

684. *Formation of 1,1-Dinitroethyl Aromatic Compounds.*

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1,1-Dinitroethyl aromatic compounds are products of the oxidation by nitric acid of certain isopropyl aromatic compounds; their structures are confirmed by synthesis from the corresponding aryl methyl ketoximes. Evidence is presented which suggests a reaction sequence involving isopropenyl group formation. 1,1-Dinitroethylbenzene is shown to be produced during the oxidation of ethylbenzene by nitric acid.

ISOPROPYL aromatic compounds are readily oxidised by 30—60% nitric acid at reflux temperature. An induction period occurs if pure nitric acid is used, so it is preferable to ensure the initial presence of nitrous acid by addition of a nitrite.

The main product of oxidation of *p*-di-isopropylbenzene under these conditions is terephthalic acid, but the highest yield which has been reported is only about 65% of the theoretical.¹ Two other stable oxidation products, one neutral, the other acidic, are readily isolated. The acidic substance can also be obtained by oxidising *p*-acetylcumene or cumic acid with 30—60% nitric acid. Both substances are converted into terephthalic acid by heating them with 30% nitric acid at 180°C, and *p*-di-isopropylbenzene itself gives terephthalic acid in 90% yield under the same conditions.

The infrared spectra of the two substances indicated the presence of nitro-groups, which, since terephthalic acid was produced on further oxidation, must be located in the side-chains. The elemental analysis of the neutral product was consistent with that of a diethyltetranitrobenzene, and the analysis of the acidic product with that of an ethyl-dinitrobenzoic acid. The stability of both substances towards further oxidation and the insolubility of the neutral substance in alkali suggested the absence of the partial structure $-\text{CH}(\text{NO}_2)-$. The substances were therefore considered to be *p*-bis-(1,1-dinitroethyl)-benzene and *p*-(1,1-dinitroethyl)benzoic acid, and these structures were confirmed by synthesis of the former from *p*-diacetylbenzene dioxime and from *p*-acetylcumene oxime, and of the latter from the oxime of *p*-acetylbenzoic acid. 2-Hydroxy-2-propyl and isopropenyl aromatic compounds also gave 1,1-dinitroethyl aromatic compounds on oxidation by 30—40% nitric acid.

1,1-Dinitroethylbenzene, which Scholl² obtained impure from acetophenone oxime and nitrogen dioxide, was similarly obtained from cumene and 40% nitric acid, and its structure was checked by synthesis by a method similar to Scholl's. It was also produced, along with 1-nitroethylbenzene, when ethylbenzene was oxidised by 40% nitric acid.

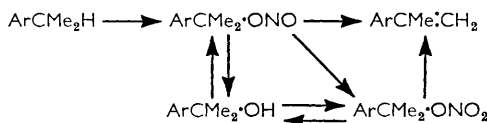
A previous example of the use of nitric acid to produce a 1,1-dinitroethyl aromatic

¹ B.P. 766,564.

² Scholl, *Ber.*, 1890, **23**, 3490.

compound is the formation of 4-(1,1-dinitroethyl)pyridine from 4-(1-hydroxymethyl-ethyl)pyridine and 4-(1,1-bishydroxymethylethyl)pyridine, either individually or as mixtures.³

The sequence of reactions whereby 1,1-dinitroethyl aromatic compounds are formed from isopropyl aromatic compounds is not obvious. Titov⁴ has reviewed the evidence on the course of nitric acid oxidation, and concluded that the acid does not participate directly in the oxidation of arylaliphatic materials, but acts as a reservoir for the formation of the active agents. These active agents, nitrogen dioxide and nitric oxide in their various forms and combinations, are expected to give three primary products from an isopropyl aromatic compound: the nitro-compound, $\text{ArCMe}_2\cdot\text{NO}_2$; the nitroso-compound, $\text{ArCMe}_2\cdot\text{NO}$; and the nitrite, $\text{ArCMe}_2\cdot\text{ONO}$. The similarity in behaviour of isopropyl, 2-hydroxy-2-propyl, and isopropenyl aromatic compounds in giving rise to 1,1-dinitroethyl aromatic compounds on oxidation suggests that the nitrite is involved, successive stages in the oxidation being as follows:



Of the possible products⁵ of addition of the nitrogen oxides to the double bond, only those with an α -nitroso- or α -nitro-group seem likely precursors of 1,1-dinitroethyl compounds. Elimination of a β -carbon atom could then conceivably occur at any stage in its further oxidation from carbinol to carboxyl.⁶ Where the α -substituent is a nitroso-group, such elimination will produce an oxime, which is a known precursor of a 1,1-dinitroethyl group. On the other hand, α -nitro-compounds are not readily converted into the corresponding *gem*-dinitro-compounds except from the nitronic acid form.⁴ It seems possible, however, either that the nitronic acid could be the first product of the β -carbon elimination, or that direct replacement of the β -carbon by a nitroso- or nitro-group could occur, so that intervention of the α -nitro-compound cannot be dismissed. The presence of hydrogen peroxide, which may be expected to reduce the nitric oxide concentration, reduces the yield of 1,1-dinitroethyl pyridine from 1-hydroxymethyl- or 1,1-bishydroxymethyl-ethylpyridine;³ this evidence supports the supposition that the nitroso route at least is involved.

EXPERIMENTAL

Melting points were determined on the hot stage of a polarising microscope. Identities were confirmed by mixed m. p. (where applicable) and i.r. spectra.

1,1-Dinitroethyl Compounds by Nitric Acid Oxidation.—In each case a few mg. of sodium nitrite were added to the nitric acid immediately before use to ensure the initial presence of nitrous acid. (i) *From p-di-isopropylbenzene.* *p*-Di-isopropylbenzene (25 g.) was refluxed with 40% nitric acid (500 ml.) for 6 hr. The mixture was filtered while still hot. On cooling, the filtrate deposited crystals which were collected, dissolved in ether, separated from a little ether-insoluble material (0.3 g.), and isolated by evaporation. The product (8.4 g.) had m. p. 165–175°; recrystallisation from water gave *p*-(1,1-dinitroethyl)benzoic acid, m. p. 170–170.5° (decomp.) (Found: C, 45.1; H, 3.7; N, 11.4. $\text{C}_9\text{H}_8\text{N}_2\text{O}_6$ requires C, 45.0; H, 3.3; N, 11.6%). The *amide*, recrystallised from dilute acetic acid, had m. p. 139–141° (decomp.) (Found: C, 45.0; H, 4.0; N, 16.8. $\text{C}_9\text{H}_9\text{N}_3\text{O}_5$ requires C, 45.2; H, 3.8; N, 17.6%). The product insoluble in hot water from the oxidation (11.0 g.) was ground, warmed with 5% sodium carbonate solution and filtered to give a neutral product (6.7 g.), purified by recrystallisation from methanol to give *p*-bis-1,1-dinitroethylbenzene, m. p. 172–173° (decomp.) (Found: C, 38.4; H, 3.5; N, 17.4. $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_8$ requires C, 38.2; H, 3.2; N, 17.8%).

³ Rubtsov, Niketskaya, and Usovskaya, *Zhur. obshechi Khim.*, 1955, **25**, 2453.

⁴ Titov, *Uspekhi Khim.*, 1952, **21**, 881.

⁵ Levy and Rose, *Quart. Rev.*, 1947, **1**, 358; Schechter and Ley, *Chem. and Ind.*, 1955, 535.

⁶ Earl, Ellsworth, Jones, and Kenner, *J.*, 1928, 2697.

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(ii) *From p-bis-1-hydroxy-1-methylethylbenzene.* The diol (2.5 g.; m. p. 172—173°) was refluxed with 30% nitric acid (50 ml.) for 4 hr. *p*-(1,1-Dinitroethyl)benzoic acid (0.55 g.), m. p. 169—170° (decomp.), was isolated as above.

(iii) *From p-acetylcumene.* The ketone (19.5 g.) was refluxed with 50% nitric acid (200 ml.) for 4 hr. *p*-(1,1-Dinitroethyl)benzoic acid (9.8 g.), m. p. 171—174° (decomp.), was isolated as above.

(iv) *From cumic acid.* Cumic acid (20 g.) was refluxed with 50% nitric acid (200 ml.) for 4 hr. The hot mixture was filtered and the insoluble product was extracted with boiling acetone. *p*-(1,1-Dinitroethyl)benzoic acid (3.1 g.), m. p. 175—177° (decomp.) was isolated by evaporation. The reaction filtrate on cooling deposited more acid (2.6 g.), m. p. 171—174° (decomp.).

(v) *From p-(1-hydroxy-1-methylethyl)benzoic acid.* The acid (2 g.) was refluxed with 40% nitric acid (20 ml.) for 5 hr. The hot mixture was filtered; the filtrate on cooling deposited *p*-(1,1-dinitroethyl)benzoic acid (0.18 g.), m. p. 171—174° (decomp.) after recrystallisation from water. The product insoluble in hot water (1.59 g.) had m. p. 313—318° (decomp.) and was completely soluble in acetone; it therefore contained little or no terephthalic acid.

(vi) *From cumene.* Cumene (40 g.) was refluxed with 40% nitric acid (400 ml.) for 3 hr. The cold mixture was extracted with sufficient ether to dissolve all the solid, and the organic layers were repeatedly extracted with 5% sodium carbonate solution, which appeared to decompose the ether-insoluble layer slowly. The ethereal layer was dried (Na₂CO₃)₂ and evaporated, and the residue (16.8 g.) was distilled; the main fraction, a pale yellow oil (9.7 g.), was 1,1-dinitroethylbenzene, b. p. 99—102°/0.4 mm., d_4^{25} 1.2457, n_D^{25} 1.5320 (Found: C, 49.5; H, 4.6; N, 13.8. C₈H₈N₂O₄ requires C, 49.0; H, 4.1; N, 14.3%).

(vii) *From isopropenylbenzene.* Isopropenylbenzene (20 g.) was refluxed with 40% nitric acid (200 ml.) for 5 hr.; the reaction was very vigorous in the early stages. The product was worked up as already described for cumene; the neutral product (5.2 g.) on distillation gave 1,1-dinitroethylbenzene (2.1 g.), b. p. 99—103°/0.4 mm., d_4^{25} 1.2457 n_D^{25} 1.5341.

(viii) *From ethylbenzene.* Ethylbenzene (40 g.) was refluxed with 40% nitric acid (400 ml.) for 5 hr. The product was worked up as described for cumene. Fractional distillation gave the following fractions (a) (8.6 g.), b. p. 90—94°/1.2 mm., d_4^{25} 1.0985, n_D^{25} 1.5208, essentially 1-nitroethylbenzene; (b) (2.4 g.), b. p. 64—68°/0.2 mm., d_4^{25} 1.1130 n_D^{25} 1.5228, mainly 1-nitroethylbenzene but containing a carbonyl impurity, probably acetophenone; (c) (3.5 g.), b. p. 83—91°/0.2 mm., d_4^{25} 1.2403, n_D^{25} 1.5298, mainly 1,1-dinitroethylbenzene but containing a carbonyl impurity, probably acetophenone. Further neutral material, distillable above 100°/0.2 mm., solidified in the still-head but was not further examined.

1,1-Dinitroethyl Compounds from Oximes.—(i) *p*-Diacetylbenzene dioxime. The dioxime (0.2 g.), m. p. 254—255°, was suspended in ether (10 ml.) together with sodium nitrite (6 g.), and 30% nitric acid (25 ml.) was added slowly with cooling and shaking. Next day the ether layer was extracted with 20% sodium hydroxide, dried, and evaporated. The residue (0.15 g.) was crystallised from methanol to give *p*-bis-(1,1-dinitroethyl)benzene (0.04 g.), m. p. 171.5—172.5°, identical with the product from nitric acid oxidation of *p*-di-isopropylbenzene (mixed m. p.; i.r. spectrum).

(ii) *p*-Acetylcumene oxime. The oxime (1.14 g.) was dissolved in ether (20 ml.) and nitrogen oxides from a nitric acid oxidation of cumene were passed through the cold solution for 10 min. The dark green solution was kept for 10 min., then 40% nitric acid (40 ml.) was added, the ether boiled off, and the mixture refluxed for 2 hr. The product (1.04 g.) was filtered off, warmed with 5% sodium carbonate, filtered off (0.63 g.), and then crystallised from methanol to give *p*-bis-(1,1-dinitroethyl)benzene (0.22 g.), m. p. 170—171.5°, identical with the product from nitric acid oxidation of *p*-di-isopropylbenzene (mixed m. p.; i.r. spectrum).

(iii) *p*-Acetylbenzoic acid oxime. The oxime, m. p. 265—268° (decomp.) (Found: C, 60.5; H, 5.2; N, 7.6. C₉H₉NO₃ requires C, 60.3, H, 5.1; N, 7.8%), was prepared from *p*-acetylbenzoic acid and purified by recrystallisation from aqueous dimethylformamide. Concentrated nitric acid (s.g. 1.42; 20 ml.) was added to a suspension of the oxime (0.316 g.) in ether (20 ml.); the vigorous reaction continued until all the ether had boiled off. The solution was allowed to cool, diluted with water (20 ml.), and filtered; after being washed with water and dried at 105° the product (0.307 g.) had m. p. 173—176°, and was identical with *p*-(1,1-dinitroethyl)benzoic acid obtained by nitric acid oxidation of *p*-di-isopropylbenzene (mixed m. p.; i.r. spectrum).

(iv) *Acetophenone oxime.* The oxime (8 g.), in ether (50 ml.), was treated with 40% nitric

acid (200 ml.), then with sodium nitrite (25 g.) in water (40 ml.); the temperature was kept below 10° throughout and for 2 hr. thereafter. The ether layer was washed with 5% sodium carbonate, dried, and evaporated. The residue (5.4 g.) was distilled; recovered acetophenone formed the first fraction, followed by 1,1-dinitroethylbenzene (3.4 g.), b. p. 78—79°/0.15 mm., d_4^{25} 1.2290, n_D^{25} 1.5322, which contained a little acetophenone (6% by analysis).

Further Oxidation.—*p*-(1,1-Dinitroethyl)benzoic acid (1.97 g.) was heated with 30% nitric acid (80 ml.) in a sealed glass tube at 140°c for 2 hr. then at 180°c for 1 hr. The product, isolated by filtration, was terephthalic acid (1.30 g.; 96% of the theoretical yield) of 99.2% purity. *p*-Bis-(1,1-dinitroethyl)benzene was similarly oxidised to terephthalic acid.

p-(1,1-Dinitroethyl)benzoic acid was recovered unchanged after refluxing for 18 hr. with 30% nitric acid; no terephthalic acid was produced.

Infrared (i.r.) Spectra.—A curious feature of the i.r. spectrum of *p*-(1,1-dinitroethyl)benzoic acid was the difference between the spectra of solid samples recovered from water and from ether or acetone. In the former, a very strong broad band, presumably due to the asymmetric stretching vibration of the nitro-groups, appeared at 6.37 μ ; in the latter, two strong sharp bands appeared at 6.32 and 6.48 μ . Further differences included the presence of a weak band at 8.01 μ in the latter, absent in the former; a much more intense carboxylic hydroxyl band, at about 10.6 μ , in the former than in the latter; movement of a moderate band, possibly due to a C-N stretching vibration, from 11.4 μ in the former to 11.3 μ in the latter; and the presence of a weak band at 14.0 μ in the former, absent in the latter. The other dinitroethyl compounds exhibited single strong broad absorption bands at 6.35—6.36 μ ; the singlet nature of the absorption of these neutral compounds, together with the variation in carboxylic-hydroxyl band intensity, suggests that the doublet form of *p*-(1,1-dinitroethyl)benzoic acid exhibits hydrogen-bonding between the nitro-groups and the carboxyl group, whereas the singlet form does not.

Corresponding moderate-to-strong bands appeared in the spectra of all four dinitroethyl compounds at 7.17—7.19, 7.36—7.38, 7.55—7.57, and 7.90—7.94 μ .

Mass Spectra.—Samples of 1,1-dinitroethylbenzene, *p*-bis(1,1-dinitroethyl)benzene, and *p*-(1,1-dinitroethyl)benzoic acid were heated at 200°, and the vapours were examined in a mass spectrometer. In no case was a parent peak detected. The spectra clearly indicated comprehensive decomposition, and in each case could be interpreted as denoting the presence of mixtures of acetophenone and benzonitrile; *p*-diacetylbenzene, terephthalonitrile, and *p*-cyanoacetophenone; *p*-acetylbenzoic acid and *p*-cyanobenzoic acid.

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