.*, 1956, **53**, 111

The most reactive bond should be the 1,2-linkage since Burns and Iball[7] have shown by quantitative crystal analysis that this is the shortest. Pullman and Berthier,[8] however, suggested on the basis of calculations of bond and valence indices by the molecular-orbital method that the 3,4-linkage has the highest bond order. Their claim that the 1,9a-bond has the next highest order is markedly at variance with the implications of the bond-length measurements. If it is assumed that the 1,2-bond is the most reactive, then reaction with ozone will involve this bond irrespective of whether ozone behaves as an electrophilic or a double-bond addition reagent. Only if it acts as a normal oxidising agent will reaction occur at the methylene group.

As formation of homophthalic acid as the main product of ozonolysis of fluorene involves complete rupture of a benzene ring it is impossible to say whether attack occurs first at the 1,2- or the 3,4-bond. If 1,2-attack is assumed a reaction scheme can be postulated as shown, based on the mechanism suggested by Criegee *et al.*[9] and applied to polycyclic hydrocarbons by Bailey.[10] The initial complex assumes the zwitterion structure (I) containing the vinylindene moiety. Another mol. of ozone then reacts to give the zwitterion (II), which on further reaction followed by decomposition with alkaline peroxide gives homophthalic acid (III).



Reagents: 1, O_3; 2, H_2O_2–NaOH.

It has previously been observed that ozonolysis of indene in ethanol gives a peroxide which could be converted into homophthalic acid in 82% yield.[11] Also 2,3-diphenylindene gives an ozonide which ultimately yields 2-phenacylbenzophenone.[12] In both these examples, as in the above scheme, the methylene group remains intact.

Similar reactions, sufficiently explained by the chart, could occur during the ozonolysis of fluorenone. The production of phthalic acid is paralleled by that of benzoic and *o*-propionylbenzoic acid on ozonolysis of 3-ethyl-2-phenylindenone.[13]

The lengths and orders of the bonds in benzo[*b*]fluorene have not been determined. Bond multiplicities indicate that the 1,2-, 3,4-, 5,5a-, and 10a,11-linkages should be the most reactive. This suggests that the compound could be regarded as a 2,3-substituted naphthalene, for which 90% of the reaction occurs at the substituted ring.[14] With benzo[*b*]fluorene this preference is not so marked: reaction with two mols. of ozone gives 30% of phthalic and 29% of homophthalic acid, as against 19% of fluorene-2,3-dicarboxylic acid obtained by reaction at the unsubstituted ring. Some unchanged benzofluorene (4·6%) was also recovered.

One step in our scheme, (V) ⟶ (III), is known to be achieved by hydrogen peroxide.[15]

In the ozonolysis of benzo[*b*]fluorenone a rather larger yield (34%) of the diacid (VI) was obtained than from the hydrocarbon. Phthalic acid was the only other product isolated. The reaction sequence is presumably similar to that for benzo[*b*]fluorene. Here scission of the ketone corresponding to (IV) would yield 2 mols. of phthalic acid and the

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[7] Burns and Iball, *Nature*, 1954, **173**, 635.

[8] Pullman and Berthier, *Bull. Soc. chim. France*, 1948, 551.

[9] Criegee *et al.*, *Annalen*, 1949, **564**, 9; 1953, **583**, 12; *Chem. Ber.*, 1954, **87**, 766; 1955, **88**, 1878.

[10] Bailey, *Chem. Rev.*, 1958, **58**, 925.

[11] Warnell and Shriner, *J. Amer. Chem. Soc.*, 1957, **79**, 3165.

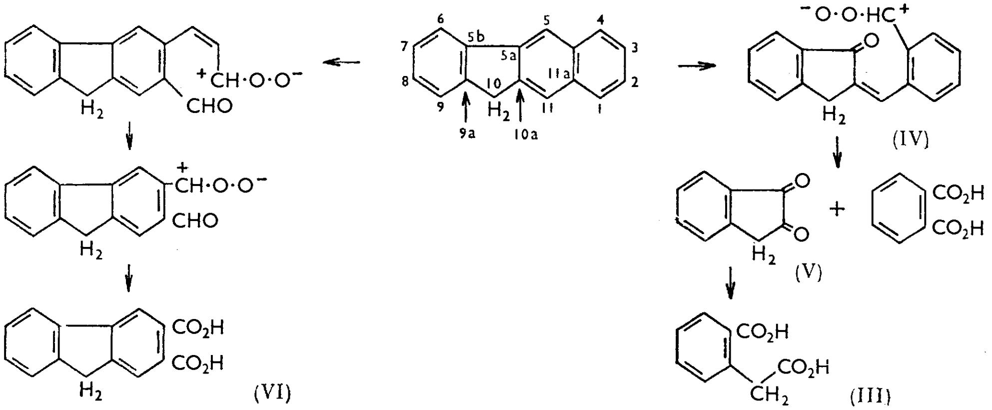
[12] Bailey, *Chem. Ber.*, 1954, **87**, 993.

[13] Frank, Eklund, Richter, Vanneman, and Wennerberg, *J. Amer. Chem. Soc.*, 1944, **66**, 1; Criegee, de Bruyn, and Lohaus, *Annalen*, 1953, **583**, 19.

[14] Wibaut and Kampschmidt, *Proc. k. ned. Akad. Wet.*, 1950, **53**, 1109.

[15] Perkin, Roberts, and Robinson, *J.*, 1912, **101**, 232.

quoted yield (36%) is based on this assumption. Thus benzo[*b*]fluorenone is attacked by ozone at both rings of the naphthalene portion to a roughly equal extent. The same rings are attacked when the ketonic is replaced by a methylene group, the one adjacent to the five-membered ring being preferred.



Experimental

Apparatus.—The electrolytic ozoniser used was similar to that described by Boer.[16] The ozone content of the output gas varied between 10 and 15% w/v depending on the construction of the anode, but with none of the anodes used was difficulty experienced in maintaining a constant output during a daily run. The ozone–oxygen mixture, dried by passage through glass spirals immersed in ethanol–solid carbon dioxide, was led into the base of a glass reaction vessel. This was equipped with a recycle stirrer placed immediately above the ozone inlet, thus giving a very effective gas–liquid contact. The amount of ozone absorbed was estimated iodometrically as the difference between the ozone content of the exit gas and that in a blank run under identical conditions.

Solvents.—The carbon tetrachloride, chloroform, and *sym*-tetrachlorethane were purified before use as described by Vogel.[17]

Decomposition of the Products of Ozonolysis.—To obtain acidic rather than aldehydic materials from the ozonolysis products, oxidative decomposition methods were used, alkaline peroxide being preferred.

Ozonolysis of Fluorene.—Fluorene, m. p. 114° (1·66 g., 10 mmoles), in chloroform (40 ml.) at 0° was treated with ozone until 20 mmoles had been absorbed. The vessel was purged with nitrogen, and 10% aqueous sodium hydroxide (20 ml.) and 30% hydrogen peroxide (10 ml.) were added. The whole was heated at 60° with stirring for 1 hr. The chloroform was distilled off and the alkaline liquors were acidified with 10% hydrochloric acid. The yellow precipitate (0·5 g.) was filtered off and chromatographed on alumina, giving unchanged fluorene (0·23 g., 13·8%), fluorenone (0·1 g., 6%), m. p. and mixed m. p. 84°,, and an orange resin (0·13 g.). The acidic filtrate was evaporated to dryness and the residue extracted with acetone in a Soxhlet apparatus. Removal of the acetone left a fawn powder (1·1 g.) which on crystallisation from 10% hydrochloric acid (charcoal) gave homophthalic acid (0·64 g., 64%), m. p. and mixed m. p. 182°; its identity was confirmed by its infrared spectrum.

When this experiment was repeated with 3 mols. of ozone all the hydrocarbon reacted, giving fluorenone (0·09 g., 6%) and homophthalic acid (1·12 g., 62%) in almost the same yield as before.

Ozonolysis of Fluorenone.—Ozone was passed through a solution of fluorenone (1·80 g., 10 mmoles) in carbon tetrachloride (60 ml.) at −20° until 20 mmoles had been absorbed (200 min.). The solution, after treatment with alkaline peroxide and removal of the solvent, was acidified with 10% hydrochloric acid. Unchanged fluorenone (0·89 g., 49·4%) was

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[16] Boer, *Rec. Trav. chim.*, 1948, **67**, 217; 1951, **70**, 1020.

[17] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., 2nd edn., p. 174.

filtered off and the filtrate evaporated to dryness. A hot acetone extract of the residue yielded a solid which on crystallisation from 10% hydrochloric acid afforded plates of phthalic acid (0·72 g., 73%), m. p. 196° (decomp.) and mixed m. p. 197° (decomp.).

Benzo[b]*fluorene*.—(*a*) The synthesis used was that described by Koelsch [4] except that an alternative method of dehydrogenation was used in the last stage. 1,2,3,4-Tetrahydrobenzo-[*b*]fluorene (2 g.) was heated under reflux for 12 hr. with a 10% palladium–charcoal catalyst (0·5 g.) in redistilled *p*-cymene (50 ml.) in a stream of carbon dioxide. After removal of the catalyst and solvent, benzo[*b*]fluorene remained as a solid residue which crystallised in plates (1·75 g., 89%), m. p. 210°, from benzene. Koelsch obtained a 22% yield of material, m. p. 204—206° by using sulphur.

(*b*) Benzo[*b*]fluorenone (13·3 g.), potassium hydroxide (13·3 g.), ethylene glycol (350 ml.), and 80% hydrazine hydrate (40 ml.) were together heated under reflux for 6 hr. Water and excess of hydrazine were distilled off until the temperature rose to 197—198°. After a further 8 hours' heating, during which the red solid hydrazone gradually disappeared, the mixture was cooled and poured into 10% hydrochloric acid (1500 ml.), and the precipitated benzo[*b*]fluorene (12·24 g., 98%), m. p. 210°, was filtered off.

Ozonolysis of Benzo[b]*fluorene*.—Benzo[*b*]fluorene (2·16 g., 10 mmoles) was ozonised in chloroform (60 ml.) at 0° until a 2-molar absorption occurred. After treatment with alkaline peroxide and removal of the solvent as before, the mixture was filtered to remove a yellow powder (0·32 g.) which was chromatographed on alumina, giving unchanged starting material (0·1 g., 4·6%) and a brown resin (0·21 g.). Acidification of the filtrate gave a powder which on crystallisation from aqueous acetone (charcoal) yielded *fluorene*-2,3-*dicarboxylic acid* (0·48 g., 19%), m. p. 264—265°, as pale yellow needles (Found: C, 70·65; H, 4·2%; equiv., 127. $C_{15}H_{10}O_4$ requires C, 70·9; H, 4·0%; equiv., 127). Its *dimethyl ester* separated from light petroleum (b. p. 100—120°) in colourless needles, m. p. 86° (Found: C, 72·1; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). Decarboxylation of the acid with copper powder and quinoline gave bifluorenylidene, m. p. and mixed m. p. 187°. The acid filtrate after removal of the fluorenone diacid was evaporated to dryness and extracted with hot acetone. Fractional crystallisation of the acetone-soluble material from ethyl acetate, in which phthalic is less soluble than homophthalic acid, followed by crystallisation of the fractions from water, gave these two acids in yields of 30% (0·46 g.) and 29% (0·50 g.) respectively.

In a repetition of this experiment the esterification of the crude fluorenedicarboxylic acid gave a small quantity, about 10%, of dimethyl fluorenone-2,3-dicarboxylate, m. p. and mixed m. p. 154°.

Benzo[b]*fluorenone*.—This was prepared in 36% yield by condensing indan-1-one with phthalaldehyde and crystallised in yellow prisms, m. p. 154°, from ethanol.[18] Indan-1-one was obtained in 57% yield by adding a solution of chromic oxide (125 g.) in acetic anhydride (1 l.) to one of indane (100 g.) in the same solvent (250 ml.) during 2 hr. at 5—10°. After a further 2 hours' stirring the mixture was poured on ice and extracted with ether. The solution was washed, dried and evaporated, and the residue distilled under reduced pressure, giving indane (13·6 g.), b. p. 85—95°/23 mm., and indan-1-one (57·3 g.), b. p. 127—130°/23 mm., m. p. 40—42°.

Ozonolysis of Benzo[b]*fluorenone*.—Benzo[*b*]fluorenone (2·30 g., 10 mmoles) was ozonised in chloroform (60 ml.) at 0° until 20 mmoles had been taken up. Treatment with alkaline peroxide and removal of the solvent yielded a yellow resin (0·18 g.) which was filtered off. Acidification of the filtrate gave crude fluorenone-2,3-dicarboxylic acid (0·99 g., 34%), m. p. 314—316°. Crystallisation from acetic acid gave yellow needles, m. p. 320—321° (sealed and open tubes) (Found: C, 66·7; H, 3·2. Calc. for $C_{15}H_8O_5$: C, 67·2; H, 3·0%). The anhydride, prepared from the acid by treatment with acetic anhydride, crystallised from this solvent in yellow needles, m. p. 322—323° (Found: C, 72·0; H, 2·5. Calc. for $C_{15}H_6O_4$: C, 72·0; H, 2·4%). It gave a dimethyl ester, yellow needles [from light petroleum (b. p. 100—120°)], m. p. 154° (Found: C, 68·9; H, 4·2. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1%). Lothrop and Coffman [19] give m. p. 250—275° for the acid, 322—323° for the anhydride, and 131—133° for the ester. Decarboxylation of the acid with copper powder and quinoline gave fluorenone (54%). The acidic filtrate after removal of the fluorenone diacid was evaporated to dryness and the residue extracted with

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[18] Thiele and Schneider, *Annalen*, 1909, **369**, 287; Thiele and Wanscheidt, *ibid.*, 1910, **376**, 269.

[19] Lothrop and Coffman, *J. Amer. Chem. Soc.*, 1941, **63**, 2564.

acetone; the extracted material gave phthalic acid (1·20 g., 36%) on crystallisation from 10% hydrochloric acid.

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