135. *Polyphenylethylenes. Part I. Preparation and Characteristics of Tetra-*p*-nitrophenylethylene.*

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Methods are described for the preparation of authentic tetra-*p*-nitrophenylethylene. In this compound the ethylenic linkage is of low reactivity but oxidation with chromium trioxide has given the epoxide, which rearranges to the pinacone under strongly acidic conditions. Tetra-*p*-aminophenylethylene has been characterised.

BY treatment of tetraphenylethylene with nitric acid (*d* 1·48) for 3 hr., Biltz [1] obtained a substance, m. p. *ca.* 100°, which he was unable to purify: on the basis of nitrogen content he considered this a tetranitro-derivative. A crystalline oxidation product, m. p. 294°, appeared to be the corresponding epoxide. Wizinger [2] accepted the nitration product as tetra-*p*-nitrophenylethylene and claimed to have reduced it to tetra-*p*-aminophenylethylene, m. p. 250°, which he also prepared from 4 : 4′-diaminobenzophenone. Bassett, Thorne, and Young [3] obtained Biltz's nitration product in yellow crystals, m. p. 274—276°, but reported no analytical figures. By the action of dinitrogen tetroxide on tetraphenylethylene Schlenk [4] obtained a compound, m. p. 292°, which he presumed identical with Biltz's epoxide.

An approach to the unambiguous preparation of these compounds was suggested by the availability of α-bromination products of di-*p*-nitrophenylmethane.[5]

Authentic tetra-*p*-nitrophenylethylene, m. p. 298—299°, was obtained in 80% yield from dibromodi-*p*-nitrophenylmethane by the action of sodium iodide in acetone (cf. Finkelstein [6]) or pyridine. Di-*p*-nitrophenylmethyl bromide reacted in acetone, to give 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane, which Biltz [1] obtained by nitration of 1 : 1 : 2 : 2-tetraphenylethane.

The ethylene was obtained from di-*p*-nitrophenylmethyl bromide by the action of sodium methoxide in methanol, presumably by a route analogous to that of self-alkylations discussed by Hauser *et al.*,[7] but a concurrent reaction led to 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane. The reaction of sodium methoxide with dibromodi-*p*-nitrophenylmethane gave some tetra-*p*-nitrophenylethylene in addition to the expected dimethoxydi-*p*-nitrophenylmethane.

The structure of the ethylene was confirmed by its formation from tetraphenylethylene

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[1] Biltz, *Annalen*, 1897, **296**, 219.
[2] Wizinger, *Ber.*, 1927, **60**, 1377.
[3] Bassett, Thorne, and Young, *J.*, 1949, 85.
[4] Schlenk, *Annalen*, 1913, **394**, 214.
[5] Gorvin, *J.*, 1955, 83.
[6] Finkelstein, *Ber.*, 1910, **43**, 1528, 1533.
[7] Hauser, Brasen, Skell, Kantor, and Brodhag, *J. Amer. Chem. Soc.*, 1956, **78**, 1653; Brasen, Kantor, Skell, and Hauser, *ibid.*, 1957, **79**, 397.

by nitration under relatively mild conditions, preferably in an equipartite mixture of nitric acid (95%) and acetic acid. This was the most generally convenient preparation since it avoided the tedious purification of di-*p*-nitrophenylmethane:[8] moreover, tetraphenylethylene, in which *ortho*-nitration is reduced by steric compression, was readily accessible through a modification of Finkelstein's procedure. Nitration with dinitrogen tetroxide gave an identical product: no evidence was found for epoxidation in this reaction and it is probable that Schlenk's " epoxide "[4] was tetra-*p*-nitrophenylethylene.

In tetra-*p*-nitrophenylethylene the *p*-nitro-groups diminish the nucleophilic character of the central double bond, the reactivity of which is already reduced by conjugation[9] and the shielding effect of the bulky aryl groups.[10] Thus, whereas tetraphenylethylene fails to add bromine but reacts with chlorine[3,6] and with perbenzoic acid,[11] the tetra-*p*-nitro-derivative appeared to react with none of these and to be unaffected by dinitrogen trioxide, osmium tetroxide, selenium dioxide, lead tetra-acetate, and performic acid. The intense red colour shown in chlorosulphonic acid suggests the presence of a complex cation, but in this medium the nitro-groups must be extensively protonated.[12]

The ethylenic linkage was attacked by stronger oxidising agents: dinitrogen tetroxide reacted very slowly, to yield 4 : 4'-dinitrobenzophenone, permanganate readily gave the same product, but with chromium trioxide in acetic acid tetra-*p*-nitrophenyloxiran (28%) was formed in addition to the benzophenone. A non-cationic complex (cf. Zeiss and Zwanzig[13]) seems a rather more probable intermediate than a carbonium ion[14] in this instance: the epoxide may possibly be formed directly by a concurrent " three-centre-type "[15] addition, similar to that suggested for epoxidation by organic per-acids.[16] Tetra-*p*-nitrophenyloxiran appeared identical with the epoxide described by Biltz.[1] It was unusually stable in acidic media but concentrated sulphuric acid produced 1 : 2-rearrangement to *p*-nitrobenzoyltri-*p*-nitrophenylmethane. This pinacone was hydrolysed immediately in alcoholic potassium hydroxide to *p*-nitrobenzoic acid and tri-*p*-nitrophenylmethane, of which the anion is deep violet.[17]

Tetra-*p*-nitrophenylethylene dissolved in concentrated nitric acid, presumably through solvation of the nitro-groups, but its stability in these solutions depended greatly on the acid concentration. Little reaction occurred in 70% nitric acid (*d* 1·42) even at 80°. In stronger nitric acids, composed largely of the rather stable monohydrate[18] H_2O,HNO_3 (>77·8%), a slow reaction proceeded at 0°, reflected in a depression in the m. p. of the largely unchanged substance recovered on dilution with water. In this concentration region (*ca.* 78—84%) nitric acid solutions at 0° reacted rapidly with tetraphenylethylene to give tetra-*p*-nitrophenylethylene, which suggested that with the more concentrated acid (" *d* 1·48," *i.e.*, *ca.* 84·5—87·5%) and extended time used by Biltz[1] an additional reaction occurred, leading to a complex product. It is proposed to discuss this later.

Tetra-*p*-aminophenylethylene, m. p. 325°, was readily prepared by reduction of tetra-*p*-nitrophenylethylene, tetra-*p*-nitrophenyloxiran, or 4 : 4'-diaminobenzophenone: its structure was confirmed by conversion into tetraphenylethylene and into 1 : 1 : 2 : 2-tetra-*p*-aminophenylethane.[1] There is no evidence available to explain the low m. p. (250°) reported by Wizinger.[2] Polynitro-compounds of low solubility, such as the epoxide, are conveniently reduced in refluxing hydriodic acid.

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[8] Staedel, *Annalen*, 1894, **283**, 153.
[9] Coulson and Jacobs, *J.*, 1949, 2805.
[10] Szwarc and Leavitt, *J. Amer. Chem. Soc.*, 1956, **78**, 3590.
[11] Lévy and Lagrave, *Bull. Soc. chim. France*, 1928, **43**, 440.
[12] Gillespie, *J.*, 1950, 2542.
[13] Zeiss and Zwanzig, *Chem. and Ind.*, 1956, 545; *J. Amer. Chem. Soc.*, 1957, **79**, 1733.
[14] Hickinbottom, Peters, and Wood, *J.*, 1955, 1360; Davis and Hickinbottom, *J.*, 1958, 2205.
[15] Skell and Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 5430.
[16] Lynch and Pausacker, *J.*, 1955, 1525.
[17] Hawthorne and Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 2549.
[18] Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722; cf. Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.

In the usual screening tests, tetra-*p*-aminophenylethylene showed no antibacterial, antiprotozoal, or schistosomicidal activity.

EXPERIMENTAL

Concentrations of nitric acid are expressed in g. of acid per 100 g. of solution.

Debrominations with Sodium Iodide.—(a) *Dibromodiphenylmethane.* To diphenylmethane (33·6 g.) was added bromine (70 g.) during 3 hr. at 120° under illumination (incandescent lamp, 200 w). The product was refluxed with sodium iodide (80 g.) in acetone (400 c.c.) for 1½ hr. The filtered precipitate was washed with acetone, acidified aqueous sodium sulphite, and water and crystallised from dioxan–ethanol. This procedure, a modification of that of Finkelstein,[6] provided a rapid and convenient route to tetraphenylethylene (*ca.* 35%, m. p. 222°).

(b) *Dibromodi*-p-*nitrophenylmethane.* Di-*p*-nitrophenylmethane was treated with an excess of bromine in boiling carbon tetrachloride (20 vols.) under illumination (200 w) for 5 hr. The solution was evaporated to dryness and the residue refluxed for 1 hr. in acetone (20 vols.) with excess of sodium iodide. By addition of acidified aqueous sodium sulphite to the concentrated solution and crystallisation of the precipitate from dioxan or from acetic acid (extractor), *tetra*-p-*nitrophenylethylene* (*ca.* 80%) was obtained in yellow prismatic needles, m. p. 298—299° [306—307° (corr.)] (Found: C, 60·8; H, 3·3; N, 11·0. $C_{26}H_{16}O_8N_4$ requires C, 60·95; H, 3·1; N, 10·9%). These formed orange-red solutions in concentrated sulphuric acid and intensely red solutions in chlorosulphonic acid; the ethylene was recovered unchanged on addition to ice.

When dibromodi-*p*-nitrophenylmethane was treated with sodium iodide in moist pyridine (25 vols.) the resulting tetra-*p*-nitrophenylethylene (84%) was accompanied by 4 : 4′-dinitrobenzophenone (11%) formed by hydrolysis. The use of glacial acetic acid as solvent gave a mixture of 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane (*ca.* 55%) (see below) and di-*p*-nitrophenylmethane.

(c) *Di*-p-*nitrophenylmethyl bromide.* When the bromide was refluxed for 3 hr. with sodium iodide in acetone the main product was 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane (40%), which crystallised in needles, m. p. 330—335° (decomp.), from pyridine–ethanol and was identical with authentic material, m. p. 330—335° (decomp.) (Found: C, 60·9; H, 3·7; N, 10·9. Calc. for $C_{26}H_{18}O_8N_4$: C, 60·7; H, 3·5; N, 10·9%), prepared by nitration of 1 : 1 : 2 : 2-tetraphenylethane.[1] Di-*p*-nitrophenylmethane (19%) was also obtained.

When the solvent was glacial acetic acid, the product consisted of di-*p*-nitrophenylmethane (62%) and a small amount of polymeric material.

Alkaline Debrominations.—(a) *Di*-p-*nitrophenylmethyl bromide.* When sodium methoxide (from 0·5 g. of sodium) was added to the bromide (3·37 g.) in refluxing methanol the mixture developed an intense violet colour. This soon changed to brown and within 1 hr. a crystalline solid was precipitated, which gave tetra-*p*-nitrophenylethylene (35—40%) and the almost insoluble 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane (6—12%) on extraction with hot acetic acid.

Potassium hydroxide in methanol gave qualitatively similar results but in certain reactions the yield of the ethane was as high as 37% without corresponding increase in the yield of the ethylene.

(b) *Dibromodi*-p-*nitrophenylmethane.* The bromo-compound (0·416 g.) was refluxed with potassium hydroxide (0·26 g.) in methanol for 7 hr. The product obtained on dilution with water crystallised from acetic acid. A small yield of tetra-*p*-nitrophenylethylene was obtained, but the main product was *dimethoxydi*-p-*nitrophenylmethane* (35%) which formed large rhombs, m. p. 157—158° (Found: C, 56·9; H, 4·2; N, 8·8. $C_{15}H_{14}O_6N_2$ requires C, 56·6; H, 4·4; N, 8·8%). This was hydrolysed by concentrated sulphuric acid to 4 : 4′-dinitrobenzophenone.

Nitration of Tetraphenylethylene.—(*a*) To a mixture of 95% nitric acid (100 c.c.) and glacial acetic acid (100 c.c.) at 0—5° was added tetraphenylethylene (10 g.) in portions. After 1½ hr. the solution was diluted with water, and the precipitate collected, dried, and crystallised from dioxan, to give tetra-*p*-nitrophenylethylene (65—70%), m. p. 298—299° unchanged by admixture with previously described material.

(*b*) Nitration with dinitrogen tetroxide [19] according to Schlenk's method [4] gave an identical product (75%).

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[19] Schlubach and Rott, *Annalen*, 1955, **594**, 65.

(*c*) Aqueous nitric acid (79%, 83%, and 87% severally) (15 c.c.) reacted with tetraphenylethylene (1·0 g.) at 0—5° at progressively faster rates to give orange-yellow solutions. The products obtained on dilution with water (after 1 hr., 20 min., and 10 min.) gave tetra-*p*-nitrophenylethylene ($>$50%). If the 87% acid was allowed to react for 3 hr. at 0° the solution gave on dilution a complex mixture from which the ethylene was isolated with difficulty and in an impure state (*ca.* 20%).

*Oxidation of Tetra-*p*-nitrophenylethylene.*—(a) *Chromium trioxide.* The ethylene (0·5 g.) was heated in acetic acid (80 c.c.) with chromium trioxide (0·5 g.) at 90—100° for 3 hr. Crystals of tetra-*p*-nitrophenyloxiran (0·14 g., 28%) separated slowly from the cooled solution; these were recrystallised from dioxan or acetic acid and formed pale yellow prisms, m. p. 294—296° (decomp.) [301—303° (corr.)] (Found: C, 59·05; H, 3·1; N, 10·3. Calc. for $C_{26}H_{16}O_9N_4$: C, 59·1; H, 3·05; N, 10·6%). Biltz[1] gave m. p. 294° [298—299° (corr.)]. The major product, obtained by dilution with water and crystallisation from acetic acid, was 4 : 4′-dinitrobenzophenone (63%). The crude products gave no colour when treated, in dioxan solution, with ethanolic potassium hydroxide.

(b) *Potassium permanganate.* In acetone solution the only product found was 4 : 4′-dinitrobenzophenone.

(c) *Dinitrogen tetroxide.* The ethylene (0·5 g.) was kept in a sealed tube at 0° in dinitrogen tetroxide[19] (10 c.c.). After 9 months it was still largely unchanged: 4 : 4′-dinitrobenzophenone (*ca.* 25%) was the only product found.

*Rearrangement of Tetra-*p*-nitrophenyloxiran.*—When the orange-yellow solution of the epoxide in concentrated sulphuric acid was left for 2 hr., p-*nitrobenzoyltri*-p-*nitrophenylmethane* was obtained on addition to ice. Crystallisation always gave solvated material, probably of clathrate nature, which lost weight slowly and incompletely when heated under reduced pressure. Dioxan gave rhombs, m. p. 188—190° (decomp.) (Found: C, 58·8; H, 3·4; N, 9·2. $C_{26}H_{16}O_9N_4,C_4H_8O_2$ requires C, 58·4; H, 3·9; N, 9·1%) (the solvate possibly contained $<$1 mol. of dioxan as the nitrogen analysis is unreliable): acetic acid gave crystals, m. p. 179—181° (decomp.) [Found: C, 57·7; H, 3·2; N, 10·0; AcOH, 6·7 (by titration), 6·1 (loss at 150—160°/1·5 mm. in 40 hr.). $C_{26}H_{16}O_9N_4,\frac{2}{3}C_2H_4O_2$ requires C, 57·8; H, 3·3; N, 9·9; AcOH, 7·0%]. A solution in dioxan–ethanol became intensely violet on addition of alcoholic potassium hydroxide; the colour disappeared on dilution with water and acidification. A solid was filtered off after the acidified solution had been made slightly alkaline, and the filtrate was reacidified and extracted twice with ether. *p*-Nitrobenzoic acid, m. p. 235—236°, was obtained from the ether by extraction with 4% sodium hydroxide solution, which was then acidified. The solid was crystallised from chloroform–ether and then from chloroform, to give tri-*p*-nitrophenylmethane, m. p. 212°, not depressed by authentic material obtained by nitration of triphenylmethane.[20] The pinacone was unaffected by chromium trioxide in acetic acid.

The epoxide was also converted into the pinacone when its orange-red solution in chlorosulphonic acid was left for 2 hr., or when it was refluxed for 1½ hr. in glacial acetic acid (20 vols.) and concentrated sulphuric acid (10 vols.). In 95% nitric acid there was no appreciable change after 24 hr. at 0°: after 25 days, 4 : 4′-dinitrobenzophenone was recovered. In 100% nitric acid, some epoxide remained after 7 days, and the benzophenone was also present, but no colour was shown with alcoholic potassium hydroxide.

*Tetra-*p*-aminophenylethylene.*—(*a*) 4 : 4′-Diaminobenzophenone (0·5 g.) in concentrated hydrochloric acid (18 c.c.) was heated for 5 hr. with granulated tin. The crystals which separated were washed with ethanol and decomposed with aqueous sodium hydroxide, to give *tetra*-p-*aminophenylethylene* as a pale yellow crystalline substance becoming green in moist air: it showed a pale green fluorescence in ultraviolet light. When purified through its ethanol-insoluble tetrahydrochloride and crystallised from ethanol (extractor) it had m. p. 325° [333—334° (corr.)] (Found: C, 79·0; H, 6·2; N, 14·3. $C_{26}H_{24}N_4$ requires C, 79·6; H, 6·2; N, 14·3%). The *tetra*-N-*acetyl derivative* had m. p. 320° (from acetic acid) (Found: C, 71·7; H, 5·8; N, 9·8. $C_{34}H_{32}O_4N_4,0{\cdot}5H_2O$ requires C, 71·7; H, 5·8; N, 9·8%).

(*b*) An identical tetra-amine was obtained by the reduction of either tetra-*p*-nitrophenylethylene or the oxiran with tin or stannous chloride in hydrochloric acid.

(*c*) When tetra-*p*-nitrophenyloxiran was refluxed for 2½ hr. in hydriodic acid, and the solution was added to aqueous sodium sulphite, tetra-*p*-aminophenylethylene was precipitated on addition of alkali.

[20] Shoesmith, Sosson, and Hetherington, *J.*, 1927, 2221.

Tetra-*p*-aminophenylethylene gave a small yield of tetraphenylethylene when its diazotised solution was refluxed with ethanol. Reduction of the base with sodium in pentyl alcohol gave 1 : 1 : 2 : 2-tetra-*p*-aminophenylethane, m. p. 270—272°, not depressed on admixture with the base, m. p. 272—274°, prepared by reduction of 1 : 1 : 2 : 2-tetra-*p*-nitrophenylethane according to Biltz's directions [1] [he gave m. p. 272° (corr.)] or by refluxing in hydriodic acid (Found: C, 79·2; H, 6·9; N, 13·9. Calc. for $C_{26}H_{26}N_4$: C, 79·2; H, 6·6; N, 14·2%). This tetra-amine, dried at 100°/0·05 mm., absorbed *ca.* $2H_2O$ reversibly from moist air.

The author thanks Messrs. K. Baker and A. G. Seaborn for experimental assistance and Mr. P. R. W. Baker for the microanalysis.

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[*Received, November 3rd,* 1958.]