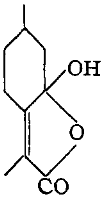
hours. Removal of solvent left an oil which deposited 0.10 g. of white plates m. p. 188–189° taken alone or mixed with the starting material. The oil, after separation of the starting material, was dissolved in ether and the ether solution was extracted once with cold 1 *M* sodium hydroxide. Evaporation of the ether yielded a faintly-yellow oil (0.16 g.) which was insoluble in dilute sodium bicarbonate and dissolved only slowly in hot 1 *M* sodium hydroxide. The cooled alkaline solution was clear and acidification with hydrochloric acid reprecipitated the oily product. The process of solution and reprecipitation was repeated twice, the oil was dried in ether solution, distilled, and analyzed.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.64. Found: C, 69.6; H, 9.59. This material had the properties expected of the lactone IX.

Summary

The structure I is proposed for the product of the autoxidation of menthofuran.



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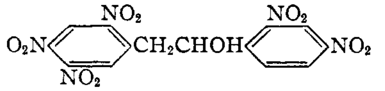
CAMBRIDGE 38, MASS. RECEIVED APRIL 26, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF QUEENS COLLEGE]

Some Experiments on the Nitration of Tetranitrobibenzyl, Tetranitrostilbene and Tolan[1]

BY A. H. BLATT* AND A. W. RYTINA[2]

The two descriptions of the nitration of the nitrobibenzyls which are to be found in the literature are not entirely consistent with each other. Will[3] reported that 4,4′-dinitrobibenzyl was easily nitrated to the 2,2′,4,4′,6,6′-hexanitro derivative, m. p. 212°, and that the same hexanitro derivative was obtained by the alkaline oxidation of TNT. Will gave no experimental details other than the melting point of the hexanitro derivative, but he stated that the analysis and other properties of the compound showed it to have the structure assigned it. Rinkenbach and Aaronson[4] reported that 2,2′,4,4′-tetranitrobibenzyl was not affected by heating with fuming nitric acid or with mixtures of fuming nitric and fuming sulfuric acids. They obtained a nitration product by dissolving tetranitrobibenzyl in fuming sulfuric acid and heating the solution to 85° for four days, then cooling, adding fuming nitric acid and heating to 85° for two days. The product, which melted at 187°, was formulated as the pentanitrodiphenylethanol (I). In one experiment starting



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with 140 g. of tetranitrobibenzyl they isolated about half a gram of a product whose melting point and nitrogen content indicated that it was identical with Will's hexanitrobibenzyl. They were unable to obtain this material by the alkaline oxidation of TNT.

We have reexamined the behavior of bibenzyl and its nitro derivatives with the following results. Bibenzyl and 4,4′-dinitrobibenzyl are nitrated to 2,2′,4,4′-tetranitrobibenzyl with 100% nitric acid. The tetranitro derivative is not affected by 100% nitric acid or by a mixture of 90% nitric acid and 95% sulfuric acid. The tetranitro compound can be nitrated further by a mixture of 90% nitric acid, 95% sulfuric acid, and 15% oleum which corresponds in composition to the mixed acid recommended for converting dinitrotoluene to TNT.[5] Tetranitrobibenzyl heated on the steam-bath for seven hours with mixed acid of the composition just described furnishes a mixture of two products: the principal and more soluble product is a colorless solid, m. p. 187°; the secondary and less soluble product is a yellow solid which melts at 212°.

The lower melting product, identical in melting point and appearance with the 187° product obtained by Rinkenbach and Aaronson, is, however, quite different. It is a pentanitrobibenzyl. The higher melting product, which corresponds in melting point to Will's hexanitrobibenzyl, has the composition to be expected for the hexanitro compound. The relationship between the two nitration products was shown by heating the pentanitro derivative in a nitrating mixture of the same composition as that in which it was formed. Under these conditions the 187° pentanitrobibenzyl is slowly nitrated to the 212° hexanitro derivative. On the basis of these results we conclude that 2,2′,4,4′-tetranitrobibenzyl is nitrated normally, but slowly, by mixed acid to yield first the 2,2′,4,4′,6-penta-

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[3] Will, *Ber.*, **47**, 712 (1914).

[4] Rinkenbach and Aaronson, THIS JOURNAL, **52**, 5040 (1930).

[5] Houben, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1941, Vol. 4, p. 183.

nitro and then the 2,2′,4,4′,6,6′-hexanitro derivatives—the location of the fifth and sixth nitro groups being assumed by analogy with the results of other aromatic nitrations.

In agreement with Rinkenbach and Aaronson we were unable to obtain hexanitrobibenzyl by the alkaline oxidation of TNT. Neither were we successful in attempts to prepare the material from trinitrobenzyl bromide by treatment with stannous chloride or with magnesium.

We also examined the behavior of 2,2′,4,4′-tetranitrostilbene toward mixed acid in order to see whether the nitro groups would decrease the tendency to polymerization shown by stilbene[6] sufficiently to permit nitration to take place. Tetranitrostilbene on treatment with mixed acid of the same composition as that used for the nitration of tetranitrobibenzyl is neither polymerized nor nitrated. Instead, oxidation takes place at the ethylenic linkage and 2,2′,4,4′-tetranitrobenzil is formed. The structure of the benzil follows from its composition, from the formation of a quinoxaline with *o*-phenylenediamine, and from the reactions of the diketone with hydrogen peroxide.

We treated tetranitrobenzil with alkaline hydrogen peroxide expecting the usual oxidative cleavage between the carbonyl groups to furnish 2,4-dinitrobenzoic acid. The product, however, was 2,4-dinitrophenol. Separate experiments showed that 2,4-dinitrobenzoic acid is not affected by alkaline hydrogen peroxide and that tetranitrobenzil does not yield 2,4-dinitrophenol on treatment with alkali in the absence of hydrogen peroxide. After these experiments had been completed, a paper by Challenger and Clapham[7] appeared in which it was shown that 2,4,6-trinitro- and 2,2′,4,6-tetranitro-stilbene were oxidized and nitrated by mixed acid to 2,2′,4,4′,6-pentanitrobenzil, and that the benzil with hydrogen peroxide in glacial acetic acid furnished trinitrobenzene and 2,4-dinitrobenzoic acid. We therefore tried the action of hydrogen peroxide in glacial acetic acid on tetranitrobenzil and found that the reaction furnished 2,4-dinitrobenzoic acid, thus completing the evidence for the structure of the benzil.

Tetranitrobenzil therefore is cleaved in two quite different ways by hydrogen peroxide: in the absence of alkali, cleavage takes place between the carbonyl groups; in the presence of alkali, cleavage takes place between a carbonyl group and a phenyl group. It is possible to write a mechanism for the reactions involved; but, until the experiments designed to test the mechanism have been tried, it does not seem profitable to discuss it.

We have also examined the behavior of tolan on attempted nitration. In order to avoid the hydration of the acetylenic linkage that takes place under the influence of sulfuric acid, we used 100% nitric acid as the nitrating agent. The reaction was vigorous and the product was an intractable, sticky, apparently polymeric material— a result that is not unexpected in view of the behavior of stilbene and the known ease of polymerization of acetylenes.

Experimental Part

2,2′,4,4′-Tetranitrobibenzyl was prepared by adding bibenzyl to ten parts of 100% nitric acid cooled in an ice-salt-bath. The reaction mixture was left in the ice–salt-bath for fifteen minutes, then left at room temperature for an hour and poured onto ice. The yield of crude product after digestion with ten parts of boiling ethanol was 90%. Two crystallizations from a mixture of equal volumes of benzene and toluene furnished the pure tetranitro compound, m. p. 171–172°, in 70% yield. The same product was obtained in 90% yield by the slow addition of 4,4′-dinitrobibenzyl[8] to nine parts of 100% nitric acid cooled in an ice-salt-bath. After one hour at room temperature, the reaction mixture was poured onto ice, the precipitate was digested for ten minutes with ten parts of boiling ethanol and crystallized from glacial acetic acid.

When one part of 2,2′,4,4′-tetranitrobibenzyl was dissolved in ten parts of 100% nitric acid, heated for one hour at 70°, left for one hour at room temperature, then poured onto ice, 95% of the starting material was recovered after digesting the crude product with boiling ethanol. When one part of tetranitrobibenzyl was dissolved at 70° in thirty parts of a mixture of 90% nitric acid and 95% sulfuric acid (1:2 by weight), and the reaction mixture was heated for a half hour at 70–95° and an hour at 95° and worked up as above, the recovery of starting material was again 95%.

Nitration of tetranitrobibenzyl was accomplished in the following way. Fifteen grams of the tetranitro derivative was dissolved by adding it to a mixture of 135 g. of 90% nitric acid and 240 g. of 95% sulfuric acid which was heated on the steam-bath. Then 120 g. of 15% oleum was added, followed by a mixture of 60 g. of 90% nitric acid and 60 g. of 15% oleum. Heating on the steam-bath was continued for seven hours, after which the reaction mixture was left overnight at room temperature and poured onto ice. The almost colorless products from five such runs were combined and washed with ethanol to furnish 65 g. of crude material which melted over the range 167–179°. This was digested with boiling benzene which left a small insoluble portion. Evaporation of the benzene solution furnished a solid which, after three crystallizations from toluene with the addition of bone black, yielded 21 g. of 2,2′,4,4′,6-pentanitrobibenzyl, m. p. 187–188°.

Anal. Calcd. for $C_{14}H_9N_5O_{10}$: C, 41.28; H, 2.23; N, 17.20. Found: C, 40.98; H, 2.28; N, 17.57.

The insoluble residue after the digestion of the main precipitate with benzene and the residues obtained by evaporation of the mother liquors from the toluene crystallizations of the pentanitrobibenzyl consisted of crude 2,2′,4,4′-6,6′-hexanitrobibenzyl. Two crystallizations from glacial acetic acid furnished 4.8 g. of the pure hexanitro derivative as a yellow–tan solid which melted at 215–217°, the exact melting point varying with the rate of heating.

Anal. Calcd. for $C_{14}H_8N_6O_{12}$: C, 37.2; H, 1.8; N, 18.6. Found: C, 37.03; H, 1.7; N, 19.0.

Conversion of Pentanitrobibenzyl to Hexanitrobibenzyl.—When 0.9 g. of pentanitrobibenzyl was treated with the mixture of 90% nitric acid, 95% sulfuric acid, and 15% oleum described in the nitration of tetranitrobibenzyl, above, and the nitration was run for sixteen hours, the yield of crude product, m. p. 150–180°, was 0.9 g. This

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[6] Lorenz, *Ber.*, **7**, 1097 (1874).

[7] Challenger and Clapham, *J. Chem. Soc.*, 1612 (1948).

[8] 4,4′-Dinitrobibenzyl is most conveniently prepared by the oxidation of *p*-nitrotoluene in methanolic potassium hydroxide solution by means of atmospheric oxygen according to Green, Davies and Horsfall, *J. Chem. Soc.*, **91**, 2079 (1907).

product was digested with 25 ml. of boiling benzene which left a residue of 0.35 g. melting at 195–205°. Crystallization of the residue from glacial acetic acid furnished pure hexanitrobibenzyl, m. p. 213–215°. The benzene extract on cooling deposited 0.25 g. of impure pentanitrobibenzyl, m. p. 165–175°; mixed with pure pentanitrobibenzyl (m. p. 187–188°) the melting point was 175–180°.

2,2',4,4'-Tetranitrostilbene was prepared from 2,4-dinitrotoluene by treatment with iodine and potassium hydroxide in methanol and piperidine.[8] When 9.7 g. of tetranitrostilbene was added to a mixture of 100 g. of 90% nitric acid and 165 g. of 95% sulfuric acid and the reaction mixture was warmed on the steam-bath, the solid dissolved. Next 85 g. of 15% oleum was added, followed by a mixture of 45 g. of 15% oleum and 45 g. of 90% nitric acid. The solution was heated on the steam-bath for seven hours, left overnight at room temperature, and poured onto ice. The solid was washed with water and ethanol and dried; weight 3.3 g. Crystallization from 200 ml. of benzene furnished 3.2 g. of pure 2,2',4,4'-tetranitrobenzil, yield, 30%.

Anal. Calcd. for $C_{14}H_6N_4O_{10}$: C, 42.56; H, 1.54; N, 14.36. Found: C, 42.63; H, 1.53; N, 14.71.

2,2',4,4'-Tetranitrobenzil is a pale yellow solid which melts at 222–223° and is almost insoluble in the ordinary solvents. It is sparingly soluble in the higher-boiling solvents such as glacial acetic acid and toluene. When 0.5 g. of the benzil was dissolved in 20 ml. of boiling acetic acid and 15 ml. of 30% hydrogen peroxide was gradually added, the first additions caused a transient precipitation, while with the last additions most of the color of the solution disappeared. A further 5 ml. of 30% peroxide was added and the reaction mixture was concentrated on the steam-bath to a volume of about 1 ml. On cooling, this residue solidified to furnish 0.55 g. of 2,4-dinitrobenzoic acid, m. p. 181–182°, which did not lower the melting point of an authentic specimen of 2,4-dinitrobenzoic acid (182–183°).

Alkaline hydrogen peroxide on the benzil leads to 2,4-dinitrophenol. To a solution of 0.2 g. of the benzil in 100 ml. of methanol was added 5 ml. of 30% hydrogen peroxide and a solution of 0.85 g. of sodium in 50 ml. of methanol. The reaction mixture was kept at the boiling point while a small precipitate formed. (The precipitate was apparently sodium carbonate for it was inorganic and liberated carbon dioxide on treatment with hydrochloric acid.) The filtrate, after removal of the precipitate, was evaporated to dryness and the residue was dissolved in 7 ml. of water. On acidification with dilute hydrochloric acid, 0.1 g. of 2,4-dinitrophenol (m. p. 111°, mixed melting point with pure dinitrophenol 111–112°) was obtained.

Tetranitrobenzil treated exactly as described in the preceding paragraph save that the hydrogen peroxide was omitted, yielded a dark brown alkali-soluble solid, which resembled the complex products generally obtained by the action of alcoholic alkali on aromatic nitro compounds and from which no dinitrophenol or any other chemical individual could be isolated.

Formation of a Quinoxaline from 2,2',4,4'-Tetranitrobenzil.—When 0.2 g. of the benzil was suspended in 125 ml. of boiling ethanol and 0.18 g. of *o*-phenylenediamine hydrochloride and 0.2 g. of potassium acetate were added and the solution was boiled for four and a half hours, the benzil slowly dissolved and a sandy yellow precipitate of the quinoxaline formed. The solid was filtered and crystallized from toluene using Darco to remove some highly colored by-products. The yield of the pure quinoxaline, m. p. 278° dec., was 0.2 g.

Anal. Calcd. for $C_{20}H_{10}N_6O_8$: C, 51.9; H, 2.16; N, 18.2. Found: C, 51.8; H, 2.46; N, 17.88.

Attempted Nitration of Tolan.—When 0.5 g. of tolan was added slowly to 20 g. of 100% nitric acid cooled in an ice–salt-bath, the reaction was vigorous. Oxides of nitrogen were evolved and a dark brown solution resulted. After the reaction mixture had been kept in the ice–salt-bath for a half hour, it was poured onto ice and the sticky brown precipitate was removed, washed with water, and dried. Two crystallizations from ethanol removed most of the color from the product, but the material was still sticky and melted over the range from 120 to 180° with decomposition.

Summary

Bibenzyl and 4,4'-dinitrobibenzyl can be nitrated to the 2,2',4,4'-tetranitro derivative readily and in good yield. The tetranitro compound is slowly nitrated by hot mixed acid to yield, first, the 2,2',4,4',6-pentanitro- and, second, the 2,2',4,4',6,6'-hexanitro-bibenzyl. 2,2'4,4'-Tetranitrostilbene is oxidized by mixed acid to the tetranitrobenzil, which undergoes a novel cleavage with alkaline hydrogen peroxide to furnish 2,4-dinitrophenol. Tolan furnished what is apparently polymeric material on attempted nitration.

FLUSHING, N. Y.

RECEIVED AUGUST 11, 1949

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Mechanism of the Reaction of Bis-β-chloroethyl Ether (β,β'-Dichlorodiethyl Ether) with Hydroxyl and Thiosulfate Ions[1]

BY PAUL D. BARTLETT* AND EDWARD S. LEWIS†

There is a structural analogy between bis-β-chloroethyl ether (β,β'-dichlorodiethyl ether) (I) and mustard gas (II).[2] The hydrolysis and displacement reactions of the latter[3–5] as well as of such "nitrogen mustards" as methylbis-β-chloroethylamine (III) and ethylbis-β-chloroethylamine[6,7] have been shown to proceed as a first-order reaction, controlled by the formation of a cyclic ethylene-sulfonium or ethylene-immonium ion. Although tertiary oxonium salts are formed far less readily[8] than either tertiary sulfonium or quaternary ammonium salts, there appeared to be a

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* Harvard University Ph.D., 1931; Faculty, 1934–.

† Harvard University Ph.D., 1947.

[1] This paper is based upon part of a thesis submitted by Edward S. Lewis for the degree of Ph.D. at Harvard University, May 10, 1947.

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[6] P. D. Bartlett, S. D. Ross and C. G. Swain, *ibid.*, **69**, 2971 (1947).

[7] P. D. Bartlett, J. W. Davis, S. D. Ross and C. G. Swain, *ibid.*, **69**, 2977 (1947).

[8] H. Meerwein, G. Hinz, P. Hofmann, E. Kronig and E. Pfeil, *J. prakt. Chem.*, N. F., **147**, 257 (1937).