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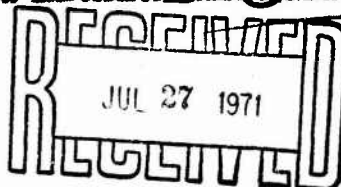
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U. S. Naval Ordnance Laboratory
White Oak, Silver Spring 19, Maryland

NAVAL ORDNANCE LABORATORY MEMORANDUM 10509



9 September 1949

AD499752

From: L. W. Kissinger
To: Explosives Division Files

Subj: Chlorination of 2,2-Dinitropropane and the Preparation of Related
Derivatives of 2,2-Dinitropropane. NOL-149

Abst: The photochemical chlorination of 2,2-dinitropropane is extremely slow. 1-Chloro-2,2-dinitropropane was produced in about 20% yield, together with a small quantity of a polychloro-compound of unknown structure. 1-Chloro-2,2-dinitropropane has also been prepared from 2,2-dinitropropanol, and 2,2-dinitro-1,3-propandiol, an intermediate in the preparation of 1,3-dichloro-2,2-dinitropropane, has been prepared from dinitromethane and formaldehyde.

Fwd: The data presented here are for the information of the Explosives Division. They may not represent the judgment of the Laboratory.

Ref: (a) Riley and Hass, Chem. Rev. 32, 405(1943).
(b) Smith and Walton, NOLM 10335, p. 14.
(c) Kissinger, NOLM 10508.
(d) OSHD 2016, p. 14.

I. INTRODUCTION

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1. It is believed to be of interest to study the detonation of experimental high explosives whose reaction products differ materially from those formed from conventional service explosives. Efforts to prepare explosives for which the mean molecular weight of the detonation products is substantially different from that of, say, TNT have led to attempts to prepare hydrogen-free explosives. With the purpose of keeping the molecular weights to be averaged as nearly alike as possible, a series of explosives with a part or all of the hydrogen replaced by halogen are being prepared by the Organic Chemistry Section. Preliminary work on the preparation of halogen derivatives of 2,2-dinitropropane is reported here.

II. Photochemical Chlorination of 2,2-Dinitropropane

2. Very little work appears in the literature on the halogenation of nitroaliphatic compounds in which the attack is on a carbon not attached to a nitro group. Riley and McBes (reference a.) studied the photochemical chlorination of mononitroaliphatic compounds and were able to prepare monochloronitro derivatives in which the chlorine atom appeared in the 1 and 2 position with respect to the nitro group.

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NOLM 10,509

3. The photochemical chlorination of 2,2-dinitropropane was studied under a variety of conditions. Under the conditions (described below) in which the most chlorination was observed the rate of chlorination was impractically slow. After 170 hours of chlorination only an equivalent of 1/2 atom of chlorine was introduced. Fractionation of this material resulted in the recovery of 45 percent of unreacted 2,2-dinitropropane and about 20 percent of 1-chloro-2,2-dinitropropane. A small fraction of material was obtained which, on analysis for chlorine, was probably a tri- or tetrachloro derivative. Nitrogen analyses however showed that only half the required nitrogen remained indicating that during this prolonged chlorination at least one of the nitro groups suffered replacement.

4. The conditions under which the above described products were obtained involved heating under reflux a solution of 2,2-dinitropropane in about 4 volumes of dry carbontetrachloride in a round - bottom flask illuminated by two sealed - beam auto spot lights (6V, 4.75A each). The chlorine was introduced into the flask through a fritted glass filter stick after preliminary drying with concentrated sulfuric acid.

5. As the chlorination of 2,2-dinitropropane proved to be so slow and another Section was having difficulty in causing the explosion of 2,2-dinitropropane itself to propagate (see reference b.), this approach was dropped.

III. Preparation of Related Derivatives of 2,2-Dinitropropane.

6. Concurrent with the chlorination of 2,2-dinitropropane the preparation of 1-chloro-2,2-dinitropropane (III) and 1,3-dichloro-2,2-dinitropropane (VI) by way of the corresponding alcohols was undertaken. 1-Chloro-2,2-dinitropropane (III) and, at the time of writing, the intermediate glycol, 2,2-dinitropropanediol-1,3(V), needed for the preparation of (VI) have been prepared.

(A) 1-Chloro-2,2-dinitropropane (III).

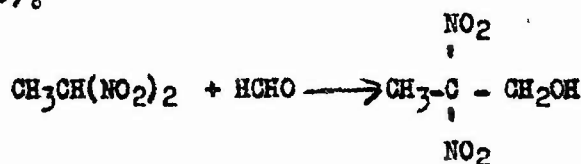
7. 1-Chloro-2,2-dinitropropane (III) was prepared by the action of phosphorus pentachloride on 2,2-dinitropropanol (II), which is readily obtainable from 1,1-dinitroethane and formaldehyde. The action of phosphorus pentachloride on 2,2-dinitropropanol (II) results in the formation of the desired chloro compound (III) in about 30-35 percent of the theoretical yield, accompanied by 15-20 percent of the theoretical yield of the phosphate ester of 2,2-dinitropropanol (IV).

8. The conditions under which these compounds were prepared were as follows:

(a) 1,1-Dinitroethane (I) was prepared as described in reference c.

(b) 2,2-Dinitropropanol (II) was prepared by heating under reflux a solution of 1,1-dinitroethane (I) in 1-1.5 molecular equivalents of 36 percent aqueous formaldehyde for 3-6 hours. The dinitropropanol was extracted from the cooled solution with ether and fractionated by distillation under reduced pressure. A fraction boiling at 72-80°C. at 2 mm. was obtained. Nitrogen analyses were correct for 2,2-dinitropropanol (II). The yield, nearly quantitative, was unaffected by the presence of dilute sulfuric acid. 2,2-

Dinitropropanol (II) melts at 79-81°C, is waxy in appearance and seems to be quite hygroscopic. It was previously prepared under an OSRD contract (reference 6.).



(I)

(II)

9. The chlorination of 2,2-dinitropropanol was accomplished by carefully mixing the alcohol with 1.5-2 molecular equivalent of phosphorus pentachloride with cooling. After the addition was complete the reaction mixture was allowed to warm to 40-50°C. spontaneously or if necessary it was heated to about 50°C. for about 1/2 hour. The solution was poured into ice water and the 1-chloro-2,2-dinitropropane (III) extracted with ether, dried over calcium chloride and fractionated by distillation under reduced pressure. 1-Chloro-2,2-dinitropropane boils at 75-77°C. at 5 mm.; it is waxy in appearance.

10. The analytical data obtained from Oakvold Laboratories on a sample of this compound are:

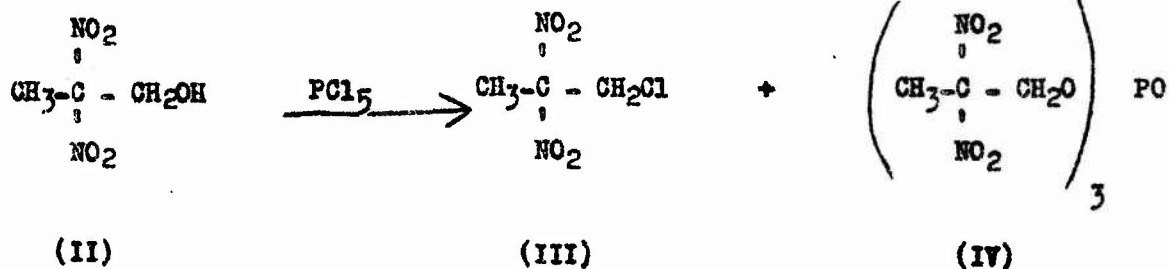
	Found	Calc'd for III
% C	21.35, 21.57	21.37
% H	2.88, 2.93	2.97
% N	14.33, 14.41*	16.62
% Cl	21.36, 21.27	21.07

11. After ether extraction of the 1-chloro-2,2-dinitropropane (III) as described above, an ether - water insoluble crystalline material melted, after crystallization from chloroform, at 155 C. Its elementary analyses are in agreement with the phosphate ester IV.

	Found	Calc'd for IV.
% C	21.80, 21.93	21.86
% H	3.24, 2.98	3.04
% N	17.20, 16.90	17.00
% P	6.12, 6.15	6.28

* The low nitrogen is in poor agreement with the calculated. However, this seems to be typical of many nitrogen determinations of these polynitro-aliphatic compounds.

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(B) 1,3-Dichloro-2,2-dinitropropane.

12. At the time of writing 2,2-dinitropropandiol-1,3 has been prepared by the action of formaldehyde on dinitromethane. Its reaction with phosphorus pentachloride is in process of being studied and will be reported upon in a subsequent NOIM.

IV. Acknowledgment:

13. The writer wishes to acknowledge the experimental work in this study above by Mr. Dean W. Jensen and Mr. Francis Taylor, Jr.

L. W. Kissinger

LWK:ahm

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