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Nathan Kornblum, and Jack Powers

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Synthesis of Aliphatic Nitro Compounds^{1,2}

NATHAN KORNBLOM AND JACK W. POWERS

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A simple new synthesis of primary and secondary nitro compounds from alkyl halides and sodium nitrite has recently been described.³ As was pointed out earlier,³ the success of this synthesis hinges upon the use of *N,N*-dimethylformamide (DMF) as the solvent.

It has now been found that dimethyl sulfoxide (DMSO) is also an effective medium for the nitro-paraffin synthesis and that its use confers certain advantages. Sodium nitrite is considerably more soluble in DMSO than in DMF;⁴ as a consequence, with DMSO much more concentrated solutions can be employed and this, in turn, makes possible shorter reaction times⁵ (Table I).

TABLE I
REACTION OF ALKYL AND CYCLOALKYL HALIDES WITH SODIUM NITRITE

Halide	Reaction Time (Hr.)		% Yield of Nitroparaffin	
	DMSO ^a	DMF ^a	DMSO	DMF
1-Bromooctane	2	6	66	60
2-Bromooctane	12	45	46	58
2-Iodoctane	4	4	58	60
Bromocyclopentane	3 ^b	42	58	57

^a Reactions conducted at room temperature unless otherwise specified. ^b At 15°C.

As can be seen from Table I, the yields in DMSO and in DMF are comparable. 1-Bromooctane, a representative primary bromide gives essentially the same yields of 1-nitrooctane in DMSO and in DMF.⁶ With 2-bromooctane, however, the 46% yield of 2-nitrooctane in DMSO solution is un-

(1) Paper XVII in the Series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(2) This research was supported by a grant from the Explosives Department of E. I. du Pont de Nemours & Co., Inc.

(3) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

(4) Thus, in a few minutes, 100 ml. of DMSO dissolves 19.2 g. of sodium nitrite whereas only 1.88 g. dissolve in 100 ml. of DMF at room temperature after 24 hr. In DMSO, urea is never added to increase the solubility of sodium nitrite in the reaction medium, whereas with DMF as the solvent urea is sometimes employed for this purpose (ref. 3).

(5) Rough rate studies made with 1-bromoheptane and with ethyl α -bromobutyrate (ref. 7) reveal that the reaction with sodium nitrite goes on at essentially the same rate in DMSO and in DMF. The shorter reaction times in DMSO are, therefore, a function of the higher concentrations which can be maintained in that solvent.

(6) While the reaction using primary iodides in DMSO was not studied, there can be little doubt that the yields of primary nitrocompounds would be comparable to those in DMF (57-61%).

mistakably lower than the 58% obtained in DMF and it seems likely, therefore, that with open chain secondary bromides the reaction in DMF can be counted on to give somewhat higher yields. With secondary iodides, as exemplified by 2-iodooctane, the two solvents give the same yields of nitro-paraffin.

In an effort to improve on the 46% yield of 2-nitrooctane, phloroglucinol^{3,7} was added to a DMSO run employing 2-bromooctane and sodium nitrite. To our surprise, the time needed for the reaction to go to completion *increased* from 12 hr. to 168 hr. and the yield of 2-nitrooctane was only 37%. From this, and other experiments with 2-iodooctane and bromocyclopentane (*cf.* Experimental), it is clear that phloroglucinol slows down the reaction of sodium nitrite with secondary halides and, if anything, decreases the yields of nitro compounds.⁸

EXPERIMENTAL

Reagents. Initially, DMSO (Stepan Chemical Co.), dried by allowing it to stand over calcium hydride for several days, and "analytical grade" sodium nitrite dried by heating overnight at 110°, were used. Runs made with the four halides listed in Table I gave the yields recorded there. Subsequently, it was found, at least for 1-bromooctane and 2-iodooctane, that the DMSO and the sodium nitrite could be used as received with no decrease in the yields of nitro compounds. Consequently it appears that, in general, precautions to maintain vigorously anhydrous conditions are unnecessary. The following is illustrative of the general procedure.

*Preparation of 2-nitrooctane from 2-iodooctane.*⁹ 2-Iodoctane (71.2 g., 0.30 mole) was poured into a stirred solution of 225 ml. dimethyl sulfoxide (DMSO) and 36 g. of sodium nitrite (0.52 mole) contained in a 500 ml. flask immersed in a water bath held at room temperature. Stirring was continued for 4 hr. The reaction mixture was poured into 600 ml. of ice water layered over with 100 ml. of petroleum ether (b.p. 35-37°). After separation, the aqueous phase was further extracted with four 100 ml. portions of petroleum ether. The combined extracts were washed with four 100 ml. portions of water and then dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the petroleum ether solution was distilled through a small column after which the residual liquid was rectified under reduced pressure. At 2 mm., 14.0 g. (30% yield) of 2-octyl nitrite (pale yellow, n_D^{20} 1.4089) came over at 32°; this was followed by a small fraction (3.9 g.), b.p. 53-56°/1 mm., (n_D^{20} 1.4111-1.4382) after which 27 g. (58% yield) of 2-nitrooctane (n_D^{20} 1.4281; b.p. 61°/1 mm.) was obtained.¹⁰ An identical experiment using dried DMSO and sodium nitrite

(7) N. Kornblum, R. K. Blackwood and J. W. Powers, *J. Am. Chem. Soc.*, *in press*.

(8) Fortunately, in those cases where phloroglucinol is indispensable (the synthesis of α -nitroesters), the reaction is intrinsically so fast that despite the retardation due to phloroglucinol it goes on at a good rate (ref. 7). Although it is highly probable that phloroglucinol also slows down the rate of reaction of alkyl halides with sodium nitrite in DMF, this point has not been investigated.

(9) Our thanks are due to Mr. D. E. Hardies for carrying out a preliminary experiment (*cf.* ref. 3).

(10) Nitroparaffins obtained from alkyl iodides sometimes have a light pink color despite their correct b.p. and n_D^{20} . This color is readily removed by allowing the nitro compound to stand in contact with a little metallic silver.

(see above) gave a 57% yield of 2-nitrooctane (n_D^{20} 1.4280). A duplicate run in which 40 g. of anhydrous phloroglucinol was present (DMSO and sodium nitrite dried as described above) was allowed to proceed for 8 hr. On working up as usual an 11% yield (5.3 g.) of 2-nitrooctane (b.p. 62°/2 mm.; n_D^{20} 1.4281) and an 11% yield (5.3 g.) of 2-octyl nitrite (b.p. 35°/3 mm.; n_D^{20} 1.4088) were isolated. In addition, there was obtained 43.4 g. of material boiling in between the nitrite ester and the nitro compound (36°/3 mm. to 58°/2 mm.); n_D^{20} 1.4117-1.4781. Since 40.6 g. out of the 43.4 g. had n_D^{20} above 1.4721 it is clear that this material is largely unreacted 2-iodooctane (n_D^{20} 1.4885).

Preparation of nitrocyclopentane. Cyclopentyl bromide (22.0 g.; 0.15 mole) was treated with a solution of 18 g. dried sodium nitrite in 100 ml. dried DMSO for 3 hr. at 15°C. On working up the reaction mixture 9.9 g. (58% yield) of nitrocyclopentane was isolated; b.p. 62°/8 mm.; n_D^{20} 1.4538.

A duplicate run to which 20 g. of anhydrous phloroglucinol had been added was conducted at room temperature. Despite the higher temperature in this run, the reaction required 10 hr. to proceed to completion (followed by titrating bromide ion liberated). The yield of nitrocyclopentane (b.p. 48°/1 mm.; n_D^{20} 1.4539) was 8.7 g. (51%).

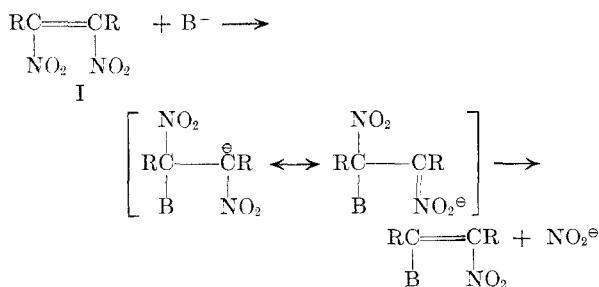
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.

Reactions of Dinitroolefins with Nucleophilic Reagents¹

WILLIAM D. EMMONS AND JEREMIAH P. FREEMAN

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1,2-Dinitroolefins (I) possess an unsaturated system which is particularly vulnerable to nucleophilic attack. In this respect they are similar to nitroaryl halides, β -chlorovinyl ketones,² and alkoxymethylenemalonic esters.³ It is not known whether these reactions are concerted or involve an unstable intermediate, but in general they may be expressed as follows:



It has previously been shown that dinitroolefins react with amines to form β -aminonitroolefins^{4,5}

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

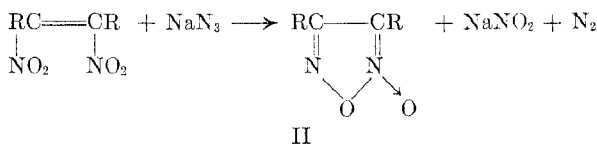
(2) For leading references, see E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 2318 (1956).

(3) L. Claisen, *Ann.*, **297**, 1 (1897).

(4) L. B. Clapp, J. F. Brown, and L. Zefel, *J. Org. Chem.*, **15**, 1043 (1950).

(5) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **78**, 3405 (1956).

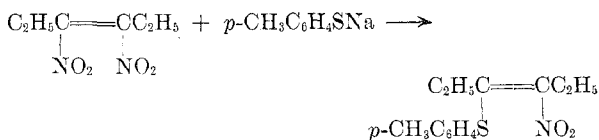
and with alkoxide ion.⁴ It has now been found that they also react very rapidly with azide and thiolate ions. With azide ion, nitrogen was evolved and the product was a furoxan (II). The structure of these compounds was established by reference to their



elementary analyses and characteristic infrared spectra.⁶ In addition one of the compounds, dimethylfuroxan, was synthesized independently by the action of dinitrogen tetroxide on dimethylglyoxime.

The production of furoxans under the gentle conditions of this reaction is of interest. First of all, it furnishes what appears to be a general route to dialkyl furoxans, up to now a relatively inaccessible group of compounds. Secondly, their process of formation must be fundamentally different from that of benzofuroxans from *o*-nitrophenyl azides.⁷ The latter reaction is a thermal one occurring at temperatures around 100-150°. The azide-dinitroolefin reaction occurs almost instantaneously at room temperature with a vigorous evolution of nitrogen suggesting a concerted ionic process.

Both *cis*- and *trans*-3,4-dinitro-3-hexene reacted with sodium *p*-toluenethiolate to produce the same 3-*p*-toluenethio-4-nitro-3-hexene (III), presumably the *trans* isomer. This compound proved to be an oil and was converted to the corresponding sulfone for identification. This reaction was not ex-



amined with the other dinitroolefins, but is presumed to be a general reaction.

Four pairs of dinitroolefins, the *cis* and *trans* isomers of 1,2-dinitrostilbene, 2,3-dinitro-2-butene, 3,4-dinitro-3-hexene, and 2,3-dinitro-2-hexene were examined in the azide and amine reactions. In each case only one product was obtained from each pair. The formation of only one compound is to be expected in the case of furoxan formation. In the aminonitroolefin series the *cis* form appears to be stabilized by hydrogen bonding.⁵ It was originally thought that different isomers or isomer ratios might be obtained in the thiolate reaction in view of the recent report of different isomer ratios resulting from the reaction of thiolate ions with *cis* and *trans*- β -chlorocrotonic esters.⁸ Apparently in the dinitroolefin series a relatively long-lived inter-

(6) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

(7) J. Boyer and F. Canter, *Chem. Revs.*, **54**, 35 (1954).

(8) D. Emyr Jones, and C. A. Vernon, *Nature*, **176**, 791 (1955).