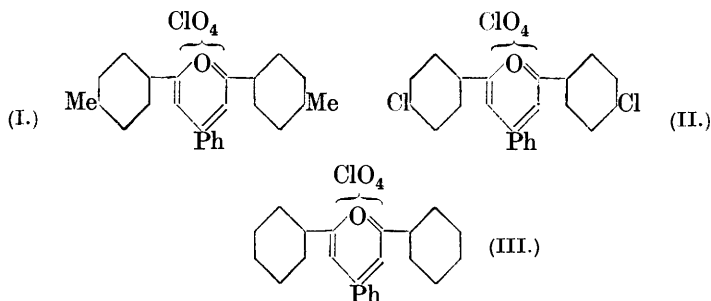


441. Nitration of Di-*p*-tolyl- and Di-*p*-chlorophenyl-phenylpyrylium Perchlorates.

By (MISS) H. E. JOHNSTON and R. J. W. LE FÈVRE.

SINCE toluene is nitrated more rapidly, and chlorobenzene less rapidly, than benzene, the 2- and the 6-substituted phenyl group of (I) and (II) might be expected to undergo substitution, compared with the corresponding groups in 2 : 4 : 6-triphenylpyrylium perchlorate (III), similarly faster and slower respectively. If, therefore, both (I) and (II) could be shown to undergo *p*-nitration in the 4-phenyl nucleus, the similar substitution of (III) could be regarded as certain (see preceding paper).



The trinitrations of both (I) and (II) proceeded exactly as did that of (III). The products were practically pure and were shown to contain one *p*- and two *m*-nitro-groups by the following observations :

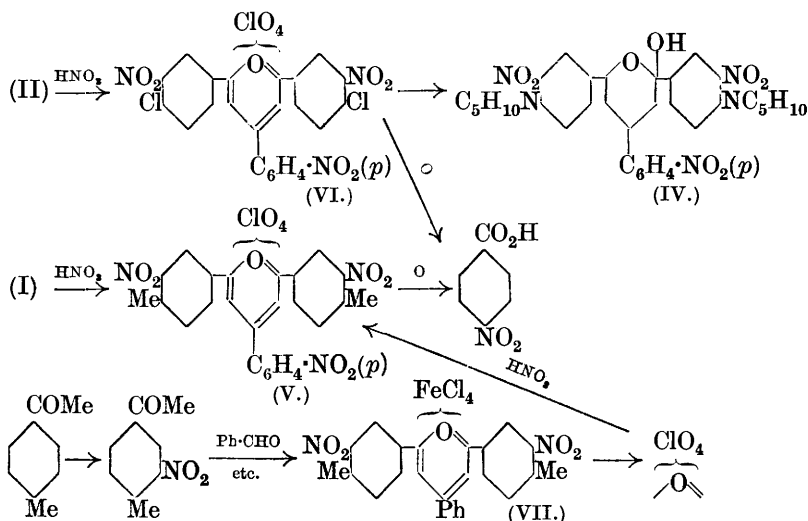
(a) Both products gave *p*-nitrobenzoic acid on oxidation.

(b) The nitration product (VI) from (II), contains a di-(*o*-chloro-nitro)-structure, since it reacted with piperidine to form a *trinitrodi-piperidinotriphenylpyranol* (IV).

(c) 3-Nitro-4-methylacetophenone, benzaldehyde, acetic anhydride, and ferric chloride gave by the usual procedure 2 : 6-di-(2'-nitro-*p*-tolyl)-4-phenylpyrylium ferrichloride (VII), the corresponding *perchlorate* of which was transformed by fuming nitric acid into a substance identical with the trinitration product (V) from (I).

It is therefore evident that the orienting influence of the oxonium pole in substances (I), (II), and (III) on the 2- and the 6-phenyl group must be strong enough to produce *m*-substitution. Had it been weak enough to allow *op*-substitution in case (III), a uniform product would not have been formed from (II), where the $-I$ effects of halogen and oxonium oxygen are in competition, but, instead, a mixture showing some *o*-substitution in the two *p*-chlorophenyl

nuclei. The fact that this does not occur strengthens the evidence for the constitution given in the previous paper to the trinitro-derivative of (III).



The results obtained with (I) are easily explicable. The normal *op*-activating tendency of methyl enhances the activities of the positions in the 2 : 6-ditolyl groups least deactivated by the oxonium pole. Substitution therefore occurs in these positions alone.

EXPERIMENTAL.

4-Phenyl-2 : 6-di-*p*-tolylpyrylium Ferrichloride.—To a mixture of *p*-methylacetophenone (130 g.), Ph·CHO (48 g.), and Ac₂O (240 c.c.), anhyd. FeCl₃ (100 g.) was added slowly : the mixture was finally heated for 10 min. on the steam-bath. The ferrichloride deposited on cooling was washed twice with AcOH and dried at 100° (yield, 60 g.), forming large, deep red prisms, m. p. 257—258°.

4-Phenyl-2 : 6-di-*p*-tolylpyranol.—A solution of the ferrichloride (5 g.) in acetone (150 c.c.) was stirred into H₂O (2 l.) containing NaOAc (cryst., 50 g.). After some hr., the orange ppt. was collected, washed with H₂O, and extracted from Fe(OH)₃ by boiling EtOH. Partial pptn. of the hot extract with H₂O gave the pyranol as a cream-coloured solid, m. p. about 100°. The yellow cryst. *picrate*, m. p. 259—260° (decomp.), was obtained from an alc. solution of its components (Found : N, 7.8. C₃₁H₂₃O₅N₃ requires N, 7.4%).

4-Phenyl-2 : 6-di-*p*-tolylpyrylium Perchlorate.—To a boiling solution of the pyranol (4 g.) in methylated spirit (800 c.c.), HClO₄ aq. (*d* 1.2; 150 c.c.) was added. The yellow cryst. *perchlorate* (3.2 g.) which slowly separated had m. p. 278—280° after recrystn. from AcOH-HClO₄ aq. (Found : C, 68.7; H, 4.8. C₂₅H₂₁O₅Cl requires C, 68.7; H, 4.8%).

Nitration. The perchlorate (1 g.) was dissolved in HNO₃ (*d* 1.5; 30 c.c.) at

0°, and H₂O (ca. 10 c.c.) then added, until pptn. began, followed by H₂O (30 c.c.) containing NaClO₄ (10 g.) (temp. below 0° throughout). The yellow ppt. was washed with EtOH; it then had m. p. 266—268° (mixed with un-nitrated material, ca. 238°), rising to 271—273° after recrystn. from AcOH-HClO₄ aq. (Found: N, 7.4. C₂₅H₁₈O₁₁N₃Cl requires N, 7.5%).

Synthesis of 2 : 6-Di-(2'-nitro-p-tolyl)-4-phenylpyrylium Perchlorate.—Quantities of Ph·CHO, 3-nitro-4-methylacetophenone (m. p. 60—61°; from 4-methylacetophenone by the method of Errera; *Gazzetta*, 1891, **21**, 92), Ac₂O, and FeCl₃ equiv. to those used in the prepn. of compound (VII) in the previous paper were kept at room temp. for 3 weeks. The crude amorphous ferrichloride then obtained was suspended in NaOAc aq. at 60° for 1 hr. after filtration, the residue was boiled with spirit, and the hot extract diluted with HClO₄ aq. until crystn. began. A yellow perchlorate, m. p. 275—277°, was obtained.

Nitration. The perchlorate, nitrated in exactly the same way as the parent compound, gave a product, m. p. 269—270° (after drying at 100°) not depressed in admixture with substance (V) (Found: N, 7.7. Calc.: N, 7.5%).

Oxidation of Substance (V).—The crude nitro-perchlorate (1 g.), suspended in boiling 6*N*-H₂SO₄, was treated with KMnO₄ (10 g.). After 10 min., the liquid was filtered hot and decolorised with SO₂. On cooling, white crystals, m. p. 210—220°, were deposited in small quantity; more were obtained from the residue by extraction with hot H₂O. After one crystn. from H₂O, the product melted at 236—238°, alone or mixed with *p*-nitrobenzoic acid.

2 : 6-Di-p-chlorophenyl-4-phenylpyrylium Ferrichloride.—This was obtained in red prisms (13 g.), m. p. 295°, when FeCl₃ (16 g.), Ph·CHO (7 g.), *p*-chloroacetophenone (21 g.), and Ac₂O (36 c.c.) were heated on the steam-bath for 1 hr., and the product washed with a little AcOH.

Perchlorate (II).—This was obtained from the ferrichloride (12 g.) in acetone (200 c.c.) and dil. NaOAc aq. (4 l.), the product, after 24 hr., being treated in boiling methylated spirit (½ l.) with HClO₄ aq. (*d* 1.2; 90 c.c.). The perchlorate (6 g.) crystallised from PhNO₂-AcOH in daffodil-yellow elongated plates, m. p. above 300°.

Nitration. The perchlorate (2 g.) dissolved in HNO₃ (*d* 1.5; 50 c.c.) without much evolution of heat. After ½ hr., the solution was cooled to 0°, and H₂O (20 c.c.) added until pptn. began, followed by 70 c.c. of sat. NaClO₄ aq. The product, after being washed with abs. EtOH, was a bright yellow, cryst. powder m. p. ca. 230° (decomp.), and 240—245° (decomp.) after crystn. from AcOH-HClO₄ aq. (Found: N, 6.1. C₂₃H₁₂O₁₁N₃Cl₃ requires N, 6.8%). Oxidation with KMnO₄ produced *p*-nitrobenzoic acid.

4-p-Nitrophenyl-2 : 6-di-(m-nitro-p-piperidinophenyl)pyranol.—The nitration product (VI) (2 g.) was heated with piperidine (5 c.c.) at 100° for ½ hr., the red solution diluted with H₂O, and the excess of piperidine removed in steam. On cooling, the residue formed a brittle, dark red glass, m. p. 76—78°, which could not be crystallised. Its solutions in pyridine and EtOH were dark red, and that in AcOH permanganate-purple (Found: N, 10.5. C₃₃H₃₃O₈N₅ requires N, 11.1%).

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