caused the precipitation of a fine white solid. Two extractions with ether were made and the ether was allowed to evaporate. The residue after several recrystallizations from methyl alcohol melted at 69–70°. This was shown to be 3,5-dibromo-2,4,6-trimethylisobutyrophenone by the method of mixed melting points.

The Action of Ethylmagnesium Bromide on α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone.—Several experiments similar to that described for methylmagnesium chloride were run with ethylmagnesium bromide. The tribromo compound was in all cases smoothly converted into the dibromo compound. In two runs the reaction mixture was treated for long intervals with carbon dioxide before being decomposed with water. The product was the same as in those runs in which no carbon dioxide was used. No acid could be isolated in any case.

Summary

α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone (III) has been prepared by the bromination of isobutyrylmesitylene (IV) and of α-bromoisobutyrylmesitylene (I).

Treatment with methylmagnesium chloride or ethylmagnesium bromide transformed the tribromo compound (III) into an enolate (VI) which reacted with water to give 3,5-dibromo-2,4,6-trimethylisobutyrophenone (V).

The structure of the dibromo compound (V) was proved by its synthesis from III by zinc reduction and by the fact that bromination reconverted it into the tribromo compound.

Urbana, Illinois

[Contribution from the Chemical Research Laboratories, Picatinny Arsenal]

THE NITRATION OF SYM.-DIPHENYLETHANE[1,2]

By Wm. H. Rinkenbach[3] and H. A. Aaronson[4]

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Although various workers have reported the preparation and properties of a number of nitro derivatives of symmetrical diphenylethane (dibenzyl), it was considered advisable to carry out a more thorough investigation of the nitration of this compound. The object of this study was to determine the practicability of preparing the symmetrical hexanitro derivative by direct nitration, although it was considered probable that steric hindrance would prevent the formation of a high yield of hexanitrodiphenylethane.

Several dinitrodiphenylethanes are recorded in the literature, the 4,4'-dinitro compound being the most important. Stelling and Fittig[5] prepared this compound by the direct nitration of diphenylethane with nitric acid (sp. gr. 1.52) and reported the simultaneous formation of the 2,4'-

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[1] Published by permission of the Chief of Ordnance, U. S. War Department.

[2] Work undertaken at the suggestion of Mr. Lambert Thorpe.

[3] Chief Chemist, Picatinny Arsenal, U. S. War Department.

[4] Assoc. Organic Chemist, Picatinny Arsenal, U. S. War Department.

[5] Stelling and Fittig, *Ann.*, 137, 260 (1866).

dinitro compound. It has been found possible to obtain 4,4'-dinitrodiphenylethane with a yield of 95% of the theoretical by the use of nitric acid having a specific gravity of only 1.42 according to the following procedure.

Thirty-five grams of diphenylethane was added to 105 g. of nitric acid (sp. gr. 1.42). There was no appreciable evolution of heat. The mixture was slowly heated and the temperature was maintained between 70 and 80° for six hours while being stirred. At the end of this time an oily layer below the spent acid was visible. After cooling, the mixture was drowned in ice water, filtered on a Büchner funnel and the retained nitro compound was washed thoroughly with water, air-dried and weighed; yield, 50.0 g. as compared with 52.5 g. calcd. This material was purified by repeated recrystallization from ethanol.

The pure 4,4'-dinitrodiphenylethane so obtained was in the form of light yellow needles which were found to melt at 180.5° (corr.). The melting point of this compound has been reported as being 178[6] 180–182[7] and 182°[8] by various workers, and particular care was taken in determining the above value with at hermometer calibrated by the U. S. Bureau of Standards.

Braun and Rawicz[9] reported the preparation of 2,4,2',4'-tetranitrodiphenylethane, obtaining a 70% yield of this compound when diphenylethane was added to ten times its weight of fuming nitric acid (sp. gr. 1.53) at −15°, allowing to stand at room temperature for one hour, and drowning in ice water. It was found possible to obtain 2,4,2',4'-tetranitrodiphenylethane with a yield of 90 to 95% by the use of the following procedure: 50 g. of diphenylethane was added slowly to 500 g. of fuming nitric acid (95%) which was stirred continuously and maintained at a temperature lower than 30°. When the mixing was complete the temperature was slowly raised to about 70° in the course of two and one-half hours, and maintained at this point for four hours. After cooling and standing overnight, heating at 70° was continued for two hours. Stirring was continued for two hours during cooling. The mixture was then drowned in ice water and filtered through a Büchner funnel. The retained solid was washed thoroughly with water to remove acid and with alcohol to remove any unnitrated diphenylethane. air-dried and found to weigh 91 g. Repeated recrystallizations of this material from benzene and toluene yielded pale yellow needles.

The pure compound so prepared was found to melt at 170.9° (corr.) as compared with the value 168–169° reported by Braun and Rawicz. It is insoluble in hot or cold ethanol, slightly soluble in ether or chloroform and appreciably soluble in hot benzene, toluene, acetone, acetic acid, ethylene dichloride or acetylene tetrachloride. It is non-hygroscopic and explodes in five seconds when heated at 380°. In spite of this, the compound is not detonated by the impact of a 2 kg. weight falling 34 inches; nor is it detonated by 0.4 g. of mercury fulminate or by 0.4 g. of tetryl with 0.23 g. of mercury fulminate in the sand test. However, when 0.40 g. of cyclotrimethylenetrinitramine with 0.23 g. of mercury fulminate is used, detonation takes place and the tetranitrodiphenylethane is found to crush 21 g. of sand as compared with 30 g. crushed by the same weight of trinitrotoluene.

Several attempts to prepare 2,4,2',4'-tetranitrodiphenylethane by the use of mixtures of sulfuric and nitric acids gave negative results. The diphenylethane was dissolved in 95% or in fuming (103%) sulfuric acid by heating to 110° and, after cooling,

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[6] Leppert, *Ber.*, **9**, 15 (1876).

[7] Green, Davies and Horsfall, *J. Chem. Soc.*, **91**, 2079 (1907).

[8] W. Will, *Ber.*, **47**, 704 (1914).

[9] Braun and Rawicz, *ibid.*, **49**, 802 (1916).

a mixture of 95% sulfuric and fuming nitric (95%) acids or of fuming sulfuric and fuming nitric acids was added. After heating at 80 to 100° for from two to four hours, the mixture was cooled and drowned in ice water. Very little separation of solid material resulted and only a small quantity of the tetranitro compound was recovered. Only traces of other compounds were obtained by extracting the water solutions with organic solvents, neutralizing with sodium carbonate and extracting again. It would appear that the use of mixed acids for nitration results in almost complete decomposition of the diphenylethane.

The only reference to a nitro derivative of diphenylethane higher than the tetranitro compound found in the literature is a statement by Will[8] that 2,4,6,2′,4′,6′-hexanitrodiphenylethane is readily formed by the nitration of the dinitro compound and can also be prepared by the oxidation of 2,4,6-trinitrotoluene in the presence of alkalies. He gave no details of either method, but gave the melting point of the hexanitro compound as 212°.

Further nitration of tetranitrodiphenylethane by the use of fuming nitric acid or mixtures of fuming nitric and sulfuric acids caused no additional nitration, the unchanged tetranitro compound being recovered in each case. A number of attempts to prepare the hexanitro compound by the oxidation of trinitrotoluene in the presence of alkalies, using the method of Green, Davies and Horsfall,[7] gave negative results, even with the addition of ammonium persulfate to the solution. An effort to replace one or more hydrogen atoms of the methylene groups with the nitrate group was made, using the method of Walther and Wetzlich.[10] These workers found that hydrobenzoin dinitrate was formed by boiling diphenylethane with silver nitrate in glacial acetic acid; but when 2,4,2′,4′-tetranitrodiphenylethane was substituted for diphenylethane in this procedure, only the unchanged tetranitro compound was recovered.

It was considered possible that a preliminary sulfonation of tetranitrodiphenylethane over an extended period might render nitration possible. A new compound was prepared by the following procedure: 142 g. of tetranitrodiphenylethane was added to 100 g. of fuming sulfuric acid (103%), and the temperature was maintained at 85° for four days. After cooling, 500 g. of fuming nitric acid (95%) was added, and the temperature was slowly raised to 85°. This temperature was maintained for two days, and the mixture was then cooled and drowned in ice water. The separated solid was caught on a Büchner funnel, washed thoroughly with water and air-dried. The weight was found to be 100 g.

On recrystallizing from toluene, the solution became black and the deposited crystals were contaminated with a dark material. Washing with alcohol and with ether removed this and when the alcohol and ether solution was evaporated to dryness, a few grams of a black, gummy residue was obtained. Repeated recrystallization of the crystalline material from toluene gave a pure product consisting of fine, pale cream-colored needles which melted at 187.3°.

Because of the melting point, the material prepared as described above was thought to be a new compound, and investigation showed it to be α-2,4,5-trinitrophenyl-β-2,4-dintrophenylhydroxyethane. The constitution of the compound was established by analysis.

Anal. Calcd.: C, 39.38; H, 2.14; N, 16.56. Found: C, 39.58; H, 2.38; N, 16.56.

From these results the empirical formula $C_{14}H_{10}N_5O_{11}$ was calculated, while that of the pentanitrohydroxy compound is $C_{14}H_9N_5O_{11}$. Since the empirical formula of the tetranitro compound is $C_{14}H_{10}N_4O_8$, it appeared probable that the new compound contained only nine hydrogen atoms, since

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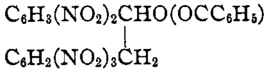
[10] Walther and Wetzlich, *J. prakt. Chem.*, **61**, 174 (1854).

one nitrogen and three oxygen atoms had been added. The value found by the determination of hydrogen is believed to be high because of the difficulty in obtaining accurate results with so small a percentage present, but is within the experimental error. If this is granted, it is apparent that either a nitrate (NO_3) group has replaced one of the hydrogen atoms of the ethylene linkage, or a nitro (NO_2) group has replaced a hydrogen atom in one of the benzene rings and an oxygen atom has been added to the ethylene linkage or formed a phenol derivative.

Molecular weight determinations, with trinitrotoluene as the solvent, gave values of 417 and 427 (av., 422) as compared with 423 for α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane and 407 for pentanitrodiphenylethane. This confirms the presence of eleven oxygen atoms instead of the ten required for a pentanitro derivative.

A diphenylamine–sulfuric acid test for the presence of a side-chain nitrate or nitrite group gave a negative result. The sodium hydroxide test for a phenolic group[11] also gave a negative result. These results indicate that a nitro group has been substituted in one of the benzene rings and that the additional oxygen is attached to the ethylene linkage, probably to form a –CHOH– group.

The presence of a non-phenolic hydroxyl group was confirmed by treatment with benzoyl chloride in pyridine solution. A brownish powder melting at about 200° with decomposition was obtained. This was found to have a nitrogen content of 13.68% as compared with a theoretical value of 13.3% for



$$\begin{array}{l} C_6H_3(NO_2)_2CHO(OCC_6H_5) \\ \qquad\qquad\quad | \\ C_6H_2(NO_2)_3CH_2 \end{array}$$

These results indicate that two nitro groups are attached to one benzene ring, three to the other, and that one of the CH_2 groups had been oxidized to a CHOH group. The problem of determining the position of the third nitro group in one benzene ring and the position of the CHOH group with reference to the trinitrophenyl group was attacked as follows.

A portion of the pentanitrohydroxy compound was placed in a solution of chromic oxide in glacial acetic acid and the solution was boiled under a reflux condenser for sixty-two hours. After cooling, two compounds were isolated. One was slightly contaminated with the second, but melted at 188° and had a nitrogen content of 16.08%. This is believed to be sufficient identification as 2,4,5-trinitrobenzoic acid, which melts at 190–191° and has a nitrogen content of 16.35%.

The second compound did not melt even when heated to 275° and contained 11.16% of nitrogen. That it was an acetic ester was shown by hydrolyzing it with sulfuric acid in the presence of ethanol, when ethyl acetate was formed. This indicates that this compound has the constitution $C_6H_3(NO_2)_2CH(OOCCH_3)$, the theoretical nitrogen content of which is 11.72%.

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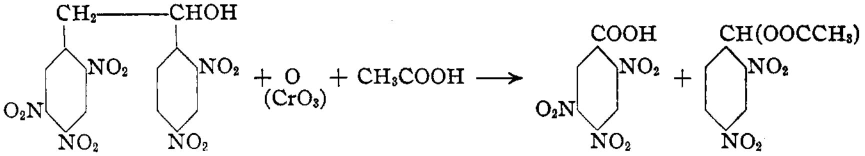
[11] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. 87.

The foregoing facts indicate that the compound under investigation is α-2,4,5-trinitrophenyl-β-2,4-dinitrophenyl-hydroxyethane and that treatment with chromic oxide and glacial acetic acid gave rise to the reaction



This compound is very slightly soluble in alcohol or ether, but is appreciably soluble in hot benzene, toluene, acetone, ethylene dichloride or acetylene tetrachloride. When heated at 360°, it explodes in five seconds and explodes when subjected to the impact of a 2-kilogram weight falling 18 inches or more. It cannot be detonated by 0.4 g. of mercury fulminate, but when initiated with 0.25 g. of tetryl and 0.25 g. of mercury fulminate in the sand test, it crushes 21 g. of sand.

The formation of α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane is of unusual interest, as the direct effects of steric hindrance are easily recognizable. It is thought probable that prolonged sulfonation does no more than serve to introduce a nitro group in the 5-position instead of the 6-position normally substituted in the trinitration of monoalkylbenzene compounds. The introduction of the nitro group in the 5-position prevents oxidation of the adjacent β-methylene. The oxidation of the methylene group is evidently limited to one stage by the steric hindrance effect of the nitro groups already present in the compound and evidently is subsequent to the introduction of one of the nitro groups; otherwise both methylene groups would be oxidized and no nitration would take place, as the introduction of a third nitro group is more difficult than the oxidation of a methylene group.

The limitation of oxidation as an effect of steric hindrance is confirmed by results obtained in efforts to condense two molecules of α-2,4,5-trinitrophenyl-β-dinitrophenylhydroxy-ethane with the elimination of one molecule of water from the two hydroxyl groups. When the compound was dissolved in and heated with 95% sulfuric acid or a mixture of fuming sulfuric acid and phosphorus pentoxide, the unchanged compound was recovered. As such condensations are relatively easy when less complex hydroxy compounds are used, and the 2,4-dinitro compound recovered on splitting with chromic oxide was esterified by the glacial acetic present, the inhibitive effect of steric hindrance in α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane is great, although the preparation of a benzoate was not difficult.

In the course of this study, the pentanitrohydroxy compound was prepared several times. From the products of nitration in one case, using 140 g. of tetranitrodiphenylethane, there was isolated about 0.5 g. of a compound melting at 209°, and having a nitrogen content of 18.48%. This is undoubtedly the symmetrical hexanitrodiphenylethane mentioned by Will[8] as melting at 212° (18.59% N). In spite of repeated attempts to prepare more of this material, none was obtained. It is apparent that this compound is formed in very small amount under even the most favorable conditions.

Summary

1. Modified methods of preparing 4,4′-dinitro- and 2,4,2′,4′-tetranitrodiphenylethane with high yields have been developed. Accurate melting point determinations of these pure compounds, as well as other properties, have been recorded.
2. A new compound has been prepared by the nitration of tetranitrodiphenylethane and identified as α-2,4,5-trinitro-phenyl-β-2,4-dinitrophenylhydroxyethane. The important properties of this compound have been determined.
3. 2,4,6,2′,4′,6′-Hexanitrodiphenylethane is formed in very small amount under even the most favorable conditions of nitration.
4. The effects of steric hindrance in the formation of nitro derivatives of diphenylethane have been evaluated.

DOVER, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

MAGNESIUM DIALKYLS. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF AN ALKYLMAGNESIUM HALIDE

BY HENRY GILMAN AND ROBERT E. BROWN

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Introduction

In extension of studies concerned with the preparation of phenylmagnesium chloride in the absence of a solvent,[1] some apparently anomalous reactions were observed when alkyl halides were heated with magnesium. This necessitated an investigation of the related magnesium dialkyls.

Hallwachs and Schafarik[2] were the first to prepare an organomagnesium compound, and this they did by heating ethyl iodide with magnesium. The solid reaction product when heated gave a colorless, volatile liquid which they said contained traces of the magnesium diethyl. Then Cahours,[3] by a like reaction, obtained an entirely volatile product which he considered magnesium diethyl. At a much later time, Löhr[4]

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[1] Gilman and Brown, THIS JOURNAL, **52**, 3330 (1930).

[2] Hallwachs and Schafarik, *Ann.*, **109**, 206 (1859).

[3] Cahours, *ibid.*, **114**, 227, 240 (1860).

[4] Löhr, *ibid.*, **261**, 48, 72 (1891). See, also, Fleck, *ibid.*, **276**, 129 (1893), who used the mercury diethyl method of preparation described by Löhr. Extensive studies on the direct action of RX compounds and magnesium have been made by Spencer and co-workers. *J. Chem. Soc.*, **93**, 68, 1821 (1908).