## THE CHEMISTRY OF NITROIMIDES.

3. ALKALINE HYDROLYSIS AND ALCOHOLYSIS OF NITROIMIDES AND THEIR REACTIONS WITH AMMONIA, AMINES, AND POTASSIUM IODIDE

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In report [1] it was shown that in the case of the alcoholysis and especially in the case of the hydrolysis of nitroimides, the splitting of the N-NO<sub>2</sub> bond is clearly caused by preliminary protonation. It is natural to postulate that in the case of alkaline hydrolysis and solvolysis, where protonation is ruled out, the tendency for the splitting of the N-NO<sub>2</sub> bond of nitroimides would be diminished. In the present work we shall examine the reactions of nitroimides with KOH in H<sub>2</sub>O, EtOH, and MeCN, as well as with NH<sub>3</sub>, RNH<sub>2</sub>, and KI, i.e., nucleophiles, which also rule out preliminary protonation of nitroimides.

It was found that some nitroimides, viz., N-carbethoxynitrourethane (Ia), nitrophthalimide (Ib), and nitrosuccinimide (Ic), react with OH<sup>-</sup> or OR<sup>-</sup> anions to form products of the nucleophilic attack at the center with the largest  $\delta^+$ , i.e., the carbonate or carbonyl C atom:

 $(EtO_2C)_2NNO_2 \longrightarrow \begin{pmatrix} KOH + H_2O \\ \hline KOH + EtOH & 96\% \\ \hline (Ia) & 86\% \end{pmatrix} EtO_2CNNO_2K$ 

In [2] it was shown that the alkaline hydrolysis of Ib proceeds with the evolution of  $N_2O$  and the formation of phthalic acid. The primary alkaline hydrolysis product, i.e., N-nitrophthalic acid monoamide, could not be isolated.

We showed that the alkaline alcoholysis of Ib also results only in the production of potassium phthalate. The treatment of Ib with KOH in MeCN produced a very hydrolytically unstable compound, which decomposed violently with the evolution of gases and was converted into potassium phthalate during an extraction attempt. This compound is clearly the product of the nucleophilic attack at the CO group, i.e., salt II:



The alkaline hydrolysis and solvolysis of Ic proceeds in a similar manner with the production of the potassium salt of succinic acid.

The direction of the reaction of nitrosaccharin (Id) with KOH is greatly dependent on the nature of the solvent and the nucleophile. For example, the treatment of Id with KOH in  $H_2O$  results in splitting of the N-CO bond. In the IR spectrum of the product formed (III) there are bands at 1580 (CO) and 1410 cm<sup>-1</sup> (NO<sub>2</sub>), which are characteristic of potassium benzoate [1550 cm<sup>-1</sup> (CO)] and salts of aromatic nitrosulfamides [1410 cm<sup>-1</sup> (NO<sub>2</sub>)]:



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2563-2571, November, 1981. Original article submitted February 18, 1981. Upon the transition from the OH<sup>-</sup> anion to the more basic OR<sup>-</sup> anion (the Edwards nucleophilic constant for OH<sup>-</sup> equals 17.48, and that for OR<sup>-</sup> equals 11.24 [3]), a second product of the alkaline alcoholysis of Id, viz., potassium salt V, was discovered in the reaction mixture in addition to dipotassium salt IV [1]. In the IR spectrum of V there are bands at 1720 (CO) and 1410 cm<sup>-1</sup> (NO<sub>2</sub>), which are characteristic of ethyl benzoate [1720 cm<sup>-1</sup> (CO)] and salts of aromatic sulfonylnitroamides. This salt (V) formed when we treated the previously described ethanolysis product of Id [1] with an equimolar quantity of KOH in EtOH:



Thus, the alkaline alcoholysis of Id produces two nucleophilic splitting products:



The treatment of Id with KOH in MeCN results in splitting of the N-SO2 bond:

(Id) 
$$\xrightarrow{\text{KOH}}_{\text{MeOH}}$$
 (IV)  $\overrightarrow{76\%}$ 

Such a direction of the reaction in a solvent capable of solvating the electrophilic centers is clearly attributable to the blocking of the approach of the nucleophilic particle to the highly solvated C atom of the carbonyl group.

In the foregoing reactions the nitro group of the nitroimides was not subjected to nucleophilic attack. However, this law is not general. For example, when N-tosylnitrourethane (Ie) is reacted with KOH, the carbomethoxy group and the nitro group are subjected to nucleophilic attack. We found that upon the transition from the less basic OH<sup>-</sup> ion to the OR<sup>-</sup> ion, the yield of the product of the splitting of the N-NO<sub>2</sub> bond drops

		MeCN	$T_{5}NKNO_2 + 420$	TsNKCO <sub>2</sub> Me
$T_{\alpha}N(NO)COM_{\alpha}$	кон	H <sub>2</sub> O	15 % 26%	74%
(Ie)		EtOH	46%	37%

In the case of the reaction of KOH with benzoylnitrourethane (If), on the other hand, the yield of the product of the splitting of the  $N-NO_2$  bond increases upon the transition from the OH<sup>-</sup> anion to OR<sup>-</sup>:

$$\begin{array}{c} PhCON(NO_2)CO_2Et \xrightarrow{KOH} \middle| \xrightarrow{H_1O} EtO_2CNKNO_2 + EtO_2CNKCOPh \\ \hline (If) & 43\% & 40\% \\ \hline 33\% & 62\% \end{array}$$

The reaction of N-nitromethanesulfonimide (Ig) with water or alcoholic potassium hydroxide results in the elimination of the nitro group:

$$(MeSO_2)_2NNO_2 \xrightarrow{KOH} (MeSO_2)_2NK$$
  
95-99%

The data on the alkaline hydrolysis and solvolysis of the nitroimides are summarized in Table 1.

A comparison of the data on the hydrolysis of the nitroimides and their reactions with the OH<sup>-</sup> anion as well as the alcoholysis of the nitroimides and their reactions with the OR<sup>-</sup> anion reveals that the tendency of the anions to undergo elimination of the NO<sub>2</sub> group decreases.

	Nucleophilic attack at functional group (yield of final reaction product, %)								
Nitroimide	KOH+H <sub>2</sub> O		KOH+MeCN			KOH+Et+OH			
	CO	SO2	NO2	co	S02	$NO_2$	CO	<i>s</i> 0₂	NO2
$(EtO_2C)_2NNO_2$ (Ia)	96						86		
CO NNO <sub>2</sub> (Ib)	65			68			77		
	98				-		98 `	· · ·	
CO $NNO_2(Id)$ $SO_2$	64				76		58	20	
$TsN(NO_2)CO_2Me$ (Ie)	26		74	13		86	46		36
PhCON (NO <sub>2</sub> ) CO <sub>2</sub> Et (If)	43		40				33		62
$(MeSO_2)_2NNO_2$ (Ig)			99	l			l		95

# TABLE 1. Interaction of Nitroimides with KOH

Alkaline hydrolysis and alcoholysis affect several electrophilic centers in nitroimides. This may be attributed to the increased activity of the OH<sup>-</sup> and OR<sup>-</sup> anions. Attention should be focused on the fact that nitroimides which contain a sulfonyl residue display a greater tendency to undergo elimination of the NO<sub>2</sub> group in reactions with OH<sup>-</sup> or OR<sup>-</sup> ions. The nitroimides which contain two sulfonyl residues undergo splitting exclusively at the N-NO<sub>2</sub> bond.

In the case of the ammonolysis or aminolysis of nitroimides, preliminary protonation is also ruled out. It may be expected that the nucleophilic attack should be directed at the center with the largest  $\delta^+$ .

In fact, such a direction of the reaction is realized in the case of the aminolysis of all the nitroimides investigated (Ia-Ig). The reaction of Ia with NH<sub>3</sub> or with morpholine results in the synthesis of nitrourethane salts:



The ammonolysis of Ib results in the formation of VI, whose IR spectrum contains bands at 1670, 1620 (CO), and 1410 cm<sup>-1</sup> (NO<sub>2</sub>). A comparison of the IR spectra of VI, a nitrobenzamide salt [1640 (CO) and 1410 cm<sup>-1</sup> (NO<sub>2</sub>)], and benzamide [1670 cm<sup>-1</sup> (CO)], as well as the conversion of VI upon contact with atmospheric moisture in phthalimide, allow us to assign it the following structure:



The treatment of Ib with morpholine produces salt VII, which is converted by acidification into nitroamide VIII. In the IR spectrum of VIII there are bands at 1730 (CO) and 1630 cm<sup>-1</sup> (NO<sub>2</sub>), which are characteristic of nitrobenzamide:



The ammonolysis of nitrosuccinimide (Ic) also proceeds with opening of the imide ring; however, the primary reaction product could not be isolated in this case. It is noteworthy that the compounds which have a nitramine grouping on an aliphatic acyl residue are often unstable. Thus, N-nitroacetamide cannot be recovered in the individual state [4]. The ammonolysis of Ic proceeds with the formation of a salt of succinamic acid, which is converted by heating into succinimide



The ammonolysis of nitrosaccharin (Id) takes place with splitting of the N-CO bond of the imide ring. In the IR spectrum of IX there are bands at 1670 and 1620 (CO) and 1460 cm<sup>-1</sup> (NO<sub>2</sub>). A comparison of the IR spectrum of IX, benzamide, and the ammonium salt of p-toluene-sulfonylnitramide, as well as the data from the elemental analysis of IX, allow us to assign the following structure to it:



The reaction of Id with morpholine or tert-butylamine also takes place with splitting of the N-CO bond. In the IR spectra of X and XI there are bands which are characteristic of salts of aromatic sulfonitramides (1440 and 1435 cm<sup>-1</sup>).



The reactions of Ie with  $NH_3$  and morpholine produce, respectively, the ammonium salt of p-toluenesulfonylnitramide and urethane and N-carbomethoxymorpholine and the morpholine salt of p-toluenesulfonylnitramide, which is converted into the potassium salt by treatment with alcoholic potassium hydroxide:



Thus, in this case, too, the nucleophilic attack is directed at the carbalkoxy group.

The influence of the polarity of the solvent on the direction of the splitting of nitroimides was studied in the example of the ammonolysis of Ie. The ratio of the splitting products was determined from the PMR spectra (Table 2).

From Table 2 it follows that the relative activity of the carbonate and sulfonic centers

TABLE 2. Influence of the Polarity of Solvents on the Ratio of the Ammonolysis Products of Ie $Ie \xrightarrow{NH^3}T_{SN}(NH_4)NO_2 + MeO_2CN(NH_4)NO_2 + T_{SNH_2} + MeO_2CNH_2$				
Solvent	Dipole mo- ment, D [3]	[TsNH <sub>2</sub> ]/ [MeO <sub>2</sub> CNH <sub>2</sub> ] ratio		
C <sub>6</sub> H <sub>6</sub> Et <sub>2</sub> O CH <sub>2</sub> Cl <sub>2</sub> EtOH MeCN	0,31 1,15 1,24 1,66 3,44	Only MeO <sub>2</sub> CNH <sub>2</sub> Same 1:12,5 1:3,2 1:2,4		

2,69

1:1,15

TABLE 3. Aminolysis of Nitroimides

Me<sub>2</sub>CO

Nitro <b>-</b> imide	Nucleophile	Solvent	Direction of attack on functional group (yield of final amino- lysis products, %)		
			CO	SO <sub>2</sub>	
	[		1	1	
(Ia)	NH3	MeCN	99		
(Ib)	NH3	Same	87		
(Id)	HNO	»	97		
	NH <sub>3</sub>	»	99		
	HNOO	»	94		
	t-BuNH <sub>2</sub>	»	90		
(Ie)	NH3	$Et_2O$	92		
	ны	Same	82		
(If)	$\rm NH_3$	»	95		
(Ig)	HNOO	»	86		
	NH <sub>3</sub>	$\mathrm{CH}_{2}\mathrm{Cl}_{2}$		100	
(Ih)	HNO	$\rm CH_2 Cl_2$		97	
	$\rm NH_3$	MeCN	ļ	400	

of the nitroimide in the reaction with  $NH_3$  gradually become equal as the polarity of the solvent is increased. In our opinion, the reason for this is the blocking of the highly solvated carbonate C atom upon the transition to more polar solvents and the greater accessibility of the less solvated S atom to the nucleophile. It was specially shown by TLC on Silufol that a product of the elimination of the  $NO_2$  group (a salt of N-tosylurethane) is not formed in any of the cases of the ammonolysis of Ie.

In the case of the ammonolysis of N-benzoylnitrourethane (If), the N-COPh bond is split to form benzamide and the salt of nitrourethane. The reaction of If with morpholine proceeds in a similar manner:



The ammonolysis of N-nitromethenesulfonimide (Ig) and N-nitrobenzenesulfonimide (Ih) proceeds with splitting of the N\_SO<sub>2</sub> bond:



The data on the aminolysis of the nitroimides are presented in Table 3.

Thus, splitting of the N-NO<sub>2</sub> bond is not characteristic of the aminolysis of nitroimides. The decisive factors in aminolysis are the attack at the most electron-deficient center of the nitroimide and the formation of the thermodynamically most stable anion. The anions of the nitroamides, i.e., the leaving groups in the case of the aminolysis of nitroimides, may be arranged in the following series in order of decreasing thermodynamic stability [5]:  $RSO_2NNO_2^- > ROOCNNO_2^- > PhCONNO_2^-$ .

A comparison of the data on the aminolysis of nitroimides and the reactions with the OH<sup>-</sup> or OR<sup>-</sup> anion reveals that the direction of the nucleophilic splitting is determined not only by the basicity of the nucleophile, but also by its nature. How the direction of splitting of a nitroimide will vary upon transition from a more basic nucleophile to a less basic nucleophile or from a "hard" to "soft" nucleophile cannot be predicted a priori. It may be postulated that the I<sup>-</sup> anion, which is less basic and more polarizable than NH<sub>3</sub> or the OH<sup>-</sup> ion, would preferentially attack the softest of the unsaturated electrophilic centers in the nitroimide according to the theory of hard and soft acids and bases [6]. Despite the fact that, according to this theory, all the unsaturated electrophilic atoms in nitroimides should be classified as hard acids, their hardness is not equivalent, since they have different dimensions, values of the charge  $\delta^+$ , and environments of electronegative atoms. Taking these three factors into account, we can arrange the acid residues in the following series of hardness: NO<sub>2</sub> > COOR > COR > SO<sub>2</sub>R.

In order to confirm this hypothesis, we investigated the reactions of several nitroimides with KI in acetone.

As expected, it was found that the attack of  $I^-$  is directed preferentially at the S atom of the sulfonic residue. Thus, under the action of KI, nitrosaccharin (Id) is split according to the scheme



The treatment of tosylnitroure thane (Ie) with KI also produces a product of the splitting of the  $N-SO_2$  bond:

(Ie) 
$$\xrightarrow{\text{KI}}$$
 EtO<sub>2</sub>CNKNO<sub>2</sub>, 87%

It seemed of interest to ascertain the direction of the reaction of KI with a nitroimide containing carbalkoxy and carbonyl groups. In this case, it is difficult to determine a priori which of the C atoms is harder, since the value of  $\delta^+$  is greater on the carbonyl C atom, while the carbalkoxy C atom is surrounded by a larger number of O atoms. According to the data in [7], the rate of the reaction of KI with benzoyl chloride in acetone is twice as

# TABLE 4. Reaction of Nitroimides with KI

Nitroimide	Nucleophilic attack on functional group (yield of final reaction products, %)			
•	SO2	CO		
(Id) (Ie) (If)	94 87	83		

high as the rate with ethyl chloroformate. Therefore, it may be postulated that the reaction of benzoylnitrourethane (If) with KI results in splitting of the N-COPh bond. In fact, the treatment of If with KI results in the synthesis of the potassium salt of nitrourethane, i.e., the carbonyl center of the nitroimide is subjected to nucleophilic attack:

> PhCONCO<sub>2</sub>Et  $\xrightarrow{\text{KI}}$  EtO<sub>2</sub>CNKNO<sub>2</sub>, 83% NO<sub>2</sub> (If)

The results of the reactions of the nitroimides with KI (Table 4) show that the elimination of the nitro groups from nitroimides is not characteristic of KI, just as in the case of the amines and  $NH_3$ . However, in contrast to the reactions with the amines, the thermodynamic stability of the leaving group in the reactions of the nitroimides with KI does not play a decisive role. In this case, the greater polarizability of the electrophilic center in the nitroimide and its weaker hardness are the primary factors.

#### EXPERIMENTAL

The structures of the compounds described were established on the basis of the absence of melting-point depression in mixed samples with known specimens.

<u>Reaction of Ia with KOH in Water and Ethanol.</u> A solution of 0.22 g of KOH in 10 ml of water (a) or EtOH (b) was added to 0.5 g of Ia. The mixture was stirred for several hours until the layers disappeared and evaporated to a volume of 2 ml.

This yielded 0.4 g (96%) in (a) and 0.36 g (86%) in (b) of the potassium salt of nitrourethane, mp  $189-191^{\circ}C$  (compare [8]).

<u>Reaction of Ib with KOH in Ethanol and Acetonitrile.</u> A solution of 0.58 g of KOH in 10 ml of EtOH (a) or absolute MeCN (b) was added to 1 g of Ib. The reaction mixture was stirred for 2 h (a) or 5 h (b) and evaporated to a small volume, and the precipitate was filtered. a) This yielded 0.97 g (77%) of potassium phthalate, which was identified with a known specimen according to its IR spectrum. b) The precipitate on the filter decomposed with the evolution of heat and foaming. The residue was washed with  $Et_2O$ . This yielded 0.85 g (68%) of potassium phthalate.

<u>Alkaline Alcoholysis of Ic.</u> A 0.78-g portion of KOH was added to 1 g of Ic in 7 ml of EtOH, and the mixture was evaporated after 2 h. This yielded 1.32 g (98%) of potassium succinate, mp 248-251°C, which was identified with a known specimen on the basis of its IR spectrum.

Reaction of Id with KOH in  $H_2O$ , EtOH, and MeCN. A 1-g portion of Id was given an addition of 0.5 g of KOH in 10 ml of  $H_2O$  (a), 10 ml of EtOH (b), or 20 ml of absolute MeCN (c). The mixture was stirred for 1 h, and the precipitate was filtered. a) This yielded 0.9 g (64%) of III, mp 128°C. Found, %: N 8.78.  $C_7H_4N_2O_8SK$ . Calculated, %: N 8.70. b) This yielded 0.26 g (20%) of IV, mp 380°C (compare [1]). The filtrate was evaporated. This yielded 0.79 g (58%) of V, which decomposes at 115°C (EtOH). Found, %: N 8.96.  $C_9H_9N_2O_6SK$ . Calculated, %: N 8.88. c) This yielded 0.97 g (76%) of IV, mp 380°C.

<u>Reaction of Ie with KOH in  $H_2O$ , EtOH, and MeCN.</u> A 0.5-g portion of Ie was given an addition of 0.21 g of KOH in 5 ml of  $H_2O$  (1), 5 ml of EtOH (b), or 10 ml of MeCN (c). The mixture was stirred for 15 min (a and b) or 2 h (c), and the precipitate was filtered. a)

This yielded 0.12 g (26%) of the potassium salt of p-toluenesulfonylnitramide, mp 285°C. The filtrate was evaporated. This yielded 0.31 g (74%) of the potassium salt of N-tosylurethane [9], mp 211-212°C. b) This yielded 0.21 g (46%) of the potassium salt of p-toluenesulfonyl-nitramide, mp 284°C. The filtrate was evaporated. This yielded 0.18 g (36%) of the potassium salt of N-tosylurethane, mp 211°C. c) This yielded 0.36 g (86%) of the potassium salt of N-tosylurethane (mp 211°C) and 0.06 g (13%) of the potassium salt of p-toluenesulfonic acid (mp 284°C).

<u>Reaction of If with KOH in H<sub>2</sub>O and EtOH.</u> A 0.5-g portion of If was given an addition of 0.24 g of KOH in 5 ml of H<sub>2</sub>O (a) or 5 ml of EtOH (b). The mixture was stirred for 0.5 h. a) After evaporation, a 5:1 mixture of Et<sub>2</sub>O with MeOH was added, and the precipitate was filtered. This yielded 0.15 g (43%) of potassium benzoate (mp 400°C), which was identified with a known specimen on the basis of its IR spectrum. Hydrogen chloride was passed through the filtrate for 15 min, the precipitate was filtered, and the filtrate was evaporated, dissolved in Et<sub>2</sub>O, and subjected to the passage of NH<sub>3</sub>. The precipitate was filtered, and 0.12 g (40%) of the NH<sub>4</sub>+ salt of nitrourethane, which decomposes at 171°C (compare [8]), was obtained. A 0.15-g (40%) yield of N-benzoylurethane with mp 108°C (compare [9]) was recovered from the filtrate.

b) The precipitate was filtered. This yielded 0.13 g (62%) of  $KNO_3$ , which was identified with a known specimen on the basis of its IR spectrum. The filtrate was evaporated to half of its volume, and the precipitate was filtered. This yielded 0.12 g (33%) of the potassium salt of nitrourethane, mp 197°C. The filtrate yielded 0.31 g (59%) of the potassium salt of N-benzoylurethane (mp 287°C), which was identified with a specimen obtained according to [9] on the basis of its IR spectrum.

Reaction of Ig with KOH in  $H_2O$  and EtOH. A solution of 0.11 g of KOH in 2 ml of  $H_2O$  (a) or 3 ml of EtOH (b) was added to 0.5 g of Ig at  $-5^{\circ}C$ . a) The solution was evaporated to half of its volume, 3 ml of EtOH were added, and the precipitate was filtered. This yielded 0.48 g (99%) of the potassium salt of methanesulfonimide (mp 178-180°C), which was identified with a known specimen synthesized according to [10] on the basis of its IR spectrum. b) This yielded 0.46 g (95%) of the potassium salt of methanesulfonimide, mp 180°C.

<u>Reaction of Ia-Ii with  $NH_3$ .</u> A solution of 0.5 g of the nitroimide in 20 ml of the solvent (see Table 3) was subjected to the passage of  $NH_3$  for 5 min, and the precipitate was filtered. A 0.36-g (99%) yield of the  $NH_4^+$  salt of nitrourethane, which decomposes at 171°C (compare [8]), was obtained from Ia, and 0.15 g of urethane (mp 48°C) was recovered from the filtrate.

A 0.49 g (93%) yield of VI, which decomposes at 149°C, was obtained from Ib. After several minutes of exposure to the air, VI decomposed with the evolution of NH3 and the formation of 0.33 g (87%) of phthalimide, mp 234°C. A 0.36-g yield of ammonium succinamate (mp 65°C) was obtained from Ic. Acidification of the salt with HCl led to the recovery of 0.25 g of succinamic acid, mp 155°C. Heating for 2 h at 200°C yielded 0.22 g (64%) of succinimide, mp 124°C. A 0.57-g (99%) yield of IX (mp 141°C) was obtained from Id. Found, %: N 21.36. C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>O<sub>5</sub>S. Calculated, %: N 21.40. A 0.31-g (92%) yield of the NH<sub>4</sub>+ salt of p-toluenesulfonylnitramide, which was identified with a known specimen on the basis of its IR spectrum, was obtained from Ie. A 0.3-g (95%) yield of the NH4+ salt of nitrourethane, which decomposes at 171°C, was obtained from If. The filtrate yielded 0.18 g (71%) of benzamide, mp 123°C. A 0.36-g (100%) yield of the NH4<sup>+</sup> salt of methanesulfonylnitramide (mp 177-178°C), which was identified with a known specimen on the basis of its IR spectrum, was obtained from Ig. A 0.32-g (100%) yield of the NH4<sup>+</sup> salt of benzenesulfonylnitramide (mp 194°C), which was identified by comparing its IR spectrum with that of the NH4+ salt of p-toluenesulfonylnitramide, was obtained from Ih. The filtrate was evaporated, and 0.19 g (83%) of benzenesulfonamide with mp 149°C was obtained.

<u>Reaction of Ie with NH<sub>3</sub> in Various Solvents.</u> A solution of 0.5 g of Ie in 10 ml of the solvent (see Table 2) was subjected to the passage of NH<sub>3</sub> for 5 min, evaporated, and given an addition of 10 ml of Et<sub>2</sub>O. The precipitate was filtered, and the filtrate was evaporated. The ratio of the amides o' ained was established on the basis of the PMR spectra of the reaction mixtures in CHCl<sub>3</sub>.  $\delta_{Me}$ , ppm: 2.15 (s, p-toluenesulfonamide), 3.63 (s, methylurethane).

Reaction of Ia-Ig with Morpholine. A solution of 0.5 g of the nitroimide in 20 ml of the solvent (see Table 3) was given an addition of 2 eq. of morpholine, and the precipitate was filtered. In the case of the formation of an oil, the latter was decanted. Compound Ia yielded 0.95 g of the morpholine salt of nitrourethane (mp 49-51°C), which was converted into the potassium salt by treatment with 0.25 g of KOH in 10 ml of EtOH. This yielded 0.32 g (100%) of the potassium salt of nitrourethane, mp 187°C. Compound VII was obtained from Ib, dissolved in 20 ml of absolute  $Et_2O$ , and subjected to the passage of HCl for 5 min. The precipitate was filtered, and 0.7 g (97%) of VIII (mp 134-135°C) was obtained. Found, %: N 15.02.  $C_{12}H_{13}N_3O_5$ . Calculated, %: N 15.05. Compound Id yielded 0.83 g (94%) of X, mp 191-193°C. Found, %: N 13.81.  $C_{15}H_22N_4O_7$ . Calculated, %: 13.92. An oil was isolated from Ie and treated with 0.2 g of KOH in 5 ml of EtOH. This yielded 0.38 g (82%) of the potassium salt of p-toluenesulfonylnitramide, mp 285°C. The decanted solution was evaporated, and 0.21 g (80%) of N-carbomethoxymorpholine, which was identified with a known specimen on the basis of its IR spectrum, was obtained.

An oil was recovered from If and treated with 0.15 g of KOH in 5 ml of EtOH. This yielded 0.31 g (86%) of the potassium salt of nitrourethane, mp 189°C. Compound Ih yielded 0.18 g (57%) of the morpholine salt of methanesulfonylnitramide, which was identified with a known specimen (a mixture of equimolar amounts of sulfonylnitramide and morpholine) on the basis of its IR spectrum.

<u>Reaction of Id with t-BuNH<sub>2</sub></u>. A solution of 0.5 g of Id in 10 ml of absolute MeCN was given an addition of 0.47 ml of t-BuNH<sub>2</sub>, and the solution was evaporated. This yielded 0.75 g (90%) of XI, mp 163-166°C. Found, %: N 15.16.  $C_{15}H_{26}N_4O_5S$ . Calculated, %: N 14.99.

<u>Reaction of Id with KI</u>. A stirred suspension of 1 g of Id in 10 ml of absolute Me<sub>2</sub>CO was given an addition of 1.5 g of KI, and the precipitate was filtered after 6 h. This yielded 0.88 g (94%) of IV, mp 380°C (compare [1]).

Reaction of Ie and If with KI. A stirred suspension of 0.2 g of the nitroimide in 10 ml of absolute Me<sub>2</sub>CO was given an addition of 0.1 g of KI, and the precipitate was filtered after 10 h. Compound Ie yielded 0.1 g (87%) and If yielded 0.12 g (83%) of the potassium salt of nitrourethane, mp 186°C (compare [8]).

# CONCLUSIONS

1. Several electrophilic centers, as a rule, simultaneously undergo nucleophilic attack during the alkaline hydrolysis and alcoholysis of nitroimides.

2. Nitroimides containing two  $SO_2$  groups are split under the anions of OH<sup>-</sup> or OR<sup>-</sup> ions at the N-NO<sub>2</sub> bond.

3. The aminolysis of nitroimides proceeds with splitting of the N-acyl bond. The reactivity of the acyl residues decreases along the series  $PhCO > RO_2C > RSO_2$ .

4. The polarity of the solvent plays a major role, increasing the probability of attack of the amine on the least solvated center in the nitroimide.

5. Splitting of the N-SO<sub>2</sub> bond is characteristic of the reactions of nitroimides with KI.

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