

## On Attempts to Obtain 1,2,3-Trinitropropane

by

T. ŚLEBODZIŃSKI, T. URBAŃSKI, J. BIMER, and D. SAŁBUT

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According to some authors the nitration of alkanes can yield dinitroalkanes when the reaction is carried out in gas phase between alkanes and nitrogen dioxide or nitric acid vapours present in excess.

However, this finding was questioned by other authors. They pointed out that polynitroalkanes should decompose through pyrolysis and oxidation when subjected to the action of high temperature of the gas phase nitration.

The existing controversy led us to prepare a few polynitroalkanes on a purely synthetic way in order to study their chemical properties, and particularly to examine their behaviour at high temperatures. Among the compounds in question 1,2,3-trinitropropane was chosen. The preparation of it was described by Brackebusch [1].

According to this author, the heating of 1,2,3-tribromopropane with silver nitrite to 90° produces a violent reaction manifested by the rise in the temperature to 190–200°, to form 1,2,3-trinitropropane.

No experimental details were given by this author.

When repeating the reaction described by Brackebusch we came to the following conclusions:

(1) No reaction occurs between 1,2,3-tribromopropane and silver nitrite in the presence of solvents (ethyl ether, carbon tetrachloride) at room temperature or at their boiling point.

(2) When 1,2,3-tribromopropane is heated with silver nitrite to temperatures from 95 to 140° (depending on the ratio of the reagents) a pyrolytic decomposition which occurs is accompanied by evolution of heat and increase in the temperature to 270°.

The use of gas chromatography for separation of nitroalkanes does not always give reliable results and requires special adsorbents [4]. Therefore we developed other procedure which consists in the preparation of crystalline derivatives of nitroalkanes which could be identified by comparing with standard samples [3].

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Note: This Paper forms Part LXXXVI of the series: Chemistry of nitroparaffins [2] and Part V of the series: Nitration of Paraffins [3].

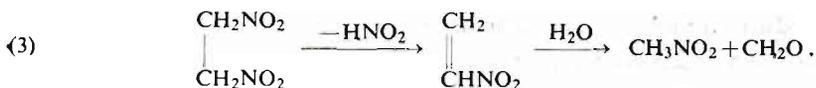
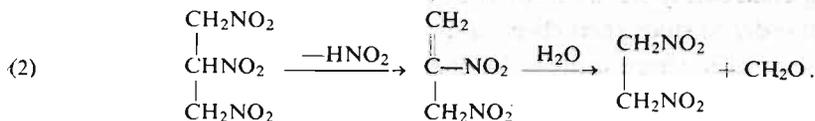
The products of the reaction were found to contain silver bromide, silver oxide and the organic fraction. The latter includes formaldehyde, nitromethane (identified as *p*-bromophenylhydrazone of nitromethanal) and a trace quantity of propane-2-on-1,3-dial (mesoxalic dialdehyde) identified as *bis* 2,4-dinitrophenylhydrazone. The latter was found identical with hydrazone of polyoxocompound formed by reduction ( $\text{SnCl}_2$  in conc.  $\text{HCl}$ ) of the nitrocompounds obtained.

Most likely propane 2-on-1,3-dial was formed in the course of thermal decomposition of 1,2,3-trinitropropane:



The decomposition yielded the product which would be identical with those of the Nef reaction, however, the mechanism is probably different as the Nef reaction occurs by acidifying the *aci*-forms of primary and secondary nitroparaffins. The presence of propan-2-on-1,3-dial can be regarded as an evidence of the formation of 1,2,3-trinitropropane followed by pyrolytic decomposition.

Similarly, the formation of nitromethane and formaldehyde can be explained as the result of thermal decomposition of the originally formed 1,2,3-trinitropropane, e.g. by the following reaction sequence:



### Experimental

1,2,3-Tribromopropane was prepared according to the known method [5].

#### Reaction of 1,2,3-tribromopropane with silver nitrite

Different molar ratios of tribromopropane to silver nitrite (from 1 : 2 to 5 : 1) were applied. The quantity of tribromopropane was in each case 106.5 g., (0.38 mol), and that of silver nitrite— from 11.7 to 116.5 g.

Silver nitrite was either added gradually to tribromopropane warmed to 90° or the mixture of both components was warmed to 90°.

The reaction was manifested by darkening of silver nitrite and evolution of, at first, white and later brown vapours. When, upon heating, the temperature reached 120—130°, an exothermic reaction started. The heating was stopped, but the temperature raised to 270—280°. The distilling off vapours were condensed.

After cooling, the liquid phase (mainly unreacted tribromopropane) was separated from solids. The solids (mainly silver bromide and oxide) were extracted with ether. The liquid phase, condensed vapour, and the ether extract were combined and dried over sodium sulphate. After evaporation of ether the liquid residue was subjected to the following examination.

## Identification of nitromethane

The liquid mixture of condensed volatile products (3.4 g. — 2 per cent of the mixture of tribromopropane and silver nitrite in proportion 1 : 2) was treated with aqueous (10%) sodium hydroxide. The clear aqueous phase was separated from an oil and a solution obtained by diazotization of an excess of *p*-bromoaniline was added. Red-orange crystalline precipitate of 4-bromophenyl-hydrazone of nitromethanal (nitroformaldehyde) (m.p. 159—160°, 0.9 g.) was obtained. It proved to be identical with a standard sample obtained by the treatment of alkaline solution of nitromethane with 4-bromophenyldiazonium acetate (m.p. 159—160°). No depression of m.p. was found when both substances were mixed. For  $C_7H_6BrN_3O_2$ , calcd. N, 17.2, found N, 16.8%.

## Identification of mesoxaldehyde

The liquid mixture of products was warmed on water bath to remove volatile substances. The remaining liquid (89.3 g.) was subjected to fractional distillation under reduced pressure: unreacted 1,2,3-tribromopropane (73.6 g.) distilled at 116—120°/30 mm., the oily reddish-brown residue (5.7 g.) which gave a clear reaction on primary nitro-group was dissolved in 30 per cent alcoholic potassium hydroxide and reduced with stannous chloride in conc. hydrochloric acid. All nitro compounds were thus transformed into carbonyl compounds. The acid solution was steam distilled and a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid was added. An orange-red precipitate of *bis*-2,4-dinitrophenylhydrazone of propan-2-on-1,3-dial (mesoxaldehyde) (0.15 g., m.p. 258—261°) was collected. It proved to be identical with a standard sample of *bis*-2,4-dinitrophenylhydrazone (m.p. 259°). Both products gave magenta-blue colour on treatment with aqueous 10 per cent sodium hydroxide. No depression of m.p. was found when both samples were mixed. For  $C_{15}H_{10}N_8O_9$  calcd.: N, 25.1, found: N, 24.8%.

DEPARTMENT OF CHEMISTRY, TECHNICAL UNIVERSITY, WARSAW  
(WYDZIAŁ CHEMICZNY, POLITECHNIKA, WARSZAWA)

INSTITUTE OF ORGANIC CHEMISTRY, POLISH ACADEMY OF SCIENCES  
(INSTYTUT CHEMII ORGANICZNEJ, PAN)



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