ARYLDINITROMETHOXYMETHANES

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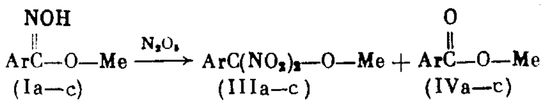
Aryldinitromethoxymethanes have been obtained for the first time by the nitration of methyl benzhydroximates by N_2O_5. Nitration of the aromatic ring in these products was carried out.

In contrast to the thoroughly studied ethers and esters of β-polynitroalcohols, only a few examples of α-polynitroalcohol ethers and esters have been reported. The methods for the preparation of such compounds are very limited in nature. Thus, ethers of dinitrofluoromethanol are formed upon the reaction of sodium alcoholates with trinitrofluoromethane [1]. α,α-Dinitrobenzyl benzoates are obtained upon the nitration of symmetric dibenzoyl hydrazine derivatives [2], while 2,2-dinitro-5-chloromethyltetrahydrofuran was obtained by treating 5,5,5-trinitro-1-chloro-2-pentanol with bases [3].

Since ketoximes and hydroxamoyl chlorides are capable of undergoing nitration to the corresponding gem-dinitro derivatives, we attempted to develop a new synthesis of ethers of α,α-dinitroalcohols by the nitration of esters of hydroximic acids. In order to check this hypothesis, we studied the nitration of methyl benzhydroximates (Ia)-(Ic) and methyl acetylhydroximate (II). The expected aryldinitromethoxymethanes (IIIa)-(IIIc) were indeed formed upon the nitration of (Ia)-(Ic) by N_2O_5 in chloroform. As in the case of oximes, deoximation occurs along with nitration, leading in this case to the formation of methyl benzoates (IVa)-(IVc). The yields of the products of nitration and deoximation are comparable (see Table 1) and together vary in the range from 68 to 73%.



$$\underset{(Ia\text{—}c)}{Ar\overset{\overset{NOH}{\|}}{C}\text{—}O\text{—}Me} \xrightarrow{N_2O_5} \underset{(IIIa\text{—}c)}{ArC(NO_2)_2\text{—}O\text{—}Me} + \underset{(IVa\text{—}c)}{Ar\overset{\overset{O}{\|}}{C}\text{—}O\text{—}Me}$$

Ar = C_6H_5 (a), p-NO_2—C_6H_4 (b), m-NO_2—C_6H_4 (c).

TABLE 1. Yields of the Products of the Nitration of Methyl Benzhydroximates (Ia)-(Ic) and Properties of Aryldinitromethoxymethanes (IIIa)-(IIIc)

Compound	Yield of $\frac{III}{IV}$, %	(III a-c)					
		Mp, °C (Bp, °C)	Found/Calculated, %			IR spectrum, ν, cm^{-1} (NO_2)	PMR spectrum CCl_4, δ, ppm
			C	H	N		
(III a)	$\frac{38}{30}$	(100/1 mm)*	$\frac{45,14}{45,29}$	$\frac{3,92}{3,80}$	$\frac{13,37}{13,21}$	1580 1320	3,87 s (MeO), 7,25–7,75 m (arom CH)
(III b)	$\frac{41}{29}$	77–78	$\frac{37,01}{37,35}$	$\frac{2,74}{2,72}$	$\frac{16,14}{16,34}$	1580 1510 1360 1320	4,0 s (MeO), 7,75–8,49 m (arom CH)
(III c)	$\frac{47}{26}$	52–53	$\frac{37,77}{37,35}$	$\frac{2,89}{2,72}$	$\frac{16,56}{16,34}$	1580 1510 1360 1320	4,03 s (MeO), 7,52–8,70 m (arom CH)

*n_D^{20} 1.5233.

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Previously unreported aryldinitromethoxymethanes are stable compounds. In particular, (IIIa) distills in vacuum without any signs of decomposition at 100°C. The dinitromethoxymethyl group is relatively stable to the action of electrophilic reagents, which permits the use of these compounds in subsequent transformations. Thus, (IIIa) was nitrated by BF_4NO_2 to give (IIIc). On the other hand, we should note that only (IVc) with a trace of (IVa) could be isolated when a nitrating mixture of nitric and sulfuric acids, concentrated nitric acid, or a mixture of HNO_3 and $(CF_3CO)_2O$ were used as the nitrating reagents.

$$\text{(IIIc)} \xleftarrow[\text{MeCN}]{BF_4NO_2} \text{(IIIa)} \xrightarrow{HNO_3/H_2SO_4} \text{(IVc)} + \text{(IVa)}$$

Methyl benzoate (IVa) is also formed in high yield upon treating (IIIa) with concentrated sulfuric acid at 0°C.

In contrast to (Ia)-(Ic), we were unable to nitrate (II) to the corresponding dinitro derivative.

EXPERIMENTAL

The PMR spectra were taken in $CDCl_3$ or CCl_4 on a Tesla BS-467 spectrometer at 60 MHz relative to HMDS. The IR spectra were taken either in KBr pellets for crystalline compounds or neat for liquid compounds on a Specord IR spectrometer. The pure products were isolated by thin-layer chromatography on Silpearl silica gel with a luminophore. Methyl hydroximates (Ia)-(Ic) and (II) were obtained by the reactions of the corresponding hydroxamoyl chlorides [4, 5] with NaOMe in methanol [6]; (Ic) was synthesized for the first time.

Methyl m-Nitrobenzhydroximate (Ic). A solution of 0.3 g (1.5 mmoles) m-nitrobenzhydroxamoyl chloride [4] in 2 ml absolute methanol was added to a solution, prepared from 0.17 g (7.4 mmoles) sodium in 3 ml absolute methanol, at 20°C. The reaction mass was stirred for 10 min at 20°C and then diluted with 20 ml water. A stream of CO_2 was introduced until the pH was brought to 7. The mixture was extracted with 20 ml chloroform, washed with 5 ml water, dried over Na_2SO_4, and evaporated. Preparative thin-layer chromatography using 9:1 benzene–acetone gave 0.19 g (65%) (Ic), mp 90-92°C. IR spectrum (ν, cm^{-1}): 3300 (OH), 1650 (C=N), 1530, 1370, 730 (arom. NO_2). PMR spectrum in $CDCl_3$ (δ, ppm): 4.07 s (CH_3, 3H), 7.35-8.55 m (arom. CH, 4H). Found, %: C 49.10; H 4.30; N 14.00. $C_8H_8N_2O_4$. Calculated, %: C 48.98; H 4.11; N 14.28.

Nitration of Methyl Benzhydroximates (Ia)-(Ic). A sample of 5 g P_2O_5 was added to a solution of 2.5 ml HNO_3 (d 1.5) in 20 ml chloroform at −20°C, stirred for 10 min at −20°C, and filtered. The solution of N_2O_5 obtained was heated to 50°C and a solution of 6.6 moles oxime (Ia)-(Ic) in 10 ml chloroform was added. The reaction mixture was stirred for 10 min at 50°C, poured onto ~30 g ice, extracted with 50 ml chloroform, washed with 15 ml water, dried over Na_2SO_4, and evaporated in vacuum. Separation of the nitration and deoximation products was carried out by preparative thin-layer chromatography with benzene as the eluent. The yields and properties of products (IIIa)-(IIIc) are given in Table 1. Products (IVa)-(IVc) were identified by comparison with authentic samples.

Nitration of Phenyldinitromethoxymethane (IIIa). a. A solution of 0.16 g (0.8 mmole) (IIIa) in 3 ml absolute acetonitrile was added to a solution of 0.13 g (1 mmole) BF_4NO_2 in 5 ml absolute acetonitrile at 0°C, stirred for 3.5 h at 0-5°C, poured onto ~10 g ice, extracted with 10 ml chloroform, washed with 3 ml water, dried over Na_2SO_4, and evaporated in vacuum. Preparative thin-layer chromatography with benzene as the eluent gave 0.06 g (38%) (IIIc), which was identical to the sample described above.

b. A sample of 0.36 g (IIIa) was added to a nitrating mixture, obtained by mixing 0.25 ml concentrated sulfuric acid and 0.35 ml nitric acid (d 1.5) at 0°C. The reaction mixture was stirred for 10 min at 0°C, diluted with 2 ml ice water, dried over Na_2SO_4, and evaporated in vacuum. Preparative thin-layer chromatography with benzene as the eluent gave 0.14 g (47%) (IVc) and 0.02 g (9%) (IVa).

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NEW COMPLEX OF MOLYBDENUM WITH DIISOOCTYLDITHIOCARBAMINE LIGANDS

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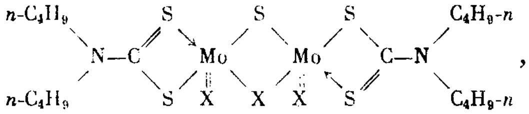
A new molybdenum(VI) complex with diisooctyldithiocarbamine ligands was synthesized by the reaction of MoO_3, di(2-ethylhexyl)amine, and CS_2 in dimethylformamide. A structure for this complex was proposed on the basis of its elemental analysis, ebullioscopic molecular mass determination, and ESR and IR spectral data.

Molybdenum complexes with dialkyldithiocarbamine ligands are used as polyfunctional supplements to lubricants [1] and olefin epoxidation catalysts [2]. Such complexes are often used as model compounds in the study of the activity of various enzymes such as nitrogenases [3].

In previous work [4], we synthesized molybdenum(V) complexes containing di-n-butyldithiocarbamine ligands. These complexes are crystalline compounds with binuclear structure, containing different numbers of sulfur or oxygen atoms in the chelate unit depending on the synthesis conditions:



where X = O or S.

The complexes synthesized have less than 1% solubility in hydrocarbon solvents at 25°C. This circumstance complicates their study and practical application. In order to increase the solubility of these molybdenum complexes, the synthesis was carried out using a secondary amine with a longer hydrocarbon chain, namely, di(2-ethylhexyl)amine.

A molybdenum complex soluble in DMF is formed upon the reaction of these components. This compound was isolated from the reaction mixture by extraction with hexane and, after removal of the solvent, purified by liquid chromatography on silica gel. This complex is a dark blue, viscous, tarry liquid with good solubility in hydrocarbon solvents. A thermogravimetric study showed that the onset of the decomposition of this complex is 185°C. The lack of ESR signals indicates that this compound is diamagnetic. This result and the stability of the complex in the air suggest that the oxidation state of molybdenum is +6.

This molybdenum complex was characterized spectroscopically. A UV band is found at 585 nm [$\varepsilon = 1.9 \cdot 10^3$ liters/(mole·cm)], which, according to Jowitt and Mitchell [5], is indirect evidence for mononuclear molybdenum complexes with dithiocarbamine ligands. The IR bands for this complex are given in Table 1, which, for comparison, also features the bands found for molybdenum complexes with n-butyl groups in the dialkyldithiocarbamine ligand [6].

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