[Contribution from the Research Laboratories of the
Aerojet-General Corporation]

THE PREPARATION OF α,ω-NITRO COMPOUNDS[1]

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Received January 17, 1955

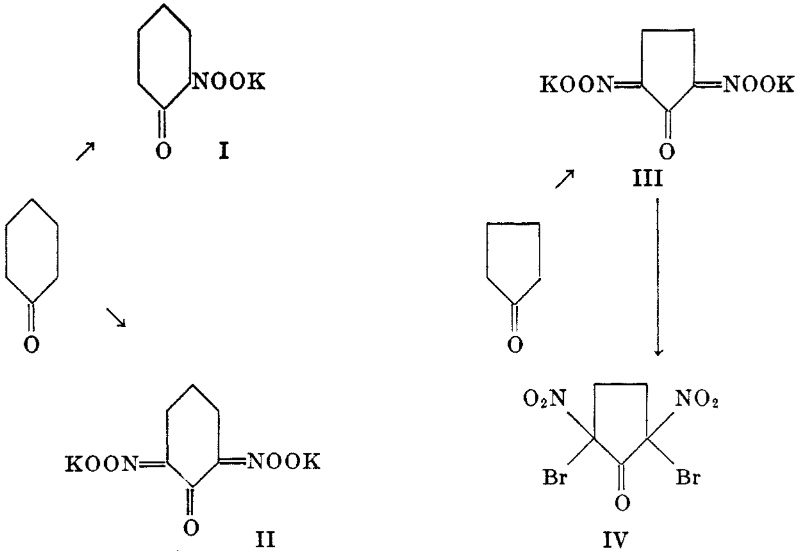
The best known method for the preparation of long chain aliphatic compounds having terminal nitro groups is that of Victor Meyer (1). The more reactive iodo compounds are prepared from available α,ω-dichloro or dibromo compounds and treated with silver nitrite:

$$Cl(CH_2)_xCl \rightarrow I(CH_2)_xI \rightarrow O_2N(CH_2)_xNO_2$$
$$x = 3 \text{ or more}$$

The terminal dinitro compounds are obtained in fair yield, but the method is time consuming and expensive. Braun and Sobecky (2) used this method for the preparation of 1,4-dinitrobutane and 1,5-dinitropentane. One special case, not involving silver nitrite was the preparation of 2,2-dimethyl-1,3-dinitropropane from acetone and nitromethane (3, 4).

While the introduction of many functional groups in the α,ω-positions of aliphatic compounds is not uncommon, nitro compounds of this type have always been considered as laboratory curiosities. Thus, there is great justification for the development of new synthetic methods for such compounds. The conversion of cyclic ketones into aliphatic dicarboxylic acids is well known. A similar technique, using cyclic ketones for conversion into α,ω-polynitro compounds might also be considered possible.

Wieland, Garbsch, and Chavan (5) described the nitration of cyclopentanone and cyclohexanone with ethyl nitrate in the presence of potassium ethoxide. They were able to prepare mono 2-nitrocyclohexanone (I), 2,6-dinitrocyclohexanone (II), and 2,5-dinitrocyclopentanone (III) in form of their *aci* potassium salts:



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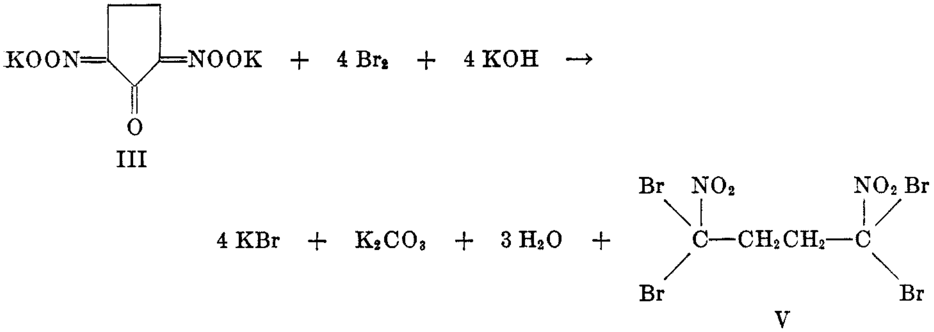
[1] This work was conducted under a contract with the Office of Naval Research.

It is known that the bromination of the salts of nitro compounds in aqueous medium gives the corresponding bromonitro compounds. When the potassium salt of 2,5-dinitrocyclopentanone was brominated in water solution a white crystalline compound was obtained. This was recrystallized several times but could not be purified to a sharply melting product. The bromine content of this mixture was 62.16% Br instead of 48.15 for the expected 2,5-dinitro-2,5-dibromocyclopentanone (IV). The analysis indicated that in addition to the bromination another reaction must have taken place. When the bromination was repeated in the presence of alkali, a sharply melting compound was obtained. The elemental analysis and the melting point were in agreement with the known 1,1,4,4-tetrabromo-1,4-dinitrobutane (2).

This new formation of aliphatic α,ω-nitro compounds is shown in the following equation:



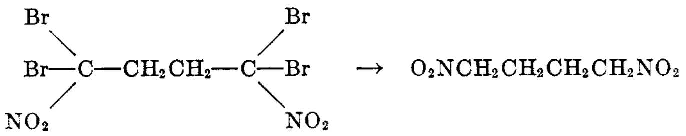
III

V

In the absence of alkali the reaction may not have proceeded to completeness and, therefore, did not lead to a uniform product.

This new method of opening cyclic ketones was also successfully applied in the case of potassium 2,6-dinitrocyclohexanone (II) to give 1,1,5,5-tetrabromo-1,5-dinitropentane, m.p. 39°.

The new method however, can only be of interest for preparative purposes if the perbromo compounds formed can be reduced to aliphatic α,ω-nitro compounds. Such reductions are well known in the literature, *e.g.* Schmidt and Trenel (6) were able to reduce bromonitroethanol to nitroethanol catalytically with a palladium catalyst in the presence of pyridine. Several other selective reducing agents such as potassium iodide, potassium cyanide, and sodium thiosulfate have been tried without apparent success. Not long ago sodium borohydride (7), a new selective reducing agent, was found to be inert toward nitro groups. Thus, when sodium borohydride was added at *p*H 3–5 to 1,4-dinitro-1,1,4,4-tetrabromobutane in methanol-water solution, the bromo groups were selectively reduced to form 1,4-dinitrobutane (V) in high yield.



V VI

D. C. Iffland and G. X. Criner (8) reported the use of sodium borohydride for the reduction of cyclic bromo nitro compounds, such as bromonitrocyclohexane, however, this method was disclosed in a patent application by the author, filed in 1951.

EXPERIMENTAL[2]

1,1,4,4-Tetrabromo-1,4-dinitrobutane (V). A solution of 7.9 g. of potassium 2,4-dinitrocyclopentanone (5) in 200 ml. of water was cooled to 0° and 35.6 g. of 20% potassium hydroxide solution was added. While stirring rapidly, 10 ml. of bromine was dropped into the alkaline solution and a yellowish-white precipitate was formed. After filtration, the crystals were dissolved in ether, dried over sodium sulfate, filtered, and the ether content was reduced by vacuum-distillation. The solution was diluted with hexane and distilled until crystals appeared. The yield was 11.5 g., m.p. 100–101° [von Braun, 100° (2)].

Anal. Calc'd for $C_4H_4Br_4N_2O_4$: C, 10.36; H, 0.87; N, 6.04; Br, 68.93.
Found: C, 10.62; H, 0.97; N, 6.56; Br, 69.99.

1,1,5,5-Tetrabromo-1,5-dinitropentane. In an Erlenmeyer flask 2.26 g. of monopotassium 2,6-dinitrocyclohexanone (5) was dissolved in 21 ml. of water and 14 ml. of 20% aqueous potassium hydroxide. The solution was cooled to 0° and bromine was added until no more was absorbed. The white precipitate was filtered and washed with water. The damp crystals were extracted with boiling hexane, the solution was concentrated, and the concentrate was chilled in a Dry Ice-acetone bath. The crystals, 0.25 g., were recrystallized from hexane, m.p. 37–38° [von Braun, m.p. 39° (2)].

Anal. Calc'd for $C_5H_6Br_4N_2O_4$: C, 12.57; H, 1.27: N, 5.86.
Found: C, 12.78; H, 1.49; N, 6.43.

1,4-Dinitrobutane (VI). A beaker provided with a stirrer, thermometer, and burette was charged with 6.8 g. of 1,1,4,4-tetrabromo-1,4-dinitrobutane in 100 ml. of methanol. A solution of 3 g. of sodium borohydride in 30 ml. of water was added dropwise. The starting *p*H was 1.5 and rose rapidly to 4–5, but was kept at *p*H 4–5 by the dropwise addition of 30% sulfuric acid. The temperature was kept below 35° during the reaction. The methanol water solution was acidified to *p*H 1.5 and vacuum-distilled to remove the methanol. The water solution contained some oil, which was dissolved in ether, and the ether solution then was dried and evaporated. The remaining oil was distilled at 1 micron and 110–115° air-bath temperature to yield 1.8 g. The oil crystallized upon cooling and was recrystallized from 5 ml. of absolute ethanol and redistilled in a high vacuum at 1 micron and 110–115° air-bath temperature. The crystals obtained had m.p. 30–33° [von Braun, 32–33° (2)].

Anal. Calc'd for $C_4H_8N_2O_4$: C, 32.43; H, 5.44; N, 18.92.
Found: C, 31.63; H, 5.38; N, 17.72.

SUMMARY

1. A new method for the preparation of α,ω-nitro compounds was developed by cleaving nitrated cyclic ketones with bromine in alkaline solution.

2. Sodium borohydride was found to be an excellent reducing agent for the conversion of aliphatic perbromo nitro compounds into aliphatic nitro compounds.

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[2] The elementary analyses were carried out in the micro analytical laboratories of Dr. Adalbert Elek, Los Angeles, California.

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