Reaction of I *with formaldehyde.* A solution of 2.0 g. of 1-α-pyrrolidyl-2-propanol in 5 ml. of water was acidified with concd. hydrochloric acid and treated with 6 ml. of 40% formalin solution. The resulting mixture was heated in a sealed pyrex tube at 117° (refluxing 1-butanol) for 4 hr. The dark brown contents of the tubes were cooled, made alkaline with 50% potassium hydroxide solution, and the base extracted with ether and dried over magnesium sulfate. Vacuum distillation gave 1.5 g. of a colorless liquid, b.p. 83–84° (21 mm.), lit.[1] b.p. 89–92° (22 mm.). The picrate melted at 174–175°, lit.[2] m.p. 174°.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.15. Found: C, 45.33; H, 4.93; N, 15.44.

In an attempt to prepare the reported oxime, 1.4 g. of VII, 0.7 g. of hydroxylamine hydrochloride and 0.6 g. of potassium hydroxide were warmed on the steam bath in 20 ml. of water for 2 hr. Working up the mixture in the manner described by Hess[1] gave no solid products.

Hydrolysis of VII. A solution of 0.25 g. of VII in 5 ml. of ethanol, 5 ml. of 1*N* hydrochloric acid, and 5 ml. of a 10% alcoholic solution of dimedone was refluxed for 2 hr., neutralized with potassium hydroxide and concentrated on the steam bath. Chilling gave a crude solid, which was recrystallized from ethanol to yield 50 mg. of the dimedone derivative of formaldehyde, m.p. and mixed m.p. 188–191.5°.

Reaction of II *with formaldehyde.* The base (1.66 g.) isolated by vacuum distillation of the product from reaction of 2.0 g. of II with formaldehyde, as described above, gave a picrate, needles from ethanol, melting at 101–103°, lit.[1] m.p. 103°.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.15. Found: C, 45.35; H, 5.03; N, 15.38.

Hydrolysis of the base in the presence of dimedone, as described above, gave the crystalline derivative of formaldehyde.

Reaction of III *with formaldehyde.* A solution of 10 g. of III in 17.5 ml. of water was acidified with 8.2 ml. of concd. hydrochloric acid, treated with 10.5 ml. of 40% formalin solution, and heated at 117° for 4 hr. The mixture was worked up as described above, affording 9.1 g. of colorless liquid, b.p. 110–113° (14 mm.), 70–72° (6 mm.), lit.[3] b.p. 108–111° (28 mm.).

Anal. Calcd. for $C_9H_{17}NO$: C, 69.70; H, 11.04; N, 9.03. Found: C, 69.31; H, 11.06; N, 9.08.

The picrate, twice recrystallized from ethanol, melted at 140.5–144°, lit. m.p. 162–163°.

Anal. Calcd. for $C_{15}H_{20}N_4O_8$: C, 46.87; H, 5.24; N, 14.58. Found: C, 46.89; H, 5.31; N, 14.71.

Hydrolysis of the base in the presence of dimedone again afforded the dimedone derivative of formaldehyde. The starting amino alcohol (III) was also recovered by crystallization and identified by its infrared spectrum.

Reaction of IV *with formaldehyde.* The reaction of 1.70 g. of IV with formaldehyde was carried out as described above, and yielded 1.50 g. of colorless product. The picrate was recrystallized twice from ethanol, and melted at 142–144°.

Anal. Calcd. for $C_{15}H_{20}N_4O_8$: 46.87: H, 5.24; N, 14.58. Found: C, 47.06; H, 5.11; N, 14.85.

Formaldehyde was isolated as the dimedone derivative when the base was hydrolyzed as described above.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

The Dinitration of *m*-Toluic Acid

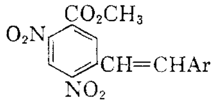
A. H. BLATT

Received February 29, 1960

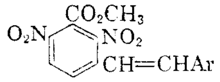
The first report of the dinitration of *m*-toluic acid is that of van Scherpenzeel[1a] who nitrated the acid in one- to two-gram quantities with 100% nitric acid and obtained in an unspecified, low yield a dinitro acid (m.p. 173°) which he formulated as 2,6-dinitro-*m*-toluic acid.[1b] From methyl *m*-toluate by the same procedure he obtained, again in an unspecified, low yield, a methyl ester (m.p. 104°) which he considered to be methyl 2,6-dinitro-*m*-toluate because it could be hydrolyzed with hydrochloric acid to the dinitro-*m*-toluic acid he had already prepared. No direct comparison was made of the two samples of the dinitro acid and no comment was made about the ready hydrolysis of a di-*ortho* substituted benzoic ester.

In the second report of the dinitration of *m*-toluic acid, Hargreaves and McGookin[2] described the use of mixed acid to furnish in 60% yield a dinitro-*m*-toluic acid which they considered to be identical with the acid obtained by van Scherpenzeel. They converted the acid to the acid chloride with thionyl chloride. From the crude acid chloride with methanol they obtained a methyl ester, m.p. 104°, which confirms the identity of their acid and van Scherpenzeel's, and a second unidentified product, m.p. 67°, which casts doubt on the homogeneity of their acid.

Since the nitration of *m*-toluic acid with 100% nitric acid was so unpromising and inconvenient, we used mixed acid and obtained consistent yields of 85% of a crude product which is a mixture containing 2,6-dinitro- and 4,6-dinitro-*m*-toluic acid in approximately equal amounts. The two acids can be separated and structures may be assigned to them from the behavior of the crude product on heating with methanol containing sulfuric acid: 4,6-dinitro-*m*-toluic acid is converted to the methyl ester (m.p. 104°) while 2,6-dinitro-*m*-toluic acid is unaffected. The two reactions, nitration and treatment with methanol and sulfuric acid, show that the earlier workers actually had in hand an impure 4,6-dinitro-*m*-toluic acid rather than the 2,6-dinitro acid as they believed. It also follows from these two experiments that 2,6-dinitro-*m*-toluic acid and its esters have not hitherto been prepared, that the description of these compounds in the literature are erroneous, and that the substituted stilbenes prepared by Hargreaves and McGookin[2] from aromatic aldehydes and the 104° methyl ester have structure I rather than the structure II that was assigned to them.



I



II

(1a) L. van Scherpenzeel, *Rec. trav. chim.*, **20**, 149–182 (1901).

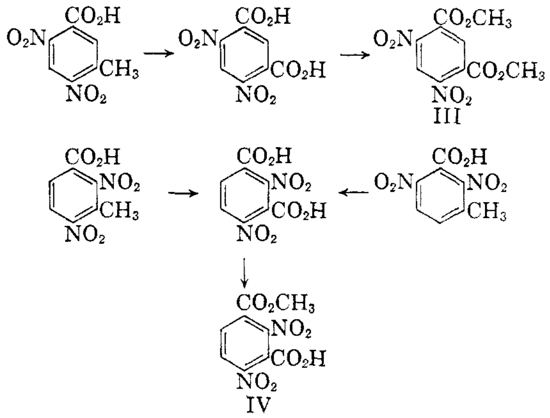
(1b) In *m*-toluic acid and its substitution products the carboxyl group and the methyl group are assigned positions 1 and 3, respectively.

(2) K. R. Hargreaves and A. McGookin, *J. Soc. Chem. Ind. (London)*, **69**, 190 (1950).

We next nitrated methyl *m*-toluate by the same procedure we had used to nitrate the acid. This furnished in quantitative yield a product that is obviously identical with the unidentified esterification product described earlier by Hargreaves and McGookin. We first thought that this product, most samples of which melt fairly sharply in the neighborhood of 65°, might be methyl 2,6-dinitro-*m*-toluate. Actually it is a mixture that contains methyl 2,6-dinitro-*m*-toluate and methyl 4,6-dinitro-*m*-toluate in about a 5 to 4 ratio. On heating with concentrated hydrochloric acid, the crude ester mixture furnishes 4,6-dinitro-*m*-toluic acid and unattacked methyl 2,6-dinitro-*m*-toluate. Nitration of methyl *m*-toluate followed by heating with hydrochloric acid is therefore a route to the 4,6-dinitro acid and the methyl ester of the 2,6-dinitro acid, which complements the nitration and esterification described in the previous paragraph both as a preparative procedure and as a basis for assigning structure.

The structure of 2,6-dinitro-*m*-toluic acid and its methyl ester are adequately established by their resistance to esterification and hydrolysis, respectively. We have considered the isomeric dinitro acid to be the 4,6- rather than the 2,4-dinitro derivative because of the identity in melting point (104°) of the methyl ester prepared by (a) esterification of the acid in question, (b) dinitration of methyl *m*-toluate, and (c) esterification of the acid obtained by the partial oxidation of 4,6-dinitro-1,3-dimethylbenzene.[3] Direct comparison of the methyl ester prepared by routes (a) and (b) has been made, but no direct comparison has been made between these samples and the ester made by route (c). Instead of preparing the ester by route (c) and comparing it with our samples, we chose to confirm its structure by the following method which is independent of the orientation of 4,6-dinitro-1,3-dimethylbenzene.

Oxidation of 4,6-dinitro-*m*-toluic acid would yield 4,6-dinitroisophthalic acid, which should esterify to the neutral dimethyl ester III. Oxidation of 2,4-dinitro-*m*-toluic acid would yield 2,4-dinitroisophthalic acid, which should esterify to the acid monomethyl ester IV. On oxidation, our presumed 4,6-dinitro-*m*-toluic acid furnished a dinitroisophthalic acid which esterified to a dimethyl ester, thus establishing the correctness of the structure of the dinitro-*m*-toluic acid as the 4,6-isomer and confirming the orientation of 4,6-dinitro-*m*-xylene and 4,6-dinitroisophthalic acid.[4] For completeness we also oxidized 2,6-dinitro-*n*-toluic acid and found, as we expected, that the resulting hitherto unknown 2,4-dinitroisophthalic acid esterifies only to the acid methyl ester IV.



The material in the preceding paragraphs provides new and somewhat different examples of the high *ortho-para* ratio in the nitration products of aromatic compounds containing a *meta*-directing group. The phenomenon and possible explanations for it have been discussed earlier[4a] so that it is necessary here only to mention by way of illustration that the nitration of benzonitrile furnishes, in addition to the principal product *m*-nitrobenzonitrile, the *ortho* and *para* nitrobenzonitriles in a ratio greater than 3:1. On statistical grounds a 2:1 ratio would be expected and steric effects should lower this ratio. *m*-Toluic acid and its methyl ester differ from the monosubstituted benzenes hitherto studied in that the 2-, 4-, and 6-positions would be activated. Statistically one would expect equal amounts of the 2,4-, 4,6-, and 2,6-dinitro derivatives, while steric factors would favor the 4,6-isomer at the expense of both the 2,4- and 2,6-isomers. One finds that all of the dinitration products are substituted in the 6-position, and that the ratio of 2-substitution to 4-substitution is about 1:1 with the acid and about 5:4 with the methyl ester. Since these ratios are based on products isolated (64% of the material was accounted for in the nitration of the acid and 80% in the nitration of the ester) we cannot say that none of the 2,4-dinitration product was formed. It is clear, however, that activation *ortho* to the nitro group is occurring and that it is sufficient to offset the considerable hindrance to substitution in the 2-position. Although our results constitute additional evidence of *ortho* activation, they do not enable us to add to or distinguish between the explanations already advanced.

Two other items should be mentioned. The first is the extraordinary solubility in water of 2,6-dinitro-*m*-toluic acid: 1 g. of the acid will dissolve

---

(3) R. D. Haworth and P. R. Jeffries, *J. Chem. Soc.*, 2069 (1951).

(4) T. Nozoe, Y. Kitahara, K. Yamane, and K. Yamaki, *Proc. Japan Acad.*, **26**, No. 8, 14–18 (1950) [*Chem. Abstr.*, **45**, 7097 (1951)] reported that nitration of hinokitiol followed by oxidation furnished 4,6-dinitroisophthalic acid, m.p. 240–241°. The acid, which was crystallized from boiling water, gave a dimethyl ester, m.p. 141°. The properties of this acid and its dimethyl ester do not agree with those of 4,6-dinitroisophthalic acid and dimethyl 4,6-dinitroisophthalate. See the Experimental section.

(4a) Pertinent references are to be found in an article by George S. Hammond and Katharine J. Douglas, *J. Am. Chem. Soc.*, **81**, 1184 (1959).

in less than 5 ml. of hot water. Presumably, the crowding and resulting nonplanarity of the four adjacent substituents prevents close packing in the crystals and favors solvation at the carboxyl group. Similar striking solubility relations are observed with the dinitroisophthalic acids. The second is that the dinitro acids and their derivatives described in this paper show the yellow color that is characteristic of dinitro aromatic compounds in acetone solution in the presence of iodide ion.[5]

EXPERIMENTAL

We are indebted to the Hercules Powder Co. for the *m*-toluic acid and methyl *m*-toluate used in these experiments.

Melting points are uncorrected.

Nitration of m-toluic acid. Isolation of 2,6-dinitro-m-toluic acid and methyl 4,6-dinitro-m-toluate. Nitrating acid was prepared from 89 ml. of chilled fuming nitric acid (*d.* 1.5) and an equal volume of chilled fuming sulfuric acid (30% sulfur trioxide) in a 500-ml., three-necked, round-bottomed flask that was fitted with a mechanical stirrer and thermometer and was surrounded by an ice-water bath. The temperature of the nitrating acid was kept between 25 and 30° during its preparation and during the subsequent nitration.

Stirring and cooling were continued while 27.2 g. (0.2 mole) of *m*-toluic acid was added in portions. As soon as the addition was complete—about 50 min. was required—the cooling bath was removed. Stirring was continued for 90 min., then the reaction mixture, which usually contained a considerable amount of precipitate, was drowned on 400 g. of ice. The solid was filtered, washed with 75 ml. of water, stirred for a few minutes with 100 ml. of water, filtered, and dried. The yield of crude product, an almost white solid that turns superficially yellow on prolonged exposure to light, averaged 38.5 g. (85%). On heating, the product begins to soften at about 155° and melts from 162 to 170°. If larger amounts of ice are used to decompose the reaction mixture or more water is used to wash the product, the yield decreases.

In order to separate the reaction products, 22.6 g. (0.1 mole) of the crude dinitro-*m*-toluic acids was dissolved in 226 ml. of cold absolute methanol and 22.6 ml. of cold concd. sulfuric acid was added. The solution, protected from moisture, was heated under reflux for 16 hr. and then chilled. The precipitate of methyl 4,6-dinitro-*m*-toluate was filtered, and the filtrate was diluted with 400 ml. of ether and shaken with one 300-ml. and two 150-ml. portions of water. The ether was then extracted with 1% aqueous sodium carbonate and dried over sodium sulfate. Evaporation of the ether left methyl 4,6-dinitro-*m*-toluate.

The sodium carbonate extract was freed of ether by a current of air, filtered if necessary, acidified with hydrochloric acid, and extracted with an equal volume of ether divided in two portions. The combined ether extracts were washed with water, dried over sodium sulfate, and evaporated to leave a residue of 2,6-dinitro-*m*-toluic acid as an off-white solid.

The average recovery in a series of these separations was 7.7 g. of crude ester (32%) m.p. 94–98°, and 7.5 g. of acid (33%) m.p. 174–178°. After it had been established that the two isomeric dinitro-*m*-toluic acids were present in approximately equal amounts in the crude dinitration product, a single separation was carried out with half the amounts of methanol and sulfuric acid called for above. This gave a 75%, instead of a 65%, recovery with a small but not significant increase in the relative amount of the 2,6- acid.

It should be possible to separate the mixture of dinitro-*m*-toluic acids without going through the esterification just described, for the 2,6-dinitro acid is far more soluble in hot water than is the 4,6-dinitro acid. (See below.) We have not attempted to work out a procedure for such a separation.

Nitration of methyl m-toluate. Isolation of 4,6-dinitro-m-toluic acid and methyl 2,6-dinitro-m-toluate. The nitrating mixture was prepared from 110 ml. of fuming nitric acid and 110 ml. of fuming sulfuric acid as described for the preceding nitration. To the stirred mixed acid, whose temperature was held between 20° and 30° by an ice-water bath, was added dropwise 30 g. (0.20 mole) of methyl *m*-toluate during 20 min. The ice bath was removed and the clear yellow solution was stirred for an hour, then poured onto 450 g. of ice. The precipitate was filtered, washed with water, and dried to yield 48 g. (quant.) of a pale yellow solid. The crude product usually melts over less than a 2° range, *e.g.*, 63–65°, with some preliminary softening.

In order to separate the nitration products, 24 g. (0.1 mole) of the crude ester mixture was suspended in 400 ml. of concd. hydrochloric acid and heated under reflux for 24 hr. during which time a slow stream of nitrogen was bubbled through the reaction mixture to reduce oxidative discoloration and to remove methanol and methyl chloride. The reaction mixture was cooled and ether was added to dissolve the dark yellow oil and admixed crystals. Water was added, the aqueous acid layer was discarded, and the ether was washed three times with water. The ether was then extracted with 1% aqueous sodium carbonate, washed with water, and dried over sodium sulfate. On evaporation, the ether left methyl 2,6-dinitro-*m*-toluate, m.p. 80–83°. The sodium carbonate extract was freed of dissolved ether by an air stream, filtered if necessary, and acidified with hydrochloric acid which precipitated 4,6-dinitro-*m*-toluic acid as an off-white solid, m.p. 166–170°.

The average recovery in a number of these separations was 12 g. of methyl 2,6-dinitro-*m*-toluate (50%) and 7 g. of 4,6-dinitro-*m*-toluic acid (30%). By extracting with ether the acidified sodium carbonate extract from which the 4,6-dinitro acid had precipitated, it was possible to increase the recovery of that acid to about 40%, but the additional material obtained in this way was of such poor quality that the extra operation was not worthwhile.

By crystallizing the crude dinitro ester mixture from methanol one can obtain reasonable amounts of methyl 4,6-dinitro-*m*-toluate, the less soluble of the two esters, and by a laborious and inefficient fractional crystallization from the same solvent one can isolate identifiable amounts of methyl 2,6-dinitro-*m*-toluate. We have not, however, been able to work out a satisfactory procedure for separating the ester mixture into its components by crystallization.

4,6-Dinitro-*m*-toluic acid is an almost colorless solid with a faint yellow cast. On exposure to direct sunlight the material turns superficially bright yellow. The acid is exceedingly soluble in the common organic solvents except ligroin or benzene. It can be crystallized from benzene (*ca.* 40 ml./g.) or water (*ca.* 50 ml./g.) with a 75% recovery. The pure acid, obtained in this way as very fine transparent crystals, melts at 178–179°.

The acid is esterified only slowly with methanol or ethanol and sulfuric acid. When 1 g. of the acid is heated under reflux with 10 ml. of methanol or ethanol and 1 ml. of concd. sulfuric acid, 16 hr. is required for complete esterification. *Methyl 4,6-dinitro-m-toluate*, obtained by esterification of the acid or by nitration of methyl-*m*-toluate, is very soluble in hot benzene, methanol, acetone, dioxane, tetrahydrofuran, dimethylformamide, or pyridine and is only very sparingly soluble in the same solvents cold. It is very slightly soluble in ether. The ester can be purified conveniently by crystallization from methanol (*ca.* 10 ml./g.; recovery, 85%). The pure ester is obtained as small pale yellow crystals that melt at 103–104°. The ester is hydrolyzed slowly by aqueous hydrochloric acid: 1.2 g. of ester heated under reflux with 20 ml. of concd. hydrochloric acid requires 16 hr. for complete hydrolysis.

---

(5) A. H. Blatt and Norma Gross, *J. Org. Chem.*, **22**, 1046 (1957).

Ethyl 4,6-dinitro-m-toluate can be prepared by esterifying the acid with ethanol as described above for the methyl ester. It can also be prepared by heating the acid, suspended in benzene, with excess thionyl chloride until the solid goes into solution (*ca.* 4 hr.), adding excess absolute ethanol, heating for a short time, and then evaporating the solvents. Both procedures give better than 90% yields. The ester is purified by dissolving it in ethanol at 35° and cooling the solution slowly. The pure ester, pale yellow crystals, melts at 47–48°.

Anal. Calcd. for $C_{10}H_{10}N_2O_6$: C, 47.24; H, 3.93. Found: C, 47.17; H, 4.11.

This ester has previously been prepared by esterification of the acid obtained by the partial oxidation of 4,6-dinitro-1,3-dimethylbenzene. It was described[6] as brown prisms, m.p. 61–62°. We have no explanation for the difference in color and melting point between the earlier sample and ours.

Oxidation of 4,6-dinitro-m-toluic acid to 4,6-dinitroisophthalic acid. The procedure was taken from that of Ruggli and Schmid for the oxidation of 4,6-dinitro-1,3-dimethylbenzene.[7] A solution of 4.6 g. of 4,6-dinitro-*m*-toluic acid in 60 ml. of concd. sulfuric acid was stirred and chilled in an ice-salt bath to −7°, then a solution of 4.6 g. of chromium trioxide in 6.5 ml. of water was added dropwise slowly enough to permit the temperature of the reaction mixture to be held below 20°. Stirring was continued until the temperature dropped to 5°, when the reaction mixture was poured onto 300 g. of ice. The precipitate of unoxidized acid, 1.2 g., identified by melting point and mixed melting point, was removed by filtration and the filtrate was extracted with 120 ml. and then 60 ml. of ether. The ether, after washing, drying, and evaporating, left 3 g. of crude dinitroisophthalic acid, which melted at 241–243° after it had been digested with hot benzene. The pure acid, crystallized by solution in nitrobenzene at 160°, was obtained as sandy transparent crystals, m.p. 246–247° dec.

Since our material melted higher than the material prepared by Ruggli and Schmid by the oxidation of 4,6-dinitro-1,3-dimethylbenzene (246° *vs.* 234°), we esterified our product not only with methanol but also with ethanol so as to be able to compare the melting point of the diethyl ester with that reported by Ruggli and Schmid.

A solution of 1.28 g. of 4,6-dinitroisophthalic acid in 22.6 ml. of absolute methanol and 2.26 ml. of concd. sulfuric acid was heated under reflux for 16 hr. during which time a large precipitate of glistening white crystals formed in the hot solution. The precipitate was filtered, the filtrate was diluted with ether, washed with water, and extracted with 10 ml. of 1% aqueous sodium carbonate. On evaporation the ether left 0.3 g. of product which, with the original precipitate, made a total yield of 1.25 g. or 88%. The strongly alkaline carbonate extract on acidification furnished a small precipitate which was rejected since the ester already obtained accounted for 88% of the starting material.

The dimethyl ester was purified for analysis by crystallization from methanol and by solution in acetone followed by addition of methanol and heating to expel most of the acetone. The pure ester, obtained as colorless glistening crystals which are moderately soluble in hot acetone and very sparingly soluble in hot methanol, melts at 162–163°.

Anal. Calcd. for $C_{10}H_8N_2O_8$: C, 42.25; H, 2.8; OCH_3, 21.8. Found: C, 42.71; H, 2.83; OCH_3, 21.35.

The diethyl ester, prepared in 86% yield in the same way as its lower homolog, melted at 126°, in satisfactory agreement with the melting point of 124° given by Ruggli and Schmid for a sample prepared from the silver salt of the acid and ethyl iodide.[7]

Anal. Calcd. for $C_{12}H_{12}N_2O_8$: C_2H_5O, 28.84. Found C_2H_5O, 28.45, 29.48.

2,6-Dinitro-m-toluic acid is an almost colorless solid with a faint yellow cast. It is very soluble in the common organic solvents except ligroin or benzene and is remarkadly soluble in hot water: 1.0 g. requires less than 5 ml. of water for solution on the steam bath and about 0.75 g. crystallizes on cooling the solution. Benzene is the most satisfactory solvent for purification: 1.0 g. of the acid dissolves in about 50 ml. of benzene and 0.75 g. can be recovered on cooling. The pure acid, obtained in large transparent chunky crystals from benzene and in very small crystals from water, melts at 182–183° with considerable sublimation.

Anal. Calcd. for $C_8H_6N_2O_6$: C, 42.48; H, 2.67. Found: C, 42.74; H, 2.81.

The hindrance to esterification of the 2,6-dinitro acid is pronounced. When 1.0 g. of the acid in 10 ml. of absolute methanol and 1 ml. of concd. sulfuric acid was heated under reflux for 16 hr.—conditions under which the isomeric 4,6-dinitro acid is quantitatively esterified—only enough of the methyl ester was formed to permit identification by melting point and mixed melting point.

Methyl 2,6-dinitro-m-toluate can be prepared by the nitration of methyl *m*-toluate (see above) and in quantitative yield from the acid by conversion to the acid chloride with thionyl chloride followed by reaction of the crude acid chloride with methanol. The ester crystallizes as large chunky pale yellow lozenges that melt at 83–84°. Its solubility is similar to but greater than that of the isomeric 4,6-dinitro ester. It is conveniently purified by crystallization from methanol (*ca.* 5 ml./g.) with an 80–85% recovery.

Anal. Calcd. for $C_9H_8N_2O_6$: C, 45.0; H, 3.33. Found: C, 45.67; H, 3.40.

The ester is resistant to hydrolysis. A suspension of 1.2 g. of the ester in 20 ml. of concd. hydrochloric acid was heated under reflux for 24 hr. in a nitrogen stream. The material solidified on cooling. It was dissolved in ether and the ether shaken out with 1% aqueous sodium carbonate. The carbonate extract on acidification gave no precipitate and an ether extract of the acidified carbonate solution yielded only about 0.06 g. of the 2,6-dinitro acid, which corresponds to about 5% hydrolysis. (The isomeric 4,6-dinitro ester is completely hydrolyzed in 16 hr. under the same conditions.) The original ether solution that had been shaken out with sodium carbonate left unhydrolyzed ester on evaporation.

Ethyl 2,6-dinitro-m-toluate was prepared by converting the acid to the acid chloride with thionyl chloride in the presence of benzene as a solvent and heating the crude acid chloride with absolute ethanol. The yield of crude ester left on evaporation of the solvents at room temperature was quantitative. The ester was purified by dissolving it in ethanol at 35°, filtering, and cooling the filtrate slowly. A second crystallization from a larger volume of ethanol diluted with a little water after filtering did not change the melting point, 58–59°. The pure ester is colorless.

Anal. Calcd. for $C_{10}H_{10}N_2O_6$: C, 47.24; H, 3.93. Found: C, 47.33; H, 3.99.

2,6-Dinitro-*m*-toluic acid was oxidized to 2,4-dinitroisophthalic acid by the procedure described above for the oxidation of 4,6-dinitro-*m*-toluic acid. The amount of unoxidized 2,6-dinitro-*m*-toluic acid that precipitated on pouring the reaction mixture into water was small: 2,6-dinitro-*m*-toluic acid is quite soluble in water. Evaporation of the ether extract gave 2.1–2.3 g. of crude product which was purified for analysis by crystallization from nitrobenzene and then from ether-petroleum ether (b.p. 60–90°). The pure acid melts at 246–247°, as does the isomeric 4,6-dinitroisophthalic acid. Mixtures of the two acids melt from 215 to 225°.

Anal. Calcd. for $C_8H_4N_2O_8$: C, 38.28; H, 1.56. Found: C, 38.22; H, 1.86.

2,4-Dinitroisophthalic acid was esterified with methanol and sulfuric acid following the procedure described above

---

[6] G. Errera and R. Maltese, *Gazz. chim. ital.*, **33**, II, 277 (1903).

[7] P. Ruggli and O. Schmid, *Helv. Chim. Acta*, **18**, 247 (1935).

for the preparation of dimethyl 4,6-dinitroisophthalate. No precipitate formed on cooling the reaction mixture so the solution was diluted with ether and shaken out three times with water to remove sulfuric acid and most of the methanol. The ether was then shaken out with 1% aqueous sodium carbonate; 20 ml. was required. The carbonate extract freed of ether was acidified and furnished the crude acid methyl ester IV in 43% yield. The poor yield is probably a result of the high solubility of the acid ester. No attempt was made to obtain more of the acid ester from the water washings or the acidified carbonate extract. The ether solution that had been extracted with sodium carbonate left no residue on evaporation showing that no neutral ester had been formed. The acid methyl ester is too soluble in aqueous methanol to permit crystallization from that solvent. For analysis, the material was crystallized from ether-petroleum ether (b.p. 60-90°). The pure methyl acid ester IV melts at 184-185°.

Anal. Calcd. for $C_9H_6N_2O_8$: CH_3O, 11.1. Found: CH_3O, 11.44.

Department of Chemistry
Queens College
Flushing, N. Y.

Reaction of Hydrogen Bromide with Conjugated Dienols[1]

R. L. Lohmar, C. R. Smith, Jr., and T. L. Wilson

Received March 7, 1960

Dimorphecolic acid, the major fatty acid of *Dimorphotheca aurantiaca* seed oil, rapidly consumes essentially one molar equivalent of hydrogen bromide in the Durbetaki titration for oxirane oxygen.[2] Formulation of this acid as 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid indicated no grouping known to consume hydrogen bromide in this manner. We report here a comparison of the behavior of dimorphecolic acid with that of two model compounds, 2,4-hexadiene-1-ol (sorbyl alcohol) and 4,6-octadiene-3-ol, when treated with hydrogen bromide in nonaqueous media.

Although several aliphatic compounds with a secondary hydroxyl group in α-position to a conjugated diene are known, their behavior toward hydrogen bromide has not been examined. Kuhn and Grundmann[3] showed that 4,6-octadiene-3-ol is readily dehydrated by *p*-toluenesulfonic acid to 2,4,6-octatriene. Heilbron and co-workers,[4] as well as Braude and co-workers,[5] examined the effect of acid catalysts on related unsaturated alcohols. They found that compounds containing the system —CH=CH—CHOH—CH=CH— showed a pronounced tendency to rearrange to secondary conjugated dienols (—CHOH—CH=CH—CH=CH—) which were readily dehydrated to trienes. Heilbron examined the action of hydrochloric acid on the closely related hex-4-ene-1-yne-3-ol and similar compounds. Rearrangement similar to that of the dienols was observed, accompanied by replacement of hydroxyl by chlorine. However, the action of hydrobromic acid led to "unstable heterogeneous products."

2,4-Hexadiene-1-ol does not consume hydrogen bromide under the conditions of the Durbetaki[6,7] titration, but 4,6-octadiene-3-ol behaves in a manner analogous to that of dimorphecolic acid. It rapidly consumes a like amount of hydrogen bromide. Ultraviolet absorption studies indicate that essentially all the dienoid absorption is preserved immediately after titration, but triene is then formed at a slower rate. Appearance of triene is accompanied by disappearance of diene, suggesting that an initially formed bromodiene is dehydrobrominated. Similar results are obtained when a chloroform solution of hydrogen bromide is used rather than an acetic acid solution. Hydrogen chloride in acetic acid is not consumed rapidly.[8] Treatment of the octadienol with two thirds the titrimetric amount of hydrogen bromide results in eventual turning of the indicator. This observation supports the interpretation of replacement followed by elimination. The presence of free acid in mixtures that had stood some time after Durbetaki titration was confirmed by the rapid neutralization of sodium carbonate dissolved in acetic acid.

Although consumption of hydrogen bromide appears to be stoichiometric or nearly so, formation of triene is not. Diene and triene are in equilibrium (Fig. 1). The molar sum of conjugated diene and triene is 75-80% of that expected. The fate of the remainder is not known, but a possibility exists that in the equilibrium reaction some of the hydrogen bromide is added to yield a nonconjugated bromodiene that would not be estimated by the spectral method used. Conversion of diene to triene is reminiscent of the results Bergström and Hansson[9] obtained by treating linoleate with *N*-bromosuccinimide. The initially formed conjugated dienoid bromide lost hydrogen bromide to form a conjugated triene. They also observed that about 30% of the bromide was not eliminated, even after prolonged refluxing.

The mechanism sequence may resemble that proposed by DeWolfe and Young[10] for the reaction of

---

[1] This is a contribution from the laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] C. R. Smith, Jr., T. L. Wilson, E. H. Melvin, and I. A. Wolff, *J. Am. Chem. Soc.*, **82**, 1417 (1960).

[3] R. Kuhn and C. Grundmann, *Ber.*, **71**, 442 (1938).

[4] I. M. Heilbron, J. T. McCombie, and B. C. L. Weedon, *J. Chem. Soc.*, **1945**, 84, and preceding papers.

[5] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, **1951**, 2085, and preceding papers.

[6] A. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[7] American Oil Chemists' Society, "Official and Tentative Methods," 2nd ed. (1958 revision), Method Cd 9-57.

[8] Miss Glenda Geisinger carried out this experiment.

[9] S. Bergström and G. Hansson, *Acta Chem. Scand.*, **4**, 435 (1950).

[10] R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).