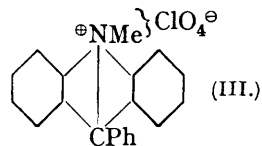
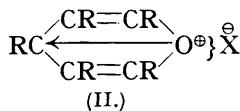
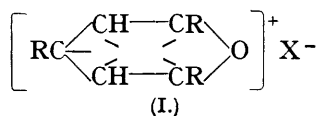


118. *Comparison of the Directive Powers of Elements having Consecutive Atomic Numbers. Part V. The Nitration of 9-Phenylxanthylum Perchlorate.*

By R. J. W. LE FÈVRE and J. PEARSON.

DILTHEY'S conclusion (*Ber.*, 1920, **53**, 261) that pyrylium salts are best formulated as "carboxonium" salts (I) is not supported by the results obtained in the nitration of 2:4:6-triphenylpyrylium perchlorate, for this substance, so formulated, would contain three phenyl groups roughly symmetrically disposed about a diffuse positive charge and the formation of 4-*p*-nitrophenyl-2:6-di-(*m*-nitrophenyl)pyrylium perchlorate (Le Fèvre and Le Fèvre, *J.*, 1932, 2894) would be unlikely. The actual result suggests that the positive charge is situated either on or close to the oxygen atom.



Further evidence in the same direction has now been found in the facts that (1) xanthylum ferrichloride is unaffected by nitric acid of a strength which dinitrates xanthone, and (2) 9-phenylxanthylum perchlorate, which Dilthey (*loc. cit.*) regards as a 9-carbonium salt (cf. also Dilthey and Wizinger, *Ber.*, 1932, **65**, 1329), readily yields a *mononitro*-derivative, which is highly resistant to further nitration, gives *p*-nitrobenzoic acid on oxidation, and is evidently 9-*p*-nitrophenylxanthylum perchlorate.

Obviously neither xanthylum ferrichloride nor 9-phenylxanthylum perchlorate contains bivalent oxygen—the presence of which would lead to di- and tri-nitration respectively—and therefore neither substance has the 9-carbonium structure which implies

it. Further, the resistance of both to nitration and to halogenation (in boiling acetic acid) indicates that formulæ which represent the pyrylium nucleus as containing an aromatic sextet are untenable, because the formation of such a sextet would deprive the two benzo-nuclei of aromatic properties.

The correct formula for the pyrylium nucleus has thus only to show: (1) intimate connexion between positions 1 : 4 and 1 : 2 (since the salts are formed from ψ -bases with hydroxyl in position 2 or 4); (2) the positive charge removed sufficiently far from the 4-position to allow p -substitution to be effected in a phenyl nucleus situated there. It is considered that these properties are adequately represented by the formula (II), which indicates that the sextet left on the 4-carbon atom by dissociation of a halide anion has been neutralised in the most obvious manner by co-ordination with the oxygen atom, which has thus become the seat of the positive charge.* All formations of pyrylium salts can be regarded similarly, co-ordination occurring at either the 4- or the 2-position as a sequel to an immobile carbinol passing into the more mobile chloride (or similarly stable anion-producing salt).

On this basis the relative stabilities of oxonium salts depend upon the relative powers of bivalent oxygen and the various anions to act as donors in a co-ordination process. Hence it is that salts with stable anions (Cl, ClO₄, etc.) are stable oxonium salts, whereas the corresponding bases are unstable, the hydroxyl (prone to co-ordination; cf. anion-tropy) readily co-ordinating on the 9-carbon atom synchronously with the displacement of the O→C dative link and the consequent appearance of a ψ -base.

On such a formula the present substitution results and those recently reported are consistent with known facts of benzene substitution. The 4-phenyl group is attached to a neutral carbon atom isolated from the positive pole by two ethylenic bonds and one long single bond, probably *ca.* 3 Å. in length. The experiments of Baker and Wilson (J., 1927, 842) having indicated that a double bond is an efficient neutraliser of inductive electronic strain (cf. Ingold, *Ann. Reports*, 1926, 131), it is evident that the chief path by which polar influences can be relayed to the 9-phenyl group is the 1 : 4-bond, *i.e.*, a distance not less than that separating pole from nucleus in the β -phenylethyltrimethylammonium salts in which *o,p*-substitution largely occurs (Goss, Hanhart, and Ingold, J., 1927, 250). Remembering, in addition, that in our cases the $-I$ effect of the oxonium pole available at the 4-carbon atom is only residual—much adjustment having been effected by the groups attached at the 2- and 6-positions—it will be conceded that the phenyl group attached to the 4-carbon atom is in a situation not unlike that of phenyl in 4-nitrodiphenyl (Fittig, *Annalen*, 1862, 124, 276) and is therefore more likely to suffer p - than m -substitution.

Action of Nitric Acid on 9-Phenyl-10-methylacridinium Perchlorate (?).—From the water-soluble methiodide of 9-phenylacridine (Bernthsen, *Annalen*, 1884, 224, 13), by interaction with hydroferrichloric and perchloric acids, we have obtained what should be 9-phenyl-10-methylacridinium ferrichloride (mentioned, but not analysed, by Bünzly and Decker; *Ber.*, 1904, 37, 2931) and perchlorate (III) respectively. The analytical data obtained for the two substances, however, and also for the picrate do not agree with a formulation such as (III).

In view of the uncertainty regarding its nature, the nitration of the perchlorate has not been examined in detail: it is fairly resistant to nitric acid, undergoing approximate mononitration by solution in this reagent at room temperature.

EXPERIMENTAL.

Xanthylum Ferrichloride.—Xanthhydrol (5 g.) was dissolved in conc. HCl (100 c.c.), and sat. FeCl₃ aq. (100 c.c.) added; a yellow cryst. ppt. formed, m. p. 195—197°.

Nitration. The ferrichloride was dissolved in HNO₃ (*d* 1.5; 50 c.c.) and left at room temp. for 1½ hr. From the solution, made up to 100 c.c. with ice, sat. FeCl₃ aq. (100 c.c.) then pptd. largely unchanged ferrichloride (mixed m. p.) (Found: N, 0.6. Calc. for mononitro-deriv.: N, 3.3%).

9-Phenylxanthylum Perchlorate.—9-Phenylxanthenol (Bünzly and Decker, *loc. cit.*) (20 g.)

* Intra-annular electron duplet transfers of this type in the case of various γ -pyrones are strongly indicated by the dipole moment measurements of Hunter and Partington (this vol., p. 87).

was dissolved in conc. HCl (250 c.c.) by warming on the water-bath, and cold conc. HCl saturated with NaClO₄ (400 c.c.) was added. The ppt. obtained (32 g.) formed orange plates, m. p. 274—275°, after three crystns. from AcOH-HClO₄ aq.

Nitration. The perchlorate was recovered unchanged after treatment for 2.7 hr. with HNO₃ (*d* 1.42) at 100°.

Five 1-g. lots of the perchlorate were separately dissolved in HNO₃ (*d* 1.5; 20 c.c.) and left for times varying from 1.5 to 28 hr. Dilution with ice to 80 c.c. and addition of 40% NaClO₄ aq. (95 c.c.) then gave orange microcryst. powders (1.5—1.6 g.) with m. p.'s varying with the time of nitration, the highest being 244—246° for the 1.5 hr. nitration product. The powders depressed (by *ca.* 40°) the m. p. of the unnitrated perchlorate, but produced no depression in each other's m. p. (Found: N, 4.1. C₁₉H₁₂O₇NCl requires N, 3.5%. C₁₉H₁₁O₉N₂Cl requires N, 6.3%). Three recrystns. of the combined material from AcOH-HClO₄ aq. gave orange plates, m. p. 257—258°.

The nitrated perchlorate (1 g.) was dissolved in a little AcOH, poured into cold H₂O (300 c.c.), and kept over-night. The ppt. formed was recrystallised from aq. EtOH, 9-*p*-nitrophenylxanthenol being obtained in stout white needles, m. p. 116—118° (Found: N, 4.6. C₁₉H₁₃O₄N requires N, 4.4%).

Oxidation of the nitration product. The pure nitrophenylxanthylium perchlorate (3 g.) was heated in a sealed tube at 170° with 10% HNO₃ (30 c.c.) for 4 hr., and the filtered yellow solution then allowed partly to evaporate in vac. over KOH. The solid obtained, after recrystn. from H₂O, had m. p. 228—230°, raised by admixture with authentic *p*-nitrobenzoic acid (Found: C, 49.8; H, 3.1. Calc.: C, 50.3; H, 3.0%).

9-p-Chlorophenylxanthenol and 9-p-Chlorophenylxanthylium Perchlorate.—To the Grignard solution prepared from *p*-chlorobromobenzene (8.5 g.), Mg (1 g.), and Et₂O (150 c.c.) was added a solution of xanthone (8 g.) in hot C₆H₆ (100 c.c.). The whole was refluxed for 1 hr. and then extracted several times with conc. HCl (total, 200 c.c.). The HCl solution was diluted with 200 c.c. of H₂O and just neutralised with NH₃ aq.; the solid obtained, recryst. from aq. MeOH, gave 9-*p*-chlorophenylxanthenol in white needles, m. p. 164° (Found: C, 73.8; H, 4.3; Cl, 11.4. C₁₉H₁₃O₂Cl requires C, 73.9; H, 4.2; Cl, 11.5%).

The xanthenol was dissolved in hot AcOH, and HClO₄ aq. (*d* 1.12) added till the solution became cloudy. The solid obtained on cooling, after recrystn. from AcOH-HClO₄ aq., gave 9-*p*-chlorophenylxanthylium perchlorate in orange-coloured needles, m. p. 280—281° (Found: C, 58.4; H, 3.1; Cl, 17.6. C₁₉H₁₂O₅Cl₂ requires C, 58.3; H, 3.1; Cl, 18.6%).

9-p-Bromophenylxanthenol, small white needles, m. p. 132—133°, and *9-p*-bromophenylxanthylium perchlorate, orange-coloured microscopic prisms, m. p. above 300°, were prepared in the same manner as the *p*-chloro-compounds, the initial materials being *p*-dibromobenzene (10.5 g.), Mg (1 g.), and xanthone (8 g.).

9-Phenyl-10-methylacridinium Salts.—To a solution of 9-phenyl-10-methylacridinium iodide in boiling H₂O was added aq. HClO₄ (and in later expts. sat. NaClO₄ aq.) till no further perchlorate was pptd. Recrystn. from AcOH-HClO₄ aq. produced long, dark yellow needles, m. p. 244—245° (Found: N, 4.4, 4.5. C₂₀H₁₆O₄ClN requires N, 3.8%). By crystn. from AcOH-70% HClO₄ (15 c.c. of each) the salt appeared as before (Found: N, 4.3%).

Addition of excess of sat. FeCl₃ aq. to a solution of 9-phenyl-10-methylacridinium iodide in hot dil. HCl produced a yellow ppt., which formed green-yellow needles, m. p. 161—162°, on recrystn. from AcOH-HCl aq. (Found: N, 3.8. Calc.: N, 2.9%).

The picrate obtained from the iodide and picric acid in hot H₂O formed yellow-green plates, m. p. 169—170° (Bünzly and Decker give 173°), after two recrystns. from EtOH-picric acid aq. (Found: N, 12.8. Calc.: N, 11.3%).

Nitration of 9-Phenyl-10-methylacridinium Perchlorate.—The crude perchlorate (1 g.) was dissolved in HNO₃ (*d* 1.5; 20 c.c.), left at room temp. for 1½ hr., and made up to 40 c.c. with ice, and sat. NaClO₄ aq. (100 c.c.) added. The orange-yellow perchlorate obtained (1 g.) had m. p. 257—262° (decomp.) (Found: N, 7.7. C₂₀H₁₅O₆N₂Cl requires N, 6.8%).

A grant from the Chemical Society is gratefully acknowledged.