CHEMISTRY OF NITRO IMIDES.

1. GENERAL METHOD FOR THE SYNTHESIS OF NITRO IMIDES

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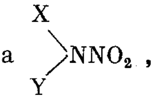
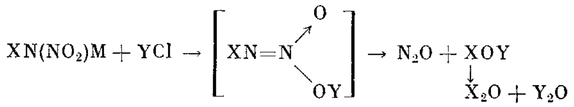
Nitro imides, viz., compounds with the general formula  $\overset{X}{\underset{Y}{>}}NNO_2$, where X and Y = RCO, RSO_2, ROCO, $ArSO_2$, etc., are closely related to triacylamines [1] or triamides [2] and can be regarded as nitrogen analogs of mixed anhydrides of mineral or organic acids. However, in contrast to anhydrides, very little study has been devoted to the chemistry of nitro imides.

The central N atom of nitro imides is bonded to three acid residues. These compounds should have multiple reactivity with respect to nucleophiles in that they act as acylating, sulfonating, or nitrating reagents. A sufficiently extensive assortment of substances and, consequently, a sufficiently general method for their preparation are necessary for a systematic study of the chemistry of nitro imides. The present communication is devoted to the development of a method of this type.

Only a few nitro imides and only two approaches to methods for their preparation have been described. The first method consists in acylation of salts of nitrourethane with ethyl chloroformate:

$$EtOCON(NO_2)K + ClCOOEt \rightarrow \underset{(I)}{(EtOCO)_2NNO_2}$$

We have established that this reaction leads to nitro imides only in exceptional cases. A reproduction of the data in [3] showed that the yield of I in toluene does not exceed 5%. The yield of I was raised to 50% only in MeCN, which is an aprotic dipolar solvent that is capable of solvating the cation and dissolves the nitrourethane salt. In the remaining cases the reaction of K or Ag salts of nitrourethane, nitrobenzamide, or p-toluenesulfonitramide with ethyl chloroformate and acetyl, bezoyl, and p-toluenesulfoyl chlorides, leads only to mixed anhydrides of the acids, which are evidently formed in the decomposition of the primary products of O-acylation of the nitro amides:

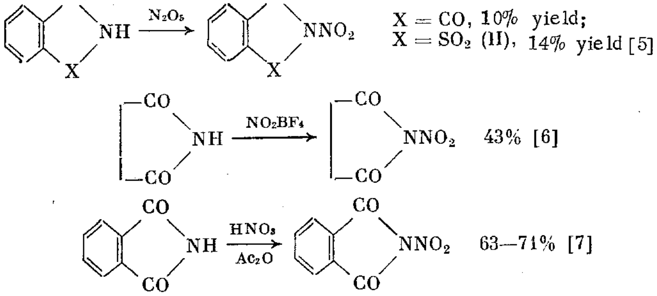


$XN(NO_2)M + YCl \rightarrow [XN{=}N(\rightarrow O)OY] \rightarrow N_2O + XOY$; $XOY \rightarrow X_2O + Y_2O$

M = K, Ag; X = Ts, ROCO; Y = Ts, ROCO, RCO.

It should be noted that the Ag salts of phthalimide and succinimide also undergo acylation to give O-acyl derivatives of the imides [4]. Thus, this approach to the preparation of nitro imides is unsuitable.

The second method for the synthesis of nitro imides consists in the nitration of imides:



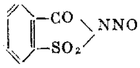
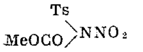
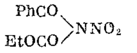
X = CO, 10% yield;
X = SO_2 (II), 14% yield [5]

43% [6]

63–71% [7]

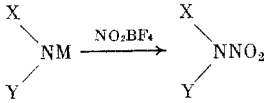
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2087-2090, September, 1981. Original article submitted February 18, 1981.

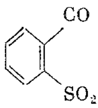
TABLE 1. Synthesis of Nitro Imides by Nitration of Salts of Imides with Nitronium Tetrafluoroborate

Nitro imide	Starting imide salt	Solvent	Yield in nitro-imide, %	mp, °C	N found/N calc., %	Empirical formula	$\nu_{as}(NO_2)$, cm^{-1}
 (II)	NH_4 [8]	MeCN	80	170			1610
 $Ts(MeOCO)NNO_2$ (III)	NH_4 [9]	MeCN	94	33	$\frac{9{,}85}{10{,}22}$	$C_9H_{10}N_2O_6S$	1630
 $PhCO(EtOCO)NNO_2$ (IV)	K [9]	MeCN	91		$\frac{11{,}81}{11{,}76}$	$C_{10}H_{10}N_2O_5$	1610
$(MeSO_2)_2NNO_2$ (V)	K [10]	CH_2Cl_2	100	73	$\frac{12{,}75}{12{,}84}$	$C_2H_6N_2O_6S_2$	1625
$(n\text{-}BuSO_2)_2NNO_2$ (VI)	K [10]	CH_2Cl_3	100	112	$\frac{9{,}61}{9{,}27}$	$C_8H_{18}N_2O_6S_2$	1630
$(PhSO_2)_2NNO_2$ (VII)	Na [10]	CH_2Cl_2	100	68	$\frac{8{,}11}{8{,}18}$	$C_{12}H_{10}N_2O_6S_2$	1625

This method is used only for the preparation of cyclic nitro imides and is evidently more general in character than the first method, although in this case also the yields of nitro imides range from 10% to 70%, most likely because of the instability of the reaction products in strongly acidic media. In this connection, we proposed a method for the synthesis of nitro imides by nitration of the salts of imides rather than the free imides with nitronium salts.

This reaction is a convenient preparative method for the production of nitro imides with various structures in 80-100% yields. We subjected the K, Na, or NH_4 salts of saccharin, N-tosylurethane, N-benzoylurethane, and imides of alkanesulfonic acids to nitration in CH_2Cl_2 or MeCN:



M = K, Na, NH_4; X = Y = RSO_2; X—Y =  ; X = Ts, Y = MeOCO (III);

X = PhCO, Y = EtOCO (IV).

The structures of the synthesized nitro imides (Table 1) were established on the basis of the results of elementary analysis and the IR spectra.

EXPERIMENTAL

Carbethoxynitrourethane (I). A 3-ml sample of ethyl chloroformate was added to a suspension of 5 g of the K salt of nitrourethane in 30 ml of absolute MeCN, and the mixture was refluxed for 6 h. The precipitate was removed by filtration, the filtrate was evaporated, and the residue was distilled to give 3 g (50%) of (I) with bp 98°C (10 mm) (see [3]).

Reaction of the K Salt of Nitrobenzamide with Ethyl Chloroformate. A mixture of 0.4 g of the K salt of nitrobenzamide, 2 ml of chloroethyl formate, and 10 ml of absolute MeCN was refluxed for 16 h, after which it was filtered, and the filtrate was evaporated to give 0.35 g (87%) of the mixed anhydride of benzoic and ethoxyformic acids. IR spectrum (ν, cm^{-1}): 1800 and 1740 (CO) (see [11]).

Reaction of the K Salt of Nitrourethane with Benzoyl Chloride. A mixture of 1 g of the K salt of nitrourethane, 0.7 ml of benzoyl chloride, and 15 ml of absolute MeCN was refluxed for 15 h, after which it was filtered, and the filtrate was evaporated to give 0.88 g (78%) of the mixed anhydride of benzoic and ethoxyformic acids.

Reaction of the Ag Salt of p-Toluenesulfonic Acid with p-Toluenesulfonyl Chloride. A solution of 0.6 g of p-toluenesulfonyl chloride in 5 ml of absolute ether was added at −10°C to a stirred solution of 1 g of the Ag salt in 20 ml of absolute MeCN, and the mixture was maintained at 20°C for 5 days. The precipitated AgCl was removed by filtration, and the filtrate was evaporated to give 0.93 g (92%) of p-toluenesulfonic acid anhydride with mp 123-124°C (see [12]). No melting-point depression was observed for a mixture of this product with a genuine sample.

Reaction of the Ag Salt of p-Toluenesulfonitramide with Acetyl Chloride. A solution of 0.22 ml of acetyl chloride in 3 ml of absolute MeCN was added dropwise to a stirred solution of 1 g of the Ag salt in 20 ml of absolute MeCN, and the mixture was maintained at 20°C for 2 days. The AgCl was removed by filtration, and the filtrate was evaporated to give 0.5 g (99%) of p-toluenesulfonic acid anhydride with mp 121-124°C. No melting-point depression was observed for a mixture of this product with a genuine sample. Acetic anhydride was detected in the filtrate by gas–liquid chromatography (GLC).

Reaction of the Ag Salt of Nitrourethane with p-Toluenesulfonyl Chloride. A solution of 0.8 g of p-toluenesulfonyl chloride in 5 ml of absolute MeCN was added to a stirred solution of 1 g of the nitrourethane salt in 20 ml of absolute MeCN, and the mixture was maintained at 20°C for 2 days. The precipitate was removed by filtration, and the filtrate was evaporated. Ether (10 ml) was added to the residue, and the resulting precipitate was removed by filtration to give 0.48 g (77%) of p-toluenesulfonic acid anhydride with mp 119-123°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

General Method for the Synthesis of Nitro Imides by Nitration of Imide Salts with Nitronium Tetrafluoroborate. An equimolar amount of nitronium tetrafluoroborate was added at −30°C to a stirred suspension of 2 g of the imide salt in 20 ml of the absolute solvent (see Table 1), and the mixture was stirred at this temperature for 20-30 min. The precipitate was removed by filtration, and the filtrate was evaporated. The solid residue was washed with alcohol.* Liquid IV was chromatographed (with Silufol as the adsorbent and benzene as the solvent) (see Table 1).

CONCLUSIONS

1. A general preparative method for the synthesis of nitro imides by nitration of salts of imides with nitronium salts was developed.

2. A number of bifunctional derivatives of nitramide that contain various combinations of carbo, sulfo, and carboxy groups were obtained for the first time.

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* The nitro imides of alkanesulfonic acids require thorough protection from air moisture. The precipitate was washed on the filter with a mixture of hexane with methylene chloride.