440. *Comparison of the Directive Powers of Elements having Consecutive Atomic Numbers. Part IV. Nitration of 2 : 4 : 6-Triphenylpyrylium Perchlorate.*

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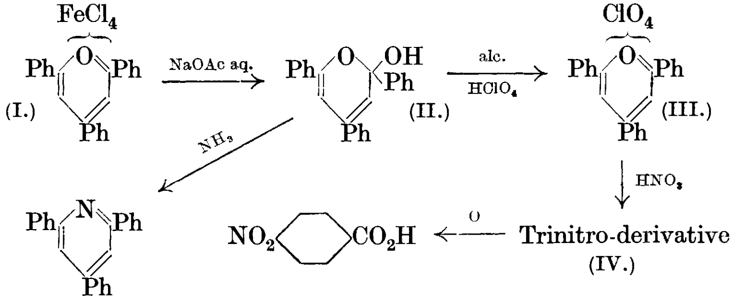
In furtherance of the aims stated in previous papers we have investigated the action of nitric acid on 2 : 4 : 6-*triphenylpyrylium perchlorate* (III). This substance was conveniently prepared from the corresponding ferrichloride (I), previously synthesised by Dilthey (*J. pr. Chem.*, 1916, **94**, 53) from benzaldehyde, acetophenone, and ferric chloride in acetic anhydride solution, by the process (I) ⟶ (II) ⟶ (III).

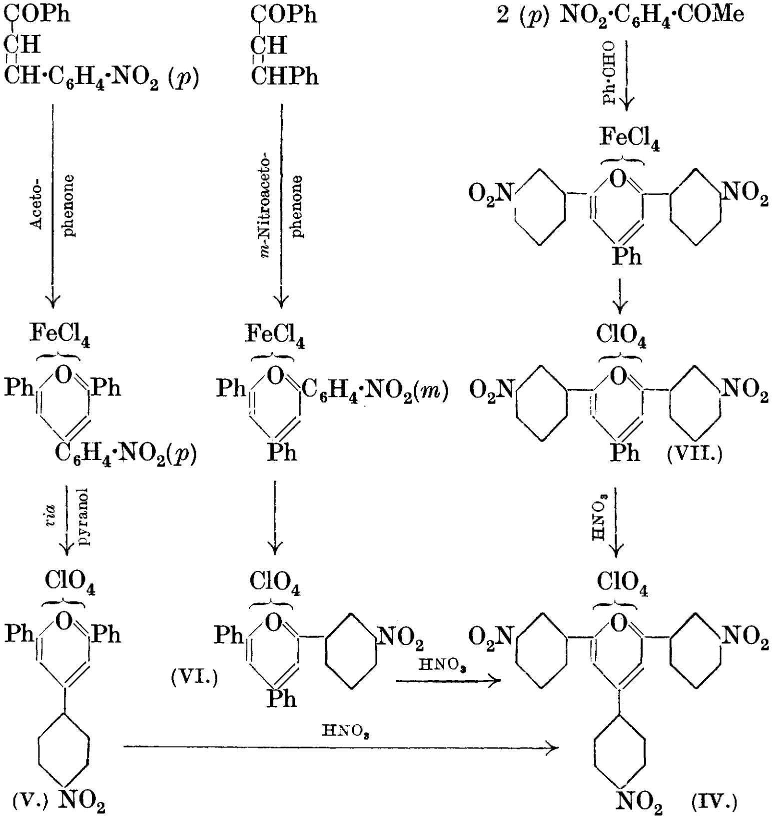
The perchlorate (III) dissolved quietly in fuming nitric acid and rapidly formed a *trinitro*-derivative (IV). Attempts to effect mononitration by adjusting the strength of nitric acid or by using sulphuric acid and potassium nitrate were unsuccessful, the substance being either trinitrated or recovered unchanged. This result was unexpected : in view of the previously noted resistance of

2-phenylbenzopyrylium salts to nitration it was thought that only one nitro-group would be easily introduced.



The constitution of the trinitro-derivative (IV) was investigated as follows :

(a) Crystallisation experiments showed that at least *ca.* 70% of (IV) was an individual substance, m. p. 276—278°.

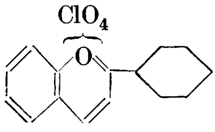


(b) Oxidation of this substance by acid potassium permanganate gave a small yield of *p*-nitrobenzoic acid, showing that one of the phenyl groups (probably the 4-phenyl group, since this is farthest from the positive pole) must have undergone *p*-nitration. From previous results the remaining nitro-groups were thought to be in *m*-positions of nuclei 2 and 6. Synthetical experiments have confirmed this view.

(c) In two cases nitro-derivatives of (I) which could not be synthesised by a process analogous to that of Dilthey (*loc. cit.*) were prepared from the appropriate (nitro)chalkones and (nitro)-acetophenones; these underwent condensation and ring formation in presence of hydrochloric acid and ferric chloride to give *ferrichlorides*, from which the corresponding *perchlorates* could be obtained.

Nitration of the 4-p-*nitrophenyl*-2 : 6-*diphenyl*- (V), 2-m-*nitrophenyl*-4 : 6-*diphenyl*- (VI), and 2 : 6-*di*-m-*nitrophenyl*-4-*phenyl*- (VII) -*pyrylium perchlorates* thus obtained produced derivatives which showed no depression in m. p. in admixture. The chief product of nitration of 2 : 4 : 6-triphenylpyrylium perchlorate therefore appears to be 2 : 6-*di*-m-*nitrophenyl*-4-p-*nitrophenylpyrylium perchlorate* (IV).

Consideration of the formula (III) suggests that the effective positivity of the 1-carbon atom of each nucleus would be less than that of the 1-carbon atom of the 2-phenyl group in the 2-phenyl-benzopyrylium salts (VIII) previously studied, because in (III) the charge of the oxygen can be partially neutralised by three electron drifts due to the — *I* actions of the phenyl groups. The similar process with the 2-phenyl-benzopyrylium salts is presumably effected as far as possible by both the 2-phenyl group and the 5 : 6-benzo-nucleus. The exact contribution of the latter part cannot be assessed directly, but the fact that 2 : 4 : 6-triphenylpyridine scarcely forms quaternary derivatives (*e.g.*, with MeI) whilst those from 2-phenylquinoline are quite stable suggests that the neutralisation is much more efficient in (III) than in (VIII).



(VIII.)

With (VIII) mononitration alone occurred, but with (III) a three-stage substitution has to be considered. The first attack will certainly be at the point farthest from the positive pole, *i.e.*, at the 4-*p*-position, and substitution, facilitated by a + *T* action of the nearest C:C double bond, will follow (cf. nitration of 4-nitro-diphenyl). The correctness of this view is supported by the fact that (V) on nitration gives (IV) in as pure a condition as when obtained directly from (III), whilst the 4-m-*nitrophenyl* analogue of (V) gives a mixture of substances.

An a priori description of the second and third stages is more difficult. The molecules of (III) are large (on a conservative estimate they lie on roughly equilateral triangles of side 14 Å.) and the outer extremities will be additionally less positive than those of (VIII), and therefore approach by kationoid reagents will be less resisted. The occurrence of some *op*-substitution in the 2- and 6- (as well as the 4-)phenyl nuclei of (III) might therefore be expected.

From the experimental point of view the weakest part of the proof admittedly lies in the methods adopted for proving the identity of the nitration products from (III), (V), (VI), and (VII), for, apart from the observation of physical similarities under the microscope in the various crystalline substances obtained from hot nitrobenzene solution, there was available only the determination of mixed melting points. All the m. p.'s involved are high and are also largely decomp. points. If, therefore, in addition these salts have low molecular depressions of freezing point, little depression of m. p. could be expected even in cases of non-identity. A further uncertainty arises from the inability to isolate any product of oxidation other than *p*-nitrobenzoic acid (although at least one case can be quoted as a precedent for this—cf. Ingold, Ingold, and Shaw, J., 1927, 813). For these reasons the confirmatory experiments of the following paper were instituted.

We have not succeeded in transforming 2 : 4 : 6-triphenylpyridine, obtained from the pyranol (II) by the action of hot alcoholic ammonia, into quaternary salts. Nitration of dilute solutions of this base in sulphuric acid gave mixtures, m. p. above 300°, of tri-, tetra-, and penta-nitro-derivatives in proportions varying with the time of nitration and the quantities taken.

Alkaline potassium permanganate oxidation of a " trinitro- " product afforded some *p*-nitrobenzoic acid, but beyond this observation the nitration products were not examined since they were obviously of no use for comparative purposes.

EXPERIMENTAL.

2 : 4 : 6-*Triphenylpyrylium Perchlorate*.—The corresponding ferrichloride (Dilthey, *J. pr. Chem.*, 1916, **94**, 53) (37 g.) was shaken with H_2O (1·5 l.) containing NaOAc (cryst., 100 g.) at 80°. After 24 hr. the crude pyranol (20 g.; m. p. 118—119°) was separated and dissolved in boiling methylated spirit (1 l.), to which was then added a hot solution of $HClO_4$ (80 c.c.; *d* 1·2) in EtOH (100 c.c.). From the red solution with green fluorescence so formed, fan-shaped bundles of yellow crystals (22 g.) separated on cooling. Recrystn. from AcOH–perchloric acid gave the *perchlorate*, m. p. 288—290° (Found: C, 67·8; H, 4·4. $C_{23}H_{17}O_5Cl$ requires C, 67·6; H, 4·2%).

Nitration of 2 : 4 : 6-*Triphenylpyrylium Perchlorate*.—The perchlorate (8 g.) was dissolved in HNO_3 (*d* 1·52; 160 c.c.) at 0° and left for ½ hr. Dilution was performed, at 0°, by stirring in successively AcOH (160 c.c.), $HClO_4$ (300 c.c.; *d* 1·2), and ice-H_2O (400 c.c.). After 2½ hr. the solid was washed with EtOH and air-dried, giving a yellow powder (9·2 g.), m. p. 240—260° (Found : N, 7·5. A trinitro-derivative requires N, 7·7%). Recrystn. from AcOH (2700 c.c.) gave 7·8 g., m. p. 262—265°. One crystn., however, from $PhNO_2$, with greater loss of material, gave yellow micro-needles, m. p. 276—278° (Found : C, 50·7; H, 2·7; N, 7·8. $C_{23}H_{14}O_{11}N_3Cl$ requires C, 50·8; H, 2·6; N, 7·7%).

Nitrations were also performed in which the HNO_3 solutions were left for 1—24 hr., but the results were no better.

Oxidation of the above Nitration Product.—(a) Six nitration expts. (0·5 g. of material in each) were left aside for several weeks. The gums produced, which later solidified, were united and crystallised from much hot H_2O (norit), giving *p*-nitrobenzoic acid (Found : N, 8·7. Calc. : N, 8·4%), m. p. and mixed m. p. 238—239°.

(b) To the nitration product (1 g.), suspended in 4*N*-H_2SO_4 (50 c.c.) at 90°, $KMnO_4$ (6 g.) was added, followed after 10 min. by excess of hot H_2O; the hot solution was then decolourised by SO_2 and filtered. On cooling, *p*-nitrobenzoic acid (m. p. 231—233°; after recrystn., m. p. 239—240°; yield, 0·13 g.) separated from 200 c.c. of solution. Since the solubility of the acid is 0·04 g./100 c.c. of solution, the total yield was approx. 0·21 g., *i.e.*, 60%. No *m*-nitrobenzoic or benzoic acid could be detected.

Preparation of the Necessary Nitrochalkones.—*p*-Nitrochalkone (20 g.) and *m*-nitrochalkone (33 g.), cream-coloured needles, m. p. 157—159° and 138—140° respectively, from AcOH, were prepared from 40% NaOH aq. (25 g.) and *p*- or *m*-nitrobenzaldehyde (15 g.) and acetophenone (15 g.) in EtOH (200 g. for the *p*-nitro-, and 120 c.c. for the *m*-nitro-chalkone).

p-Nitrobenzylidene-*m*-nitroacetophenone, m. p. 176—179°, and *m*-nitrobenzylidene-*m*-nitroacetophenone, m. p. 210°, were prepared from 40% NaOH aq. (2·5 c.c.) and *m*-nitroacetophenone (2 g.) and *p*- or *m*-nitrobenzaldehyde (1·5 g.) in EtOH (200 c.c.) at 0°.

Preparation of 4-p-*Nitrophenyl*-2 : 6-*diphenylpyrylium Ferrichloride.*—A solution of the crude *p*-nitrochalkone (20 g.) and acetophenone (9·6 g.) in Ac_2O (160 c.c.) was saturated with dry HCl and, after the addition of $FeCl_3$ (28 g.), heated on the steam-bath for ½ hr. After 3 days, the cryst. deposit was collected, washed with AcOH, and dried at 100° (yield, 4·5 g.). The *ferrichloride* formed red-brown needles, m. p. 209—212°, from AcOH (Found : N, 2·9. $C_{23}H_{16}O_3NCl_4Fe$ requires N, 2·5%).

4-p-*Nitrophenyl*-2 : 6-*diphenylpyrylium Perchlorate.*—A solution of the ferrichloride (3 g.) in acetone (50 c.c.) was added drop by drop to well-shaken NaOAc (100 g. in 1 l. of H_2O), the ppt. washed with H_2O (yield, 2·5 g.), dissolved in methylated spirit (400 c.c.), and boiled with $HClO_4$ (10 c.c.; *d* 1·2). The *perchlorate* separated on cooling as golden-yellow leaflets (1·2 g.), m. p. above 300° (Found : N, 2·9. $C_{23}H_{16}O_7NCl$ requires N, 3·1%).

4-m-*Nitrophenyl*-2 : 6-*diphenylpyrylium Ferrichloride.*—This was prepared in the same way as the 4-*p*-nitrophenyl isomeride (heating for 1½ hr.). It formed red crystals, m. p. 237°, from AcOH (Found : N, 2·6%). Yield, 10 g. from 33 g. of *m*-nitrochalkone.

4-m-*Nitrophenyl*-2 : 6-*diphenylpyrylium Perchlorate.*—The corresponding pyranol (17 g. of moist paste), obtained as described above (ferrichloride, 5 g.; acetone, 100 c.c.; NaOAc, 150 g.; H_2O, 2 l.), was dissolved in hot

EtOH (2 l.), and the filtered solution treated with $HClO_4$ (100 c.c.; *d* 1·2) in hot EtOH (100 c.c.). On cooling, 2 g. of light brown plates, m. p. 241—242°, separated (Found: N, 2·9%).

2-m-*Nitrophenyl*-4 : 6-*diphenylpyrylium Ferrichloride*.—Chalkone (7·5 g.), *m*-nitroacetophenone (6 g.), Ac_2O (35 c.c.), and $FeCl_3$ (12 g.) were heated on the steam-bath for 1½ hr. Cooling and filtration then furnished golden-yellow needles (6 g.), m. p. 216—218° (Found: N, 2·6%).

2-m-*Nitrophenyl*-4 : 6-*diphenylpyrylium Perchlorate*.—The ferrichloride (5 g.) in acetone was diluted with NaOAc aq. (3 l.), the pyranol produced was dissolved in 2 l. of boiling EtOH, and excess of $HClO_4$ aq. added. The yellow *perchlorate* separated slowly, m. p. 277—278° after crystn. (Found: N, 3·2%).

2 : 6-*Di*-m-*nitrophenyl*-4-*phenylpyrylium Ferrichloride*.—*m*-Nitroacetophenone (8·2 g.) and Ph·CHO (2·4 g.) in Ac_2O (20 c.c.) were heated with $FeCl_3$ (5 g.) on the steam-bath for 4 hr. After 12 hr. the usual treatment gave a yellow microcryst. powder, m. p. 229—232° (Found: N, 4·7. $C_{23}H_{15}O_5N_2Cl_4Fe$ requires N, 4·7%).

2 : 6-*Di*-m-*nitrophenyl*-4-*phenylpyrylium Perchlorate*.—The crude pyranol obtained from the ferrichloride (2 g.), acetone (100 c.c.), and NaOAc (200 g. in 2 l. of H_2O) was dissolved in hot EtOH (1 l.), and $HClO_4$ (50 c.c.; *d* 1·2) added. The *perchlorate* crystallised on cooling as orange-brown plates (1·8 g.), m. p. 291° (Found: N, 5·5. $C_{23}H_{15}O_9N_2Cl$ requires N, 5·6%).

2 : 4 : 6-Tri-*m*-nitrophenylpyrylium ferrichloride and 2 : 6-di-*m*-nitrophenyl-4-*p*-nitrophenylpyrylium ferrichloride could not be prepared by the above methods.

Nitration of the Foregoing Perchlorates.—(a) A solution of 4-*p*-nitrophenyl-2 : 6-diphenylpyrylium perchlorate (0·3 g.) in HNO_3 (6·5 c.c.; *d* 1·52) was kept for ½ hr. and then treated at 0° with AcOH (6·5 c.c.), $HClO_4$ aq. (17 c.c.), and H_2O (18 c.c.) in the order stated. After ¼ hr., filtration and EtOH-washing gave 0·3 g. of orange-yellow crystals, m. p. 245—250°, raised to 270—271° by crystn. from $PhNO_2$ (Found: N, 7·7. $C_{23}H_{14}O_{11}N_3Cl$ requires N, 7·7%). The mixed m. p. with the trinitration product from (III) (m. p. 276—278°) was 271—274°.

(b) 4-*m*-Nitrophenyl-2 : 6-diphenylpyrylium perchlorate, treated exactly as in the previous case, gave a product, m. p. 150—210°.

(c) Similar treatment of 2 : 6-di-*m*-nitrophenyl-4-phenylpyrylium perchlorate produced 0·3 g. of light orange-yellow crystals, m. p. 268—270°, raised slightly by admixture with the nitration product (IV) (Found: N, 7·9%).

(d) 2-*m*-Nitrophenyl-4 : 6-diphenylpyrylium perchlorate, treated as in (a), gave orange-yellow crystals, m. p. 265—270°, raised by addition of (IV) (Found: N, 7·8%).

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