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PECULIARITIES OF THE NITRATION OF SECONDARY POLYNITROALKANES

L. T. Eremenko, G. V. Oreshko,
and M. A. Fadeev

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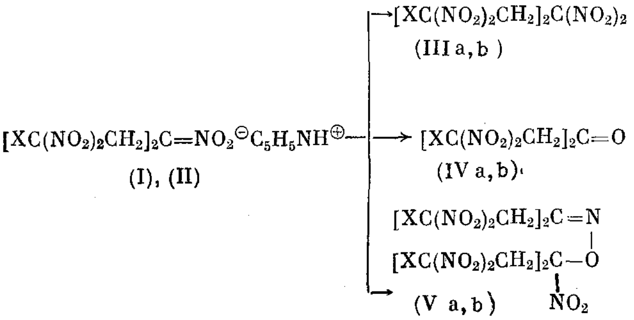
The nitration of salts of unsubstituted secondary nitroalkanes $RR'C = NO_2^{\ominus}$ by nitronium tetrafluoborate [1], as well as the oxidative nitration by Ag [2] or Na [3, 4] nitrites in alkaline or neutral medium, is well known. However, gem-dinitro compounds are not formed in the case when R or R' is an electron-acceptor group [5]. The nitration of compounds of this kind by nitric acid or nitrating mixtures has received little study; only two examples of the production of gem-dinitro derivatives for $R = R' = CH_2C(NO_2)_3$ [6] and $R = R' = CH_2C(NO_2)_2Me$ [7, 8] are shown.

Our preliminary experiments have shown that the nitration of 1,5-disubstituted 1,1,3,5,5-pentanitropentanes proceeds complexly and is accompanied by side reactions, which are dominant under definite conditions.

In this work we studied the reactions of salts of the indicated compounds with various nitrating systems. It was shown that the main and side processes are determined by the composition of the nitrating systems and lead to the formation of the following products:



$X = NO_2$(a), F (b).

In anhydrous $HNO_3-H_2SO_4$ systems at a 5-10% HNO_3 content, when the equilibrium

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}$$

is almost entirely shifted to the right [9], the main products of the reaction with (I) or (II) are (Va, b) and (IVb), respectively (Table 1). In the system containing 10% HNO_3, (IIIa) and (IIIb) are formed in negligible yields.

When water is introduced into the system ($HNO_3:H_2SO_4:H_2O$ = 10:85:5), the dissociation of HNO_3 according to the indicated equation is sharply reduced, and the reaction with (I) proceeds by C-nitration in the 3 position with a 43% yield (IIIa) and oxidation with the formation of (IVa) and (Va).

Nitration of (I) and (II) by HNO_3-H_2O systems at HNO_3 concentrations of 98-70%, which are characterized by the presence of a large amount of nonionized HNO_3 [10] and a negligible amount of $NO_2^{\oplus}$ (in systems up to 5% H_2O) [9], leads primarily to products of C-nitration (IIIa, b) up to 65%, as well as (IVa, b) as a result of oxidation processes of the Neff reaction. In this case the nitrating ability of the HNO_3-H_2O system is preserved down to a 70% HNO_3 content, which agrees with the data of [7]. At lower HNO_3 concentrations, nitration does not occur, evidently on account of the insolubility of the nitro

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TABLE 1. Results of the Nitration of Salts of Fluoro- and Nitro-Substituted 1,1,3,5,5-Pentanitropentanes

Salt of polynitropentane to be nitrated	Nitrating system, %				Reaction products, %		
	HNO_3	H_2SO_4	$(Ac)_2O$	H_2O	(III)	(IV)	(V)
(I)	5	95	0	0	0	0	57
	10	90	0	0	1	0	57
	10	85	0	5	43	13	8
	98	0	0	2	64	26	0
	95	0	0	5	65	20	0
	90	0	0	10	65	13	0
	80	0	0	20	50	11	0
	70	0	0	30	20	0	0
	36	0	64	0	65	9	0
(II)	5	95	0	0	0	22	8
	10	90	0	0	8	18	0
	98	0	0	2	51	35	0
	80	0	0	20	18	23	0

derivatives under these conditions, and nitronic acids are isolated, which is confirmed by the data of [11].

The products of nitration were isolated from the reaction mass by the addition of conc. H_2SO_4 or a saturated aqueous solution of $NaNO_3$ (IIIa, b)-(Va, b), identified after crystallization according to the IR and PMR spectra by comparison with known samples, produced according to [6, 12-14].

We have undertaken an attempt to produce gem-dinitro derivatives using other nitrating systems. Upon action of the HNO_3-Ac_2O system on (I), we obtained (IIIa) with a 65% yield; however, C-nitration does not occur when $NO_2^{\oplus}BF_4^{\ominus}$, N_2O_4, $ClNO_2$ are used in aprotic solvents.

Thus, the nitration of salts of secondary polynitropentanes is effective only when systems in which the nitrating agent is $YONO_2$, when Y = H, Ac, are used.

The reaction proceeds through the formation of a nitronic acid [15], followed by protonation and the formation of an intermediate adduct with $YONO_2$. The formation of ketones (IVa, b) can be explained by reactions of oxidation [13, 16, 17] or hydrolysis [18], while that of O-esters of oximes (Va, b) can be explained by redox reactions of salts of secondary polynitroalkanes in acid media, proceeding with the participation of a nitronic acid [19].

EXPERIMENTAL

Pyridinium salts (I) and (II) were produced according to [20]. Sulfuric acid, grade pure, was used without additional purification. The nitric acid used was anhydrous, freshly redistilled. The yields of the products are cited in Table 1.

Interaction of (I) with the $HNO_3-H_2SO_4$ System (General Procedure). To 270 ml of the nitrating mixture, a suspension of 10 mmoles (I) and 50 ml CCl_4 was added at −10°C with mixing. After 30 min the reaction mass was filtered off and extracted with 2 × 50 ml of CCl_4. The precipitate was washed with water, dried, and recrystallized from CCl_4. We isolated (Va), t. dec. 144-145°C (compare with [19]). The extract was washed with conc. H_2SO_4 and evaporated under vacuum. The residue was recrystallized twice from CCl_4; (IIIa), mp 48-48.5°C, was isolated (compare with [6]).

Interaction of (I) with the $HNO_3-H_2SO_4-H_2O$ System. Under the conditions of the preceding experiment we isolated (IIIa) and (Va). Additional extraction of the acid mixture with CH_2Cl_2 yielded (IVa), t. dec. 100-101°C (compare with [13]).

Interaction of (II) with the $HNO_3-H_2SO_4$ System. a) To 270 ml of the anhydrous nitrating mixture with a 5% HNO_3 content, a suspension of 10 mmoles (II) in 50 ml CCl_4 was added at −10°C with mixing. After 30 min the acid layer was removed, extracted with 50 ml of CCl_4, and the extract combined with the organic layer. The solvent was evaporated under vacuum, and the residue crystallized from CF_3COOH. We isolated (Vb), mp 64-65°C (compare with [14]).

b) Interaction with the $H_2SO_4-HNO_3$ nitrating system, containing 10% HNO_3, was conducted under the conditions of experiment (a); however, (IIIb) was isolated from CCl_4, mp 48-49°C (compare with [12]).

Nitration of (I) or (II) by the HNO_3-Ac_2O System. a) To 35 ml of HNO_3 of the indicated concentration (see Table 1), a suspension of 10 mmoles (I) or (II) in 50 ml CCl_4 was added at −30°C with mixing. After 20 min, 150 ml of conc. H_2SO_4 was cautiously poured in, and the mixture was mixed for 15 min, maintaining the temperature no higher than −120°C. The precipitate was filtered off and recrystallized from CF_3COOH. We isolated (IVb), t. dec. 100-102°C, or (IVb), t. dec. 110-112°C (compare with [13]). The filtrate was extracted with 2 × 50 ml CCl_4, and the combined extracts washed with 30 ml of conc. H_2SO_4 and evaporated under vacuum. The residue was recrystallized from CCl_4 or CF_3COOH, (IIIa), mp 47.5-48.5°C; (IIIb), mp 48-49°C.

b) Under the conditions of experiment a), the reaction products were isolated by adding 10 ml of a 20% aqueous solution of $NaNO_3$ at −30°C. The organic layer was removed, and the acid mixture extracted with 2 × 30 ml of CCl_4 at 0 to −5°C. The combined extracts were washed with 30 ml of 80% H_2SO_4 and 2 × 30 ml of conc. H_2SO_4. This solution was evaporated under vacuum, the residue recrystallized from CCl_4 (IIIa), mp 47.5-48.5°C; (IIIb), mp 48-49°C.

Nitration of (I) by the HNO_3-Ac_2O System. To the nitrating mixture of 1 mole of 100% HNO_3 and 1.1 moles Ac_2O, a suspension of 10 mmoles (I) in 50 ml of CCl_4 was added at −20°C with vigorous mixing. After 20 min of mixing, 250 ml of conc. H_2SO_4 was added, and the mixture extracted with 2 × 50 ml of CCl_4. The combined extracts were washed with 50 ml of conc. H_2SO_4 and evaporated under vacuum. The residue was recrystallized from CCl_4 or CF_3COOH. We isolated (IIIa), mp 47.5-48.5°C. The reaction mixture was additionally extracted with 2 × 50 ml CH_2Cl_2. The extract was washed with 50 ml of conc. H_2SO_4, evaporated under vacuum, and the residue recrystallized from CF_3COOH. We isolated (IVa), t. dec. 100-102°C.

Interaction of (I) with $NO_2^{\oplus}BF_4^{\ominus}$. To a solution of 2.3 g (5 mmoles) (I) in 20 ml of dry $MeNO_2$, we added 1.3 g (10 mmoles) of $NO_2^{\oplus}BF_4^{\oplus}$ at −40°C with vigorous mixing. After mixing of the reaction mass for 1 h, 100 ml of conc. H_2SO_4 was poured in, and the mixture was extracted with 2 × 30 ml of CH_2Cl_2. The extract was washed with conc. H_2SO_4, evaporated under vacuum, and the residue recrystallized from $CHCl_2$. We isolated 1.1 g (57%) 1,1,1,3,5,5,5-heptanitropentane, t. dec. 103-104°C (compare with [21]).

Interaction of (I) with N_2O_4. To a solution of 2.3 g (5 mmoles) (I) in 40 ml of CH_2Cl_2, a solution of 2 g (22 mmoles) N_2O_4 in 20 ml of CH_2Cl_2 was added at −20°C with mixing. After mixing for 1 h at −15°C, the products were isolated according to a) and b).

a) The N_2O_4 and part of the solvent were distilled off under vacuum, the residue washed with 2 × 30 ml of 50% H_2SO_4 and 2 × 30 ml of conc. H_2SO_4 and evaporated under vacuum. Recrystallization from $CHCl_3$ yielded 1 g (52%) 1,1,1,3,5,5,5-heptanitropentane, t. dec. 103-104°C.

b) The reaction solution was washed with 2 × 30 ml of conc. H_2SO_4 and evaporated under vacuum. Recrystallization of the residue from CCl_4 yielded 1.2 g (62%) (Va), t. dec. 144-146°C.

Interaction of (I) with $ClNO_2$. The isolation was conducted according to b) under the conditions of the preceding experiment. We obtained 0.9 g (42.5%) of 3-chloro-1,1,1,3,5,5,5-heptanitropentane, mp 68-69°C (compare with [20]).

CONCLUSIONS

In the interaction of salts of 1,1,1,3,5,5,5-heptanitro- or 1,5-difluoro-1,1,3,5,5-pentanitropentanes with nitrating systems based on HNO_3, 1,1,1,3,3,5,5,5-octanitro- or 1,5-difluoro-1,1,3,3,5,5-hexanitropentanes, 1,1,1,5,5,5-hexanitro- or 1,5-difluoro-1,1,5,5-tetranitropentan-3-ones, the O-bis-(2,2,2-trinitroethyl)nitromethyl ether of bis(2',2',2'-trinitroethyl)carboxime or the O-bis(2-fluoro-2,2-dinitroethyl)nitromethyl ether of bis(2'-fluoro-2',2'-dinitroethyl)carboxime are formed. The ratio of the reaction products depends on the composition of the nitrating system. The data obtained permit us to consider that the nitrating reagent is a nonionized form of $HONO_2$ or $AcONO_2$.

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OXIDATIVE REARRANGEMENT OF CYCLOALKANONE CYANHYDRINS: EFFICIENCY OF VARIOUS OXIDANTS AND OXIDANT SYSTEMS

Yu. N. Ogibin, S. K. Gorozhankin,
and G. I. Nikishin

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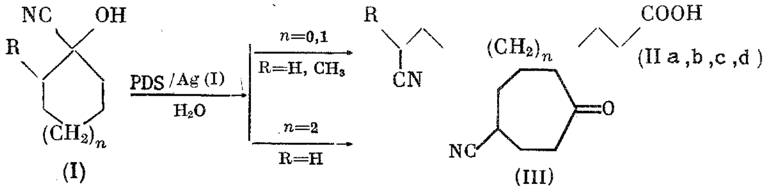
547.47'052:547.514.472

By the action of the sodium peroxydisulfate (PDS)/Ag(I) oxidant system, cyclopentanone and cyclohexanone cyanhydrins (CH) (Ia, b) undergo oxidative rearrangement to 5- and 6-cyanoalkanoic acids (IIa, b), while cycloheptanone CH (Ic) rearranges to 4-cyanocycloheptanone (III) [1]:



R = H, $n = 0$ (a), 1 (b), 2 (c), R = CH_3, $n = 0$ (d), R = CH_3, $n = 1$ (e)

Under the rearrangement conditions the resulting cyanoalkanoic acids become actively involved in oxidative decarboxylation [2]. Consequently, the selectivity of the conversion of Ia, b to acids IIa, b does not exceed 60%. Under similar conditions the rearrangement product of Ic (4-cyanocycloheptanone, III) does not undergo secondary conversions, so that the rearrangement of Ic to III proceeds with significantly higher selectivity (85%) [1].

The purpose of the present work was to find oxidants and oxidant systems that could efficiently initiate cycloalkanone CH rearrangement and would, at the same time, be unreactive

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