(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%).

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# Reactions of Dinitroolefins with Nucleophilic Reagents[1]

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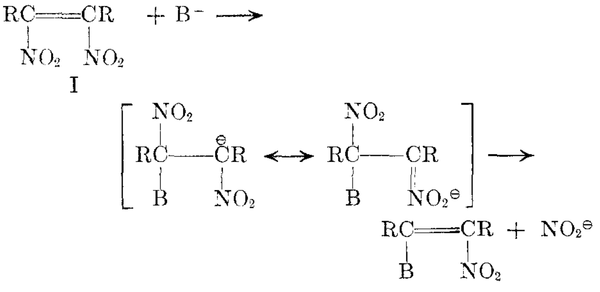
1,2-Dinitroolefins (I) possess an unsaturated system which is particularly vulnerable to nucleophilic attack. In this respect they are similar to nitroaryl halides, β-chlorovinyl ketones,[2] and alkoxymethylenemalonic esters.[3] It is not known whether these reactions are concerted or involve an unstable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



I

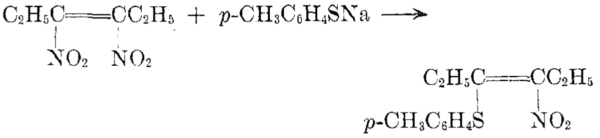
$$\underset{\text{NO}_2}{\text{RC}}{=}\underset{\text{NO}_2}{\text{CR}} + \text{B}^- \longrightarrow \left[\overset{\text{NO}_2}{\underset{\text{B}}{\text{RC}}}-\overset{\ominus}{\underset{\text{NO}_2}{\text{CR}}} \longleftrightarrow \overset{\text{NO}_2}{\underset{\text{B}}{\text{RC}}}-\underset{\text{NO}_2^{\ominus}}{\text{CR}}\right] \longrightarrow \underset{\text{B}}{\text{RC}}{=}\underset{\text{NO}_2}{\text{CR}} + \text{NO}_2^{\ominus}$$

It has previously been shown that dinitroolefins react with amines to form β-aminonitroolefins[4,5] 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.

II

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



$$\underset{\text{NO}_2}{\text{C}_2\text{H}_5\text{C}}{=}\underset{\text{NO}_2}{\text{CC}_2\text{H}_5} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SNa} \longrightarrow \underset{p\text{-CH}_3\text{C}_6\text{H}_4\text{S}}{\text{C}_2\text{H}_5\text{C}}{=}\underset{\text{NO}_2}{\text{CC}_2\text{H}_5}$$

Four pairs of dinitroölefins, 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 aminonitroölefin 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-

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[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. Zeftel, *J. Org. Chem.*, **15**, 1043 (1950).

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

[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).

TABLE I

PREPARATION OF FUROXANS

| Furoxan | Dinitroölefins (Mol.) | Yield, % | B.p., °C. (Mm.) | $n_D^{20}$ | Analysis Calcd. C | Calcd. H | Calcd. N | Found C | Found H | Found N | Infrared Bands$^6$ $\gamma$ Cm.$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,4-Dimethyl$^{10}$ | trans-2,3-Dinitro-2-butene$^5$ (0.05) | 75 | 60–62 (1.3) | 1.4832 | ... | .. | ... | ... | .. | ... | 1616, 1165, 1041, 996, 850 |
| 3,4-Diethyl | 3,4-Dinitro-3-hexene$^{12}$ (0.03) | 70 | 66–67 (0.1) | 1.4775 | 50.68 | 7.09 | 19.71 | 51.19 | 7.23 | 19.98 | 1600, 1142. 1037, 955, 843 |
| 3-Propyl-4-methyl | 2,3-Dinitro-2-hexene$^5$ (0.04) | 62 | 63–64 (0.15) ) | ... | 50.68 | 7.09 | ... | 50.72 | 7.09 | ... | 1600, 1150. 1015, 977, 847 |

mediate is generated and assumes the more stable, presumably the *trans* configuration.

EXPERIMENTAL[9]

*Preparation of furoxans.* Table I summarizes the data on the preparation of furoxans. All were prepared by exactly the same method which is outlined below for diphenylfuroxan.

*Diphenylfuroxan.* To a suspension of 2 g. (0.03 mole) of sodium azide in a mixture of 90 ml. of ethanol and 10 ml. of methanol was added a solution of 3 g. (0.01 mole) of *cis*-1,2-dinitrostilbene.[13] Gas evolution began immediately and heat was evolved. The solution gradually became orange as reaction continued. After the addition was completed, the mixture was heated under reflux for 1 hr., then poured into water and extracted with ether. After drying, the organic extracts were concentrated and the solid residue was recrystallized from ethanol to yield 2.3 g. (86%) of 3,4-diphenylfuroxan, m.p. 115–117° (lit.[14] m.p. 114–115°).

*Reaction of sodium p-toluenethiolate with 3,4-Dinitro-3-hexene.* A solution of 6.2 g. (0.05 mole) of *p*-toluenethiol in 50 ml. of absolute ethanol was added to a solution of 1.2 g. (0.05 g. atom) of sodium in 50 ml. of absolute ethanol. The resulting solution was cooled to 10–20° and 8.7 g. (0.05 mole) of either *cis* or *trans*-3,4-dinitro-3-hexene[5] in 25 ml. of ethanol was added slowly. An immediate precipitation of sodium nitrite occurred. The mixture was allowed to stand at room temperature for 30 min. It was then filtered, poured into water, and extracted with ether. The ether extracts were washed thoroughly with 10% sodium hydroxide solution, dried, and concentrated. There was obtained 10 g. (80%) of a yellow oil, whose infrared spectrum indicated it to be the desired nitroölefin derivative.

The oil was heated under reflux with 45 ml. of 30% hydrogen peroxide in 150 ml. of glacial acetic acid for 1 hr. The product, 3-*p*-toluenesulfonyl-4-nitro-3-hexene, was isolated in the usual manner and upon several recrystallizations from benzene-petroleum ether (30–60°) melted at 100–101.5°; yield 5 g. (55%).

*Anal.* Calcd. for $C_{13}H_{17}NO_4S$: C, 55.10; H, 6.05; N, 4.94. Found: C, 55.02; H, 6.29; N, 4.77.

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[9] We are indebted to Dr. Keith S. McCallum for infrared interpretations.

[10] This infrared spectrum of this material was identical with that of authentic material (generously supplied by Dr. C. O. Parker) prepared by the action of dinitrogen tetroxide on dimethylglyoxime.[11]

[11] R. Scholl, *Ber.*, **23**, 3490 (1890).

[12] L. E. Bisgrove, J. F. Brown, and L. B. Clapp, *Org. Syntheses*, in press. We are indebted to Dr. Clapp for a preprint of this preparation.

[13] K. N. Campbell, J. S. Shavel, and B. K. Campbell, *J. Chem. Soc., Am.* **75**, 2400 (1953).

[14] E. Beckmann, *Ber.*, **22**, 1588 (1889).

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# Substituted Acrylonitriles from Heterocyclic Aldehydes and 3,4-Dimethoxyphenylacetonitrile

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In the course of studies in these laboratories a series of nine substituted acrylonitriles has been prepared by the condensation of heterocyclic aldehydes with 3,4-dimethoxyphenylacetonitrile. Two of these acrylonitriles (see Table I) have since been reported by Castle and Seese.[1] All of the compounds were screened as candidate hypotensive agents and were found to be inactive.

EXPERIMENTAL

The heterocyclic aldehydes used were all commercially available except julolidine-9-carboxaldehyde which was prepared by the method of Smith and Yu.[2]

*α-3,4-Dimethoxyphenyl-β-(3-pyridyl)acrylonitrile.* To a solution of 1.8 g. (0.01 mole) of 3,4-dimethoxyphenylacetonitrile and 1.1 g. (0.01 mole) of pyridine-3-aldehyde in 50 ml. of absolute ethanol was added 0.1 g. of potassium hydroxide. The solution was heated on the steam bath for 1 hr., then diluted with 25 ml. of water and chilled in an ice bath. The yellow crystals which appeared were filtered, washed with 15 ml. of 50% (vol.) ethanol, and recrystallized from 35 ml. of Methyl Cellosolve.

This procedure was followed in preparing the 2-quinolyl, 4-quinolyl, 3-isoquinolyl, 2-thienyl, and 2-furyl derivatives using the appropriate heterocyclic aldehyde. The 2-furyl derivative was recrystallized from 80% ethanol.

*α-3,4-Dimethoxyphenyl-β-(4-pyridyl)acrylonitrile.* A solution of 1.8 g. (0.01 mole) of 3,4-dimethoxyphenylacetonitrile and 1.1 g. (0.01 mole) of pyridine-4-aldehyde in 25 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride. The mixture was allowed to remain at room temperature for 2 days. It was then poured onto ice and the re-

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[1] R. N. Castle and W. S. Seese, *J. Org. Chem.*, **20**, 987 (1955).

[2] P. A. S. Smith and T. Y. Yu, *J. Org. Chem.*, **17**, 1281 (1952).