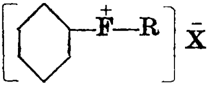
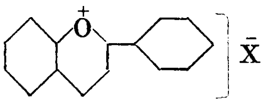
CCCLXXI.—*The Orienting Influence of Oxonium Oxygen. The Nitration of 2-Phenylbenzopyrylium Perchlorate and Ferrichloride.*

By Raymond James Wood Le Fèvre.

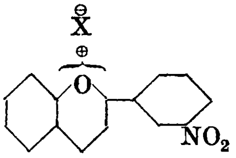
Among those elements which become orienting poles by passing into the " onium " state, the element with the numerically largest positive nucleus will be the most electron-attracting and, therefore, where aromatic substitution is concerned, the least *op*-directing. Hence, also, the most difficult nitrations (compare Ingold and Shaw, J., 1927, 2918), in which *m*-derivatives alone would be formed, must be expected among the hypothetical fluorinium salts (I). Similarly, oxonium-containing kations (*e.g.*, 2-phenylbenzopyrylium, II) should undergo substitution with less readiness and with a higher resulting yield of *m*-substituted product than the analogously constituted ammonium group (*e.g.*, 2-phenylquinolinium).



(I.)



(II.)



(III.)

The failure of previous attempts to discover the orienting nature of oxygen (Le Fèvre, J., 1928, 3249) by the nitration of dibromoxanthone in sulphuric acid solution was probably due to rapid nitration of the free xanthone (containing bicovalent oxygen) present in small quantities in equilibrium with the corresponding xanthonium salt, which would be attacked by nitric acid to a very small extent only (see later, and compare Vorländer's explanation of the *op*-nitration of *N*-phenyl-γ-pyridone).

The nitrations of the ferrichloride and perchlorate of 2-phenylbenzopyrylium (II) now to be described proceeded in the anticipated manner, being exceedingly difficult to effect and giving the 3′-*nitro*-compounds (III), the nitro-group having, as usual, entered the nucleus more remote from the positive pole (compare Drumm, Reilly, and Moore, J., 1928, 563). The constitution (III) was confirmed by direct synthesis from *m*-nitroacetophenone and salicylaldehyde. The nitration products were never obtained in yields greater than *ca.* 86%, but were in all cases practically pure. The 14% deficiency may have been due to (1) destruction of 3′-nitro-2-phenylbenzopyrylium salts by nitric acid (this undoubtedly did occur, the maximum yield of nitro-product being obtained by about 40 hours' nitration at the ordinary temperature), (2) hydrolysis and subsequent oxidation of the so-formed initial material (test experiments showed that, under the conditions of nitration employed, considerable destruction of salicylideneacetophenone took place), and (3) formation and destruction of the isomeric 2′- or 4′-nitrophenylbenzopyrylium salts (no 4′-*nitro-2-phenylbenzopyrylium perchlorate*, obtained synthetically from *p*-nitroacetophenone and salicylaldehyde, could be recovered after solution for 2 days in fuming nitric acid).

These results with oxonium salts and preliminary experiments (and known analogies) with the related quinolinium salts suggest that in both cases nitration in the *m*-position may predominate to such an extent that comparison will be impossible. If so, the inquiry will be extended to the benzylbenzopyrylium and benzylquinolinium groups and even to the corresponding phenylethyl compounds.

EXPERIMENTAL.

Preparation of Salicylideneacetophenone.—A hot solution of potassium hydroxide (30 g.) in water (25 c.c.) was added to a mixture of salicylaldehyde (25 g.), acetophenone (16 g.), and rectified spirit (100 c.c.). After 24 hours, the red crystalline paste of potassium salt was collected and stirred into an excess of 50% acetic acid–water. The resulting yellow powder gave pure salicylideneacetophenone (about 20 g.) after one crystallisation from spirit.

2-*Phenylbenzopyrylium Ferrichloride and Perchlorate.*—To a gently boiling solution of salicylideneacetophenone (14 g.) in glacial acetic acid (100 c.c.), concentrated hydrochloric acid (20 c.c.) was slowly added. As soon as the red colour thus produced became yellow, perchloric acid (50 c.c.; *d* 1·12) was run in, followed by 100 c.c. of cold water. The perchlorate crystallised at once in pearly yellowish-green plates (17 g.), m. p. 178—179°. Addition of almost saturated ferric chloride solution instead of perchloric acid gave the ferrichloride, which, after crystallisation from acetic acid, had m. p. 126—128° (Decker and von Fellenberg, *Annalen*, 1907, **356**, 303, give m. p. 125—129° corr.).

Nitrations of the Perchlorate.—The perchlorate was dissolved in the nitrating acid (10 parts by wt.) and after a definite time the solution was diluted with water (1 vol.), and an excess of perchloric acid added; the nitrated perchlorate then crystallised.

The nitrations with nitric acid (*d* 1·4 or 1·5) alone at 15° and at 80° for times varying from 5 minutes to 24 hours were unsatisfactory, unchanged material or gum and impure mononitro-derivative being obtained. With a mixture of sulphuric and nitric (*d* 1·5) acids (1 : 3 by vol.) at 15°, the yields of 3′-nitro-derivative obtained after 40, 48, and 89 hours were 86, 70, and 68%, respectively.

3′-*Nitro-2-phenylbenzopyrylium perchlorate* crystallised from acetic acid–perchloric acid solution in small orange prisms, m. p. 239—241° after softening from *ca.* 230° (Found : N, 4·2. $C_{15}H_{10}O_7NCl$ requires N, 4·0%).

Nitration of 2-*Phenylbenzopyrylium Ferrichloride.*—A solution of the ferrichloride (2 g.) in 20 g. of nitric acid (*d* 1·5), after being left for 68 hours at the ordinary temperature, was diluted with 20 c.c. of water, and an excess of ferric chloride solution added. The precipitated ferrichloride solidified slowly (m. p. 131—141°) and then crystallised from acetic acid as a yellow powder, m. p. 145—147°.

Synthesis of 3′-*Nitro-2-phenylbenzopyrylium Salts.*—A solution of salicylaldehyde (2·4 g.) and *m*-nitroacetophenone (3·2 g.) in 50 c.c. of 99% formic acid was treated with dry hydrogen chloride for

12 hours. The crystalline magma formed was collected, washed with hydrochloric acid, and extracted with boiling alcohol; the residue, m. p. 252°, was apparently *salicylidene*-m-*nitroacetophenone*, but satisfactory analyses were not obtained (Found : N, 6·4. $C_{15}H_{11}O_4N$ requires N, 5·2%). Addition of excess of perchloric acid to the acid filtrate gave a crystalline perchlorate, m. p. 240—243° (Found : N, 4·1. Calc. : N, 4·0%), admixture of which with the crude or recrystallised nitration product of 2-phenylbenzopyrylium perchlorate (see above) raised the m. p. in both cases.

The use of concentrated ferric chloride solution in place of perchloric acid gave the corresponding ferrichloride, which, after one crystallisation from acetic acid–ferric chloride solution, had m. p. 146—150° and caused no depression in the m. p. of the nitration product of 2-phenylbenzopyrylium ferrichloride when mixed with it.

Synthesis of 4'-Nitro-2-phenylbenzopyrylium Perchlorate.—Salicylaldehyde (1·2 g.), *p*-nitroacetophenone (1·6 g.), and formic acid (20 c.c.) were treated as in the case of the analogous *m*-nitro-derivative. A precipitate of salicylidene-*p*-nitroacetophenone (?), m. p. 297—298°, was obtained as golden needles. The formic acid filtrate, after slight dilution, was repeatedly extracted with chloroform until the latter was no longer coloured green. Treatment with an excess of perchloric acid then gave *4'-nitro-2-phenylbenzopyrylium perchlorate* as dark orange needles with a copper-bronze reflex; m. p. *ca.* 220°, decomp. *ca.* 225° (Found : N, 4·2%).

As a rough indication of the amounts of 2'- and 4'-nitro-2-phenylbenzopyrylium perchlorates which were (if at all) contaminating the nitration product from 2-phenylbenzopyrylium perchlorate, the m. p. of a mixture of 1 part of the 4'-nitro-compound and 10 parts of 3'-nitro-2-phenylbenzopyrylium perchlorate (m. p. 240—243°) was determined. The mixture began to shrink at 190°, definitely softened at *ca.* 205°, and ran at 211°. The crude nitration product generally softened at 225—230° and ran at *ca.* 236—237°.

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