[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

Benzopyrylium Salts. IV. Nitration of 2,3-Diphenyl-benzopyrylium Perchlorate

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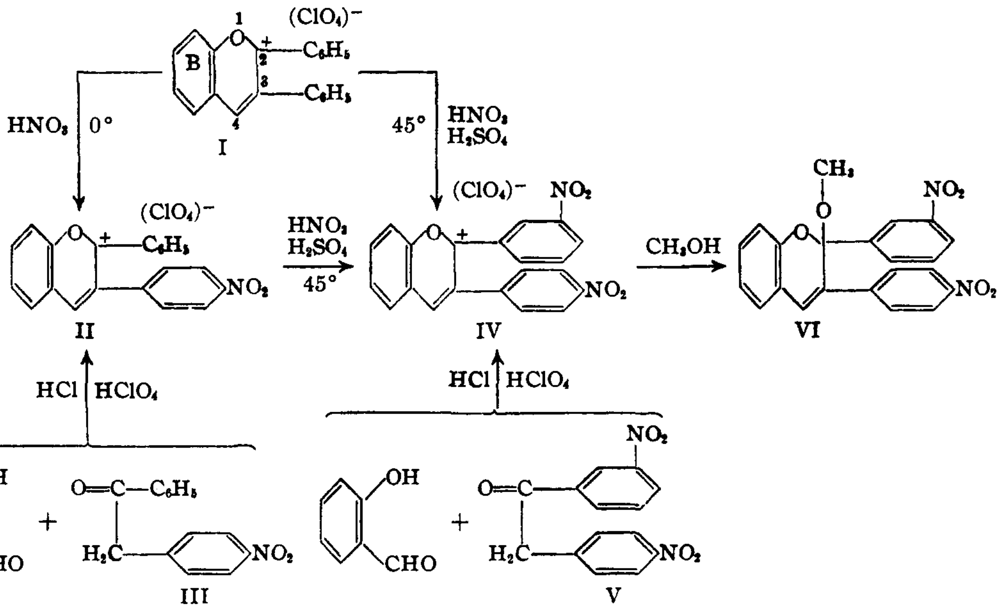
One of the most interesting reactions of flavylium salts is their behavior on nitration. Le Fevrè[1] showed that nitration of flavylium perchlorate produced the 3'-nitro derivative. In the present investigation the nitration reactions have been extended to a study of 2,3-diphenylbenzopyrylium perchlorate (I) in order to establish the orientation of the substituents and relative ease of substitution in the two phenyl groups.



Treatment of 2,3-diphenyl-benzopyrylium perchlorate (I) with fuming nitric acid at 0° produced a 53% yield of the mono-nitro derivative (II). The latter was best purified and characterized by conversion to its ferrichloride. The structure of II was established by synthesis from salicylaldehyde and α-(*p*-nitrophenyl)-acetophenone (III). The perchlorates and ferrichlorides of the two samples of compound II were identical.

When the original perchlorate (I) was treated with concentrated nitric and sulfuric acids at 45° a 93% yield of a dinitro derivative was obtained. Exactly the same product could be obtained by nitration of the mono-nitro derivative (II). The structure of this dinitrodiphenylbenzopyrylium perchlorate was shown to be that represented by formula (IV) by synthesis from salicylaldehyde and α-(*p*-nitrophenyl)-*m*-nitroacetophenone (V). The three samples of compound IV were shown to be identical by analyses, mixed melting points and conversion to the same methoxy derivative (VI).

The above experiments show that under mild conditions of nitration a nitro group is introduced into the *para* position of the phenyl group in position 3 of the flavylium salt (I) and that under more drastic conditions an additional nitrogroup is introduced in the meta position of the phenyl group in position 2.

The position taken by a group entering the benzene ring is fundamentally dependent on the charge of the atom already attached to the ring.[2] If the charge is zero or negative the entering group goes into the ortho or para position whereas a considerable positive charge sends the entering group to the meta position. The results of the present nitration experiments are in agreement with the carbonium structure for these salts[3] which in the present case is represented by formula I. Using the approximation method of Latimer and Porter[2a] the charge on carbon atom 2 is about +1.2 whereas the charge on carbon atom 3 is about 0.

It is remarkable that no nitration products were obtained with substituents in Ring B of formula I. Examination of the reaction mixtures showed that no additional nitro derivatives were produced in these experiments with 2,3-diphenyl-

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(1) Le Fevrè, *J. Chem. Soc.*, 2771 (1929); Le Fevrè and Le Fevrè, *ibid.*, 1988 (1932); Le Fevrè, Le Fevrè and Pearson, *ibid.*, 37 (1934).

(2) (a) Latimer and Porter, THIS JOURNAL, **52**, 206 (1930); (b) Price, *Chem. Rev.*, **29**, 32 (1941).

(3) Shriner and Moffett, THIS JOURNAL, **63**, 1694 (1941).

benzopyrylium perchlorate. The nitration of other benzopyrylium salts is being studied in an effort to locate such substitutents since it is important in connection with other possible resonance structures of I.

Experimental

Nitration of 3-Phenylflavylium Perchlorate at 0°.—To 10 cc. of yellow, fuming nitric acid cooled in an ice-salt bath was added slowly with shaking 2 g. of 3-phenylflavylium perchlorate. When solution was complete, it was poured onto 25 g. of ice. The resulting precipitate was removed by filtration and dissolved in ether. An excess of 72% perchloric acid was cautiously added and the 3-(*p*-nitrophenyl)-flavylium perchlorate which separated at once was collected on a filter and repeatedly washed with absolute ether. The yield was 1.2 g. (53.5%). After two recrystallizations from glacial acetic acid it melted with decomposition at about 217°. For further purification a sample of the perchlorate was dissolved in concentrated hydrochloric acid and an excess of ferric chloride, also dissolved in concentrated hydrochloric acid, was added. 3-(*p*-Nitrophenyl)-flavylium ferrichloride separated as a yellow precipitate which was removed by filtration and crystallized twice from glacial acetic acid. A yellow crystalline product was obtained which melted at 136–137°.

Anal. Calcd. for $C_{21}H_{14}O_3NFeCl_4$: C, 47.95; H, 2.68; Fe, 10.62. Found: C, 47.89; H, 3.21; Fe, 10.78.

3-(*p*-Nitrophenyl)-flavylium Perchlorate and Ferrichloride.—Dry hydrogen chloride was passed for two hours into a suspension of 1.4 g. (0.01 mole) of α-(*p*-nitrophenyl)-acetophenone (prepared by the method of Petrenko-Kritschenko[4] from *p*-nitrophenylacetyl chloride and benzene by the Friedel-Crafts reaction), 1.35 g. (1.15 cc., 0.011 mole) of salicylaldehyde, and 2.7 g. (1.5 cc., 0.02 mole) of 72% perchloric acid in 40 cc. of glacial acetic acid. On standing at room temperature, crystals of 3-(*p*-nitrophenyl)-flavylium perchlorate separated. After two days the crystals were collected on a filter, washed with absolute ether, and recrystallized from glacial acetic acid yielding 4.0 g. (93.5%) of yellow crystals, which after a second recrystallization melted at 235–237° with decomposition.

Anal. Calcd. for $C_{21}H_{14}O_7NCl$: N, 3.28. Found: N, 3.28.

A sample of this perchlorate was converted to the ferrichloride as described above yielding yellow crystals of 3-(*p*-nitrophenyl)-flavylium ferrichloride which melted at 137–138°. When mixed with the ferrichloride from the nitration product no depression of the melting point occurred.

Anal. Calcd. for $C_{21}H_{14}O_3NFeCl_4$: C, 47.95; H, 2.68; Fe, 10.62. Found: C, 47.77; H, 2.90; Fe, 10.66.

Nitration of 3-Phenylflavylium Perchlorate at 45°.—Ten grams of 3-phenylflavylium perchlorate was dissolved in 40 cc. of concentrated sulfuric acid, cooled in an ice-salt bath, and 40 cc. of cold concentrated nitric acid was slowly added with shaking and cooling. This solution was warmed for five minutes at 45° and then poured onto ice. The resulting precipitate was removed by filtration, dissolved in ether, and an excess of 72% perchloric acid was cautiously added. The 3-(*p*-nitrophenyl)-3′-nitroflavylium perchlorate which separated was collected on a filter and repeatedly washed with absolute ether. The yield was 11.5 g. (93%) of a light yellow crystalline powder which melted at about 145–150° with decomposition. Repeated recrystallization either from glacial acetic acid containing a little perchloric acid, or from a mixture of acetic acid and nitromethane, yielded a product which melted at 258–258.5° with decomposition.

Anal. Calcd. for $C_{21}H_{13}O_9N_2Cl$: N, 5.93. Found: N, 5.90.

A sample of this perchlorate was dissolved in methanol by refluxing. When cooled, pale yellow crystals of the methoxy derivative separated, which after recrystallization from methanol with the aid of norite yielded pale yellow crystalline plates melting at 177.5–178.5°.

Anal. Calcd. for $C_{22}H_{16}O_6N_2$: N, 6.93. Found: N, 7.08.

Nitration of 3-(*p*-Nitrophenyl)-flavylium Perchlorate.—Two grams of 3-(*p*-nitrophenyl)-flavylium perchlorate was nitrated under the same conditions as in the stronger nitration of 3-phenylflavylium perchlorate. A yield of 2.1 g. (90.7%) of 3-(*p*-nitrophenyl)-3′-nitroflavylium perchlorate was obtained which, after three crystallizations, melted at 255.5–257.5° with decomposition. A mixed melting point with the dinitration product above gave no depression.

Anal. Calcd. for $C_{21}H_{13}O_9N_2Cl$: N, 5.93. Found: N, 5.92.

A sample of this perchlorate was converted to the methoxy derivative as described above. It melted at 178–179° and a mixed melting point with the methoxy derivative of the dinitration product described above gave no depression.

3-(*p*-Nitrophenyl)-3′-nitroflavylium Perchlorate and Methoxy Derivative.—Dry hydrogen chloride was passed into a solution in 20 cc. of acetic acid of 0.43 g. (0.38 cc., 0.0035 mole) of salicylaldehyde, 0.96 g. (0.58 cc., 0.007 mole) of 72% perchloric acid and 1 g. (0.0035 mole) of *m*-nitro-α-(*p*-nitrophenyl)-acetophenone, prepared by the oxidation of 1-(*m*-nitrophenyl)-2-(*p*-nitrophenyl)-ethanol which was obtained by the condensation of *p*-nitro-α-toluic acid and *m*-nitrobenzaldehyde according to the method of Harrison and Wood.[5] After two hours, crystals of 3-(*p*-nitrophenyl)-3′-nitroflavylium perchlorate had started to separate and after three hours the hydrogen chloride was stopped and the mixture allowed to stand at room temperature for two days. The yellow crystals were collected on a filter and washed with acetic acid followed by absolute ether, giving 0.99 g. (60%) of crystals melting at 254.5–255.5° with decomposition. After recrystallization from glacial acetic acid containing a little perchloric acid the compound melted at 257–258.5° with decomposition. Mixed melting points with both the perchlorates from the stronger nitration of 3-phenylflavylium perchlorate and from the nitration of 3-(*p*-nitrophenyl)-flavylium perchlorate gave no depressions.

Anal. Calcd. for $C_{21}H_{13}O_9N_1Cl$: N, 5.93. Found: N, 6.02.

A sample of this perchlorate was converted to the methoxy derivative as described above. It melted at 178–179° and mixed melting points with both the methoxy derivative from the stronger nitration of 3-phenylflavylium perchlorate and the methoxy derivative from the nitration of 3-(*p*-nitrophenyl)-flavylium perchlorate gave no depression.

Anal. Calcd. for $C_{22}H_{16}O_6N_2$: N, 6.93. Found: N, 6.85.

Summary

Mild conditions of nitration introduced a nitro-group in the para position of the phenyl group in position 3 of 2,3-diphenylbenzopyrylium perchlorate. More vigorous nitration conditions introduced an additional nitro-group in the meta position of the phenyl group in position 2. The structures of the nitration products were established by syntheses.

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(4) Petrenko-Kritschenko, *Ber.*, **25**, 2239 (1892).

(5) Harrison and Wood, *J. Chem. Soc.*, 577 (1926).