

756. Polyphenylethylenes. Part II.¹ The Epoxidation of Tetra-*p*-nitrophenylethylene by Nitric Acid.

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A major product of the oxidation of tetra-*p*-nitrophenylethylene in 90—100% nitric acid at 0° is the epoxide. An important by-product is the pinacone, the yield of which increases from zero in 90% acid to 37% in absolute nitric acid. These findings are discussed.

THE slow reaction at 0° of tetra-*p*-nitrophenylethylene in nitric acid of concentration <ca. 85% has been noted.¹ In the concentration range 85—100% the reaction accelerated greatly. Though complex over the whole range it was predominantly an oxidation, yielding tetra-*p*-nitrophenyloxiran as a major product.

In ~100% nitric acid the oxidation proceeded through a deep violet intermediate, which persisted for <1 minute at 0° (<5 minutes at -20°). Crystallisation of the product obtained on dilution with water gave the epoxide (30%) and its 1,2-rearrangement product, *p*-nitrobenzoyltri-*p*-nitrophenylmethane (23%): an estimate of the amount of pinacone (14%) and epoxide (6%) remaining in the mother-liquor was obtained from the weight of *p*-nitrobenzoic acid isolated after hydrolysis, before and after rearrangement in concentrated sulphuric acid. 4,4'-Dinitrobenzophenone (7%) was separated from the product by treatment with an excess of Girard's reagent P in 2-methoxyethanol acidified with dichloroacetic acid. The material deficit was partly accounted for by experimental losses (e.g., recovery of *p*-nitrobenzoic acid from pure pinacone was 87%, from epoxide after rearrangement 76%): no other compound could be fully characterised, but crystals (1—2%), m. p. >370°, usually separated from dioxan solutions after the epoxide. Although *p*-nitrobenzoic acid was found to be a product of the prolonged action of concentrated nitric acid on the pinacone, no appreciable amount of this could be isolated from the crude product from tetra-*p*-nitrophenylethylene. Addition of ammonium nitrate (1, 5, or 10 moles %) did not increase pinacone formation. Similarly, dinitrogen pentoxide

¹ Part I, *J.*, 1959, 678.

(4 moles %) had little effect, but a larger excess (16 moles %) increased the formation of 4,4'-dinitrobenzophenone (>20%).

Oxidation of tetra-*p*-nitrophenylethylene by nitric acid.

Nitric acid	Moles (%)	Initial colour of intermediate	Estimated yields (%) at 0°			Other products
			Pinacone	Epoxide	Benzo-phenone	
Absolute	100	Deep violet	37 (40 at -20°)	36 (33 at -20°)	7	?
98% Aq.	93	Dark brown-violet	15	55	6	A, B
95% Aq.	84	„ violet-brown	8	64	5	A, B
93% Aq.	79	„ yellow-brown	2-3	60-65	—	A
90% Aq.	72	„ „	0	>50	1	A (>40%)
In CHCl ₃	50	Green-brown	2-3	63	2	A, B

The use of nitric acid containing increasing percentages of water caused a rapid decrease in pinacone formation (cf. Table) and a corresponding increase in epoxidation (up to *ca.* 65%), while the initial colour of the intermediate complex acquired brown shades and finally lost its violet tinge. Reaction in "fuming nitric acid" (95—98%) provided a convenient preparative route either to the epoxide or, after rearrangement in concentrated sulphuric acid, to the pinacone.

At relatively low acid concentrations (*ca.* 90%) the reaction required several hours at 0°: the epoxide was still the main product (>50%), but the formation of pinacone could no longer be detected either by the appearance of a violet colour on treatment of the crude product with alcoholic potassium hydroxide or by the isolation of *p*-nitrobenzoic acid. Similarly, negligible amounts of 4,4'-dinitrobenzophenone were isolated. The main by-product was a compound, m. p. 245° (A), stable in concentrated sulphuric acid, apparently a nitroethane derivative resulting from a secondary reaction involving nitrous acid formed in the primary oxidation: though small amounts of this were isolated from the products of reaction at higher concentration (up to 98%) it was of minor importance in the range 95—100%. A compound of m. p. >280° (B), an oxidation product of (A), was also formed in reactions at intermediate concentrations. Both compounds presented difficulties in isolation and no method of estimation of yield was found: it is proposed to discuss their structure and mode of formation later.

Nitric acid in glacial acetic acid (90 moles % of HNO₃) reacted through a deep violet intermediate to give the epoxide and isolable pinacone: at 70 moles % the intermediate was yellow brown; epoxide and compound (A) were isolated but the pinacone was not detected. Nitric acid in chloroform (50 moles %) resembled aqueous nitric acid (79 moles %) as an oxidising agent (cf. Table), but dinitrogen pentoxide (31 moles %) in chloroform reacted more vigorously, though without colour change, to give much 4,4'-dinitrobenzophenone and a little of the epoxide. Oxidation with ammonium peroxodisulphate in concentrated sulphuric acid gave the pinacone as main product.

It follows, incidentally, that the substance of m. p. *ca.* 100° obtained by Biltz² by prolonged nitration of tetraphenylethylene already contained the epoxide before treatment with chromium(VI) oxide.

Discussion.—No previous example of epoxidation of an ethylenic linkage by nitric acid seems to have been reported; few epoxides, of course, could exist unchanged in this medium. Nitric acid is known sometimes to produce a glycol or its ester,³ though not necessarily through an epoxide.⁴

Epoxidation of tetra-*p*-nitrophenylethylene in 90% nitric acid, like epoxidation by

² Biltz, *Annalen*, 1897, **296**, 219.

³ Biltz, *Annalen*, 1909, **363**, 156; Wieland and Sakellarios, *Ber.*, 1920, **53**, 201; Perkin and Plant, *J.*, 1923, **123**, 676; Dunnivant, *J. Org. Chem.*, 1956, **21**, 1513; Atkinson, Kershaw, and Taylor, *J.*, 1962, 4426.

⁴ Yates and Stout, *J. Amer. Chem. Soc.*, 1954, **76**, 5110.

chromium(vi) oxide in acetic acid,^{4,5} is unaccompanied by 1,2-rearrangement and must therefore proceed with minimal separation of charge. The nature of the yellow-brown intermediate is unknown, but its failure to appear in acid weaker than *ca.* 90% (72 moles %) may indicate that unsolvated HNO₃ molecules are involved, which at lower concentrations tend to form complexes,⁶ H₂O, 2HNO₃. The intervention of nitrogen dioxide cannot, however, be excluded. The reaction in chloroform of nitric acid, but not of dinitrogen pentoxide, seems essentially similar.

In aqueous nitric acid ionic self-dehydration becomes increasingly important in the concentration range of 95–100% (>84 moles %):⁶ 2HNO₃ ⇌ H₂O + NO₂⁺ + NO₃⁻. So the reaction intermediate is formed under conditions of enhanced polarity, revealing progressive colour change and an increasing tendency to undergo internal rearrangement before yielding the end-product. The deep violet complex, though visually almost indistinguishable from the tri-*p*-nitrophenylmethide anion,¹ also resembles the violet intermediate in the oxidation of tetraphenylethylene to 9,10-diphenylphenanthrene with bromine in presence of tin(IV) chloride.⁷ Tetra-*p*-nitrophenylethylene does not react with bromine in this way, but recent evidence suggests that oxidations of this type may occur under very highly acidic conditions.

EXPERIMENTAL

Absolute nitric acid⁸ was redistilled under reduced pressure, condensing below -40° (sulphate test negative). Less concentrated acid was produced by dilution, or from "AnalaR" nitric acid (fuming); concentrations (g. per 100 g. of solution) were determined by titration with standard alkali. Tetra-*p*-nitrophenylethylene, crystallised from dioxan, was dried at 150°/0.1 mm.

General Procedure.—The ethylene (2.048 g.) was added quickly to the nitric acid (40 c.c.) at 0° (or -20°) with agitation. Dissolution was rapid, and characteristic colour changes were observed. After periods varying from 20 min. (100% acid) to 5 hr. (90% acid) the pale orange solutions were diluted with much water and filtered next day. On prolonged storage the filtrate sometimes gave a further precipitate of 4,4'-dinitrobenzophenone (1–2%). Further amounts of the benzophenone were separated from the dried solid precipitate by treatment during 3 hr. at 90° of its solution in 2-methoxyethanol (20 c.c.) with Girard's reagent P (2 g.) and dichloroacetic acid (2 g.); the mixture was diluted with much water, filtered, and heated at 100° with hydrochloric acid (one such treatment yielded most of the ketone but a little more could be isolated by repetition of the process).

The greater part of the epoxide was isolated by crystallisation of the dried solid precipitate from dioxan (15 c.c.). The filtrate on dilution with ethanol (40 c.c.) sometimes (*e.g.*, 100% and 98% acid) gave crystals of the pinacone, but in all instances pinacone in solution was estimated by addition of potassium hydroxide (2 g.) in ethanol (10 c.c.) and isolation of *p*-nitrobenzoic acid from the solution obtained after acidification, dilution to 500 c.c., and filtration at pH 10. After ether extraction at pH 1–2 the acid, m. p. 238°, was recovered from the extracts with 4% aqueous sodium hydroxide (25 c.c.); the solution was filtered, acidified with hydrochloric acid, seeded, and kept for 3 days at 0°.

For estimation of epoxide in the solid filtered from the solution at pH 10, the dried material was dissolved in concentrated sulphuric acid (40 c.c.), the solid was reprecipitated after 4 hr. by addition of ice-water, and *p*-nitrobenzoic acid was isolated after hydrolysis in dioxan-ethanol with potassium hydroxide. The solid obtained after the second hydrolysis was set aside for isolation of compounds (A) and (B) by crystallisation or chromatography.

Exploratory reactions in mixtures of 100% nitric acid and glacial acetic acid were carried out similarly, but were not examined with precision.

The ethylene in dry chloroform (40 c.c.) and 100% nitric acid (20 c.c.) was left at 0° for 25 hr. ;

⁵ Mosher, Steffgen, and Lansbury, *J. Org. Chem.*, 1961, **26**, 670.

⁶ Gillespie, Hughes, and Ingold, *J.*, 1950, 2552; Ingold and Millen, *J.*, 1950, 2612; Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.

⁷ Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1932, **54**, 3687.

⁸ Stern, Mullhaupt, and Kay, *Chem. Rev.*, 1960, **60**, 185.

there was an apparent tendency for separation into two phases.⁹ Water was added and the chloroform removed by gentle heating; subsequent treatment was as described earlier.

Reaction with Dinitrogen Pentoxide in Chloroform.—To a solution of dinitrogen pentoxide¹⁰ (6.1 g.) in dry chloroform (14.8 g.) at 0° was added tetra-*p*-nitrophenylethylene (1.024 g.), and the orange-yellow solution was left overnight at 0°. The solvent was removed in a stream of oxygen, and the product warmed with water. The filtered solid gave 0.56 g. (51%) of 4,4'-dinitrobenzophenone, m. p. 188—190°, on crystallisation from glacial acetic acid, and the mother-liquor deposited 0.03 g. (3%) of tetra-*p*-nitrophenyloxiran, m. p. 294—296° (decomp.). The residues contained mainly the benzophenone; alcoholic potassium hydroxide gave a pale violet colour indicative of a trace of pinacone.

The epoxide subjected to these conditions was recovered unchanged (70%).

Preparation of the Epoxide.—Tetra-*p*-nitrophenylethylene (20.48 g.) was added to 96% nitric acid (500 c.c.) at 0—5° with stirring. A dark violet-brown solution resulted, which became pale orange within 2½ hr. Dilution with water (3 l.) gave a yellow solid (20.7 g.) which was filtered off and dried: the filtrate gave a further precipitate of 4,4'-dinitrobenzophenone, m. p. 185° (0.34 g., 1.6%). The solid, on crystallisation from glacial acetic acid (150 c.c.), gave tetra-*p*-nitrophenyloxiran (9.7 g., 46%), m. p. 296—297° (decomp.). Recrystallisation from dioxan gave material of m. p. 301—303° (decomp.) (corr.), identical with that prepared by oxidation with chromium(VI) oxide.¹

Preparation of the Pinacone.—(a) Tetra-*p*-nitrophenylethylene (20.48 g.), added to 97.5% nitric acid (500 c.c.) at 0—5°, gave a dark brown-violet solution, pale orange after 30 min. The solid obtained on dilution with water (3 l.) was dried and dissolved in concentrated sulphuric acid (400 c.c.). The solution was poured on ice after 5 hr. and the precipitated solid collected, dried, and crystallised from glacial acetic acid to give solvated *p*-nitrobenzoyltri-*p*-nitrophenylmethane in 65—75% yield.

(b) Ammonium peroxodisulphate (0.6 g.) was added to a solution of tetra-*p*-nitrophenylethylene (0.35 g.) in concentrated sulphuric acid (8 c.c.) and left at room temperature for 24 hr. The solid obtained on addition to ice contained much unchanged material: the latter was destroyed by warming the whole for 5 min. in acetone with potassium permanganate (0.35 g.). The resulting mixture of pinacone and 4,4'-dinitrobenzophenone was crystallised twice from dioxan-ethanol, to give the solvated pinacone (0.9 g.) (22%).

Solvation of the Pinacone.—The dioxan solvate described earlier¹ appeared, on re-examination, to be a hemisolvate [Found: solvent, 7.4 (by weight loss); dioxan, 8.6 (by an infrared method). C₂₆H₁₆N₄O₉ · ½C₄H₈O₂ requires C, 58.7; H, 3.5; N, 9.8; dioxan, 7.6%]. Although this solvate crystallised from dioxan on addition of ethanol, no ethanol could be detected in the crystals by infrared examination. A solvate which crystallised from chloroform in jagged prisms on addition of carbon tetrachloride contained both solvents in not quite stoicheiometric proportions (by collection of solvent of crystallisation and analysis for each by an infrared method) (Found: C, 48.5; H, 2.5; Cl, 19.1; N, 8.0; CHCl₃, 8.3; CCl₄, 12.6. C₂₆H₁₆N₄O₉ · ½CHCl₃ · ½CCl₄ requires C, 48.8; H, 2.5; Cl, 18.7; N, 8.4; CHCl₃, 9.0; CCl₄, 11.6%). The solid foam obtained on complete drying of this solvate up to 190°/1.5 mm. had m. p. 224—226°. Unsolvated pinacone has not been obtained in an unequivocally crystalline form.

Effect of Nitric Acid on the Pinacone.—From a solution of the pinacone in 96% nitric acid, unchanged material (>10%) was recovered after 260 hr. at room temperature, together with *p*-nitrobenzoic acid (>50%). The residue, which consisted only partly of tri-*p*-nitrophenylmethanol, was not further examined.

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⁹ Paquot and Perron, *Bull. Soc. chim. France*, 1957, 529.

¹⁰ Caesar and Goldfrank, *J. Amer. Chem. Soc.*, 1946, **68**, 372.