b) The dry finely divided carboxylate salt (0.02 mole) was added portionwise over 2 h to 4.6 g of (I) at 40°. The mixture was kept at this temperature for 1.5 h, cooled, and poured into 30 ml of ice-water. The 2-fluoro-2,2-dinitroethyl ester was separated, dried with $MgSO_4$, and distilled at 0.1 mm. Yields: 3.2 g (85%) of 2-fluoro-2, 2-dinitroethyl acetate from sodium acetate; 2.4 g (60%) of 2-fluoro-2,2-dinitroethyl acrylate from potassium acrylate; and 1.6 g (80%) of 2-fluoro-2,2-dinitroethyl formate from potassium formate. The characteristics of the esters agreed with the data in [2].

CONCLUSIONS

The reaction of carboxylic acid anhydrides, acid halides, esters and salts with 2-fluoro-2, 2-dinitroethyl sulfuric acid is a general method for preparing esters of 2-fluoro-2,2-dinitroethanol.

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CONVERSION OF PRIMARY NITRAMINES TO ALKYL NITRATES BY REACTION WITH NITRYL FLUORIDE

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UDC 542.91: 547.416

In [1] we described the preparation of alkylene dinitrates by reaction of alkali-metal salts of primary N, N'-dinitramines with FNO_2. We have now found that this reaction is a general one and does not require the conversion of the nitramines into salts

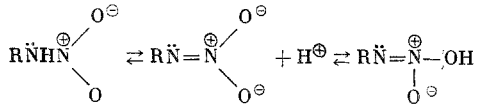
$$\left.\begin{matrix} RNHNO_2 \\ [RNNO_2]^{\ominus} M^{\oplus} \end{matrix}\right] \xrightarrow{FNO_2} RONO_2 + N_2O + F^{\ominus}(HF)$$

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, $FC(NO_2)_2CH_2$, $FC(NO_2)_2CH_2CH_2$

$$\left.\begin{matrix} (CH_2)_n[NHNO_2]_2 \\ (CH_2)_n[NNO_2^{\ominus}]_2 M^{\oplus} \end{matrix}\right] \xrightarrow{FNO_2} (CH_2)_n[ONO_2]_2 + 2N_2O + 2F^{\ominus}(2HF)$$

$n = 1, 6$

As can be seen from Table 1, the alkyl- and alkylenenitramine salts give higher yields of the nitrates than the nitramines themselves. In the case of nitroalkylnitramines, the nitrate yield is practically independent of the form of nitramine used. We think that this difference in chemical behavior is due to the higher acidity of the nitroalkylnitramines. Nitrates can also be prepared starting from amines, using the corresponding amount of FNO_2. The nitramines first formed by reaction with the excess FNO_2 are subsequently converted into nitrates. This method can be used to prepare, e. g., ethyl, n-butyl, and 2-fluoro-2, 2-dinitroethyl nitrate. To stop the reaction at the formation of primary nitramines [9], low-nucleophilicity or nonpolar solvents such as alkanes should be used, and the reaction should be performed in the presence of excess amine. Nitramines hardly react with FNO_2 in nonpolar solvents at < 0°C. On the basis of the foregoing, we can suppose that primary nitramines react with FNO_2 in the form of isonitramines or their anions. It is known that the negative charge in nitramine anions is localized practically entirely on the oxygen atoms of the nitro group [10]



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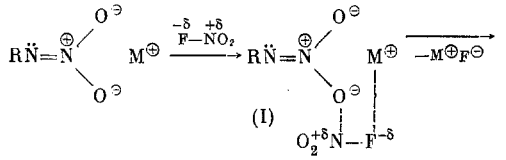
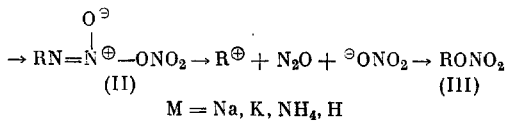
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 383-386, February, 1977. Original article submitted December 23, 1975.

TABLE 1. Reaction Products of Primary N-Nitramines and Their Salts with FNO_2

Starting material	Reaction product	Yield, % from salt	Yield, % from nitramine	bp, °C (p, torr)	n_D^{20}	Lit. data
CH_3NHNO_2	CH_3ONO_2	55	31	65 (760)	1,3753	[2]
$C_2H_5NHNO_2$	$C_2H_5ONO_2$	57	43	89 (760)	1,3852	[3, 4]
$C_3H_7NHNO_2$	$C_3H_7ONO_2$	56	37	52 (60)	1,3971	[4]
$C_4H_9NHNO_2$	$C_4H_9ONO_2$	61	39	64 (80)	1,4059	[5]
$CH_2(NHNO_2)_2$	$CH_2(ONO_2)_2$	40	25	68 (15)	1,4307	[6]
$(CH_2)_6(NHNO_2)_2$	$(CH_2)_6(ONO_2)_2$	66	35	105 (0,3)	1,4509	[5]
$FC(NO_2)_2CH_2NHNO_2$	$FC(NO_2)_2CH_2ONO_2$	79	74	53 (3)	1,4370	[7]
$FC(NO_2)_2(CH_2)_2NHNO_2$	$FC(NO_2)_2(CH_2)_2ONO_2$	79	73	22,8–23 (mp)		[8]

The overwhelming majority of alkali-metal nitramine salts are practically insoluble in CH_3CN. The reaction probably proceeds at the interface between the solid salt phase and the FNO_2 solution, and the salt probably reacts as a tight ion pair. Bearing this in mind, we can visualize a reaction mechanism involving a transition-state complex (I) in which a hard Lewis acid (the metal cation) is opposed to a negatively polarized fluorine atom displaced from the FNO_2 molecule in the form of a fluoride ion, i. e., a hard Lewis base. The reaction of hard acids with hard bases is thermodynamically favorable owing to the high stability of the resulting salts [11]

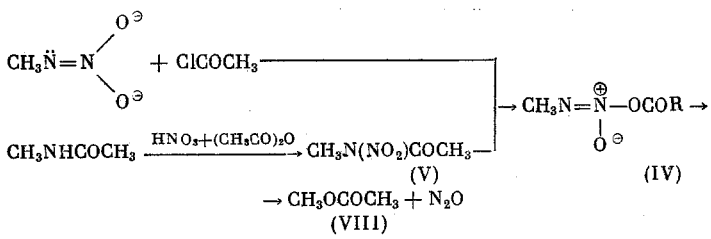




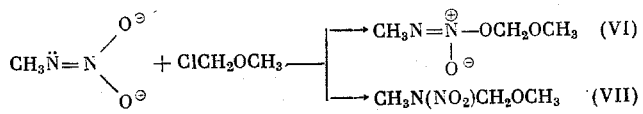
M = Na, K, NH_4, H

The reaction results in the formation of the O-nitration product, i. e., an azoxy nitrate (II). This decomposes like diazo compounds [12] to form N_2O, a nitrate anion, and a carbonium ion, and reaction of the latter two species gives the alkyl nitrate molecule. It is logical to assume that this mechanism also occurs in the reaction of FNO_2 with nitramines. It is known that nitramines readily isomerize to isonitramines [13] having a pronounced acid character. In this case, the fluorine atom in the transition-state complex is opposed to a hydrogen atom cleaved off in the form of a proton.

Our attempts to isolate the intermediate azoxy nitrate (II) were unsuccessful owing to its instability. It is known, however, that azoxy esters of this type are formed in reactions between carbonyl chlorides and nitramine salts and by thermolysis of nitramides [14], in the course of which they split off N_2O and are converted into esters. We prepared N-methylazoxy acetate (IV), which has not been described before, by reacting AcCl with the K salt of methylnitramine. The isomer of compound (IV), viz., N-methyl-nitracetamide (V), was prepared by nitrating N-methylacetamide at low temperature. On heating it is readily converted to (IV), so low-temperature vacuum distillation was used to purify (V)



In [15], azoxy ethers (VI) were prepared, together with alkoxymethylnitramines (VII), by reacting nitramine salts with α-chloromethyl ethers



On reacting (IV) and (VI) with FNO_2, we ascertained that both reactions result in the release of N_2O and the formation of methyl acetate (VIII) (66%) or dimethyl formal (IX) (53.4%). In the latter case, methylene dinitrate (X) is also formed (31.2%). Thus, azoxy esters and ethers are not actually nitrated by FNO_2 but undergo dissociation. Neither does N-methyl-nitracetamide (V) react with FNO_2; it is recovered quantitatively from the reaction. The results obtained can be regarded as evidence in favor of the fact that azoxy nitrates are involved in the reaction of nitramines and their alkali-metal salts with FNO_2.

EXPERIMENTAL

N-Methylazoxy-formal (VI). This was prepared as described in [15] by reacting the Na salt of methylnitramine with $ClCH_2OCH_3$.

N-Methylazoxy Acetate (IV). Freshly distilled AcCl (6.8 g) was added over 15 min at −25° to a stirred suspension of 10 g of the K salt of methylnitramine in 45 ml of abs. CH_3CN. The mixture was stirred for one more h at − 25° and for 6 h at 40-45°. The KCl was filtered off and washed with 10 ml of abs. CH_3CN. Yield 6.53 g (99.9%). After distilling off the CH_3CN under vacuum, the residue was distilled twice to give 3.09 g (30%) of (IV) in the form of a colorless liquid with a bp of 46-47° (15 torr), $n_D^{20} = 1.4512$. Found: C 30.8; H 5.12; N 23.5%. $C_3H_6N_2O_3$. Calculated: C 30.5; H 5.08; N 23.7%. Fundamental IR frequencies (ν, cm^{-1}): 765 (N—O), 1280 (s, N—O), 1460 (as, N—O), 1603 (N = N), 1035 (C—O), 1725 (C = 0).

N-Methylnitracetamide (V). A mixture of 18 g N-methylacetamide and 49 ml Ac_2O was treated at 2-5° over 25 min with 40.5 ml HNO_3 ($d_4^{20} = 1.5$), stirred at 5° for 30 min and at 18-20° for 3 h, and then poured into 800 ml of ice-water. The aqueous solution was extracted with CH_2Cl_2 (2 × 100 ml) and dried over $MgSO_4$. After distilling off the CH_2Cl_2, the residue was distilled twice to give 18.6 g (64.1%) of N-methylnitracetamide, bp 20-21° [1.5 torr], $n_D^{20} = 1.4674$. Found: C 30.62; H 5.24; N 23.61%. $C_3H_6N_2O_3$. Calculated: C 30.5; H 5.08; N 23.7%.

Reaction of N-Methylazoxy Acetate (IV) with FNO_2. Nitryl fluoride (3 g) was passed into a solution of 5.7 g of (IV) in 40 ml of abs. CH_3CN at −25° over 12 min. The mixture was stirred at −5 to −8° for 40 min and poured into 300 ml of ice-water. Ether extraction (1 × 110 ml) gave 2.38 g (66.6%) of methyl acetate, bp 57°/760 torr, $n_D^{20} = 1.3592$.

Reaction of N-Methylnitracetamide (V) with FNO_2. Nitryl fluoride (3 g) was passed through a solution of 5 g of (V) in 40 ml of abs. CH_3CN at −25° over 15 min. The mixture was stirred at −10° for 10 min and poured into 200 ml of ice-water. The oil phase was extracted with CH_2Cl_2 (2 × 80 ml) to give 4.56 g (91%) of N-methylnitracetamide, bp 20-21° (1.5 torr), $n_D^{20} = 1.4675$.

Reaction of N-Methylazoxy-formal (VI) with FNO_2. Nitryl fluoride (4.2 g) was passed through an intensively stirred solution of 2.8 g of (VI) in 30 ml of abs. CH_3CN at −20° over 15 min. The mixture was stirred at −5° for 25 min and poured into 250 ml of ice-water. The oil phase was extracted with dichloroethane (2 × 50 ml) to give 0.95 g (53.4%) of dimethyl formal, bp 42-44°, $n_D^{20} = 1.3534$. The dichloroethane was distilled off and the residue distilled under vacuum to give 1.02 g (31.6%) of methylene glycol dinitrate (X), bp 70-71° (18 torr), $n_D^{20} = 1.4305$ (see [10]).

The alkyl- and nitroalkyl-N-nitramines were reacted in the form of their ammonium salts, and the alkylene-N, N'-dinitramines were reacted in the form of their Na salts. Typical nitration methods are given below.

Ethyl Nitrate. a) A sample (4.3 g) of vacuum-dried ethyl-N-nitramine ammonium salt and 50 ml of abs. CH_3CN were placed in a four-necked flask equipped with a sealed stirrer, a gas inlet tube, a thermometer, and a gas outlet connected to a gas buret for sampling the gaseous reaction products. Nitryl fluoride (2.6 g) was passed through the stirred suspension at −20 to −15° over 15 min. The mixture was stirred for a further 20 min at −15 to −10°. The precipitated NH_4F was filtered off, and filtrate poured into 200 ml of ice-water, and the oil phase extracted with CH_2Cl_2 (3 × 40 ml). The combined extracts were dried over $MgSO_4$, the solvent distilled off, and the residue distilled twice to give 2.1 g (57.1%) of ethyl nitrate, bp 89° (760 torr), $n_D^{20} = 1.3852$. The yield of NH_4F was 99%.

b) Nitryl fluoride (2.6 g) was passed through a stirred solution of 3.6 g ethyl-N-nitramine in 25 ml of abs. CH_3CN at −15 to −10° over 15 min. The mixture was stirred for a further 30 min at −10 to −5°, poured into 150 ml of ice-water, and extracted with CH_2Cl_2 (3 × 25 ml). Normal working up gave 1.56 g (43.1%) of ethyl nitrate.

c) Nitryl fluoride (10 g) was passed through a stirred solution of 4.4 g ethylamine in 50 ml of abs. CH_3CN at −20 to −15° over 25 min. The mixture was kept at −10 to −5° for 30 min and then poured onto ice. Normal working up gave 1.46 g (40.3%) of ethyl nitrate.

CONCLUSIONS

1. The conversion of primary nitramine anions into alkyl nitrates with the same number of carbon atoms by reaction with nitryl fluoride is found to be a general reaction.

2. Both amines and nitramines and their salts can participate in the reaction, which takes place in nucleophilic solvents.

3. A reaction mechanism is proposed, involving azoxy nitrates formed by O-nitration of ambidentate nitramine anions. Azoxy ethers and esters are not nitrated by nitryl fluoride, but dissociate to form ethers or esters and nitrous oxide.

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REACTION OF ACYL ISOCYANATES WITH DISUBSTITUTED AMIDES AND AN INVESTIGATION OF HINDERED INTERNAL ROTATION IN AMIDINE MOLECULES

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UDC 542.91: 547.298.1: 547.239.1

Continuing our study of the reaction of acyl isocyanates with disubstituted amides, we have studied the reactions of trifluoroacetyl isocyanate (I) with DMF, dimethylacetamide (DMA), and dimethylbenzamide (DMB), and also the reaction of DMA with trichloroacetyl isocyanate.

The reaction of DMF with (I) proceeds differently from that with benzoyl and trichloroacetyl isocyanate [1]. We were unable to isolate 1-trifluoroacetylformamidine (III) because the (III) formed reacts with the (I) present in the reaction mixture to give an adduct (IV) or (V).

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