The identities of the (XVI) and (XVII) obtained in the different experiments were established by the lack of depression of the melting points in mixed samples.

CONCLUSIONS

1. When LiAlH4 is allowed to react with unsubstituted, di-, and tetra-N-alkylated bicyclic bisureas (BBU) of the octane and nonane series, reduction takes place only in the case of tetra-N-alkyl BBU, reduction of one or both carbonyl groups taking place according to the structure of the BBU.

2. Reaction of non-N-alkylated O-alkyl BBU with nucleophilic reagents results in deprotonation with the formation of bicyclic isoureas.

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N-NITRATION OF SALTS OF PRIMARY NITRAMINES BY NITRYL FLUORIDE

R. G. Gafurov, B. S. Fedorov, and L. T. Eremenko UDC 542.958.1:547.416

We have reported in previous communications [1, 2] that treatment of alkali-metal salts of nitramines with nitryl fluoride in acetonitrile results in the O-nitration of the ambident nitramine anion to form the alkyl nitrite and nitrous oxide, via the intermediate alkyl azoxynitrate.

The F-NO₂ molecule is polarized and has a dipole moment of 0.47 D [3]. The substantial contribution of the nitronium fluoride structure $FNO_2 \leftrightarrow F^{\odot}NO_2^{\oplus}$ suggests an analogy between the reactivity of FNO₂ and that of nitronium salts, which react with nitramine salts at the N atom to form N,N-dinitramines [4]. In principle, this reaction should also occur with FNO₂.

We have shown [5] that with tetraalkylammonium salts of methylnitramine, FNO₂ gives the N-nitration product (methyl-N,N-dinitramine). The yield of the latter increases, and the yield of methyl nitrate decreases accordingly, as the size of the cation increases. In the present investigation, this method of N-nitration of nitramine salts has been extended to the preparation of alkyl-N,N-dinitramines (C_2-C_5) .

 $\begin{bmatrix} R\ddot{N} = \overset{\bigcirc}{N} \\ & & \\ &$

Table 1 shows the melting points and yields of the tetramethylammonium salts of the C_1 - C_5 primary nitramines. The tetraethylammonium salts of these alkylnitramines are liquids which fail to crystallize at ~20°C.

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TABLE 1. Tetramethylammonium Salts of Primary Nitramines, [RNNO₂]^o[N(CH₃)₄]^o

R	mp, ℃	Anhydrous recrystalliza- tion solvents	Yield after purifica- tion, %
Me	$\begin{array}{r} 62-64\\ 124-126\\ 183-184\\ 241-242\\ 305-307\end{array}$	2-BuOH+Et ₂ O	80,7
Et		2-BuOH+Me ₂ CO	86,4
<i>n</i> -Pr		2-BuOH+Me ₂ CO+MeCO ₂ Et	85,1
<i>n</i> -Bu		2-BuOH+Me ₂ CO+Et ₂ O	86,2
<i>n</i> -Am		MeCN+Et ₂ O (-30°)	77,4

TABLE 2. N,N-Dinitroalkylamines $RN(NO_2)_2$, Obtained by Nitration of Tetraalkylammonium Salts of Primary Nitramines with FNO₂ in MeCN

R	Yield, %		ha °C		
	from the tetramethyl- ammonium salt	from the tetraethyl- ammonium salt	(torr)	n_D^{20}	d4 ²⁰
Et n-Pr n-Bu n-Am	54,7 54,3 62,3 51,4	68,3 70,1 67,2 67,7	40-41 (13,5) 24 (3,0) 27 (0,2) 33 (0,2)	1,4399 1,4414 1,4429 1,4444	1,296 1,224 1,159 1,082

Table 2 gives the yields and some properties of the C_2-C_5 alkyl-N,N-dinitramines which have been obtained.

Figure 1 shows the linear dependence of the d_4^{20} and n_D^{20} values for the N,N-dinitramines prepared, which is characteristic of homologous series of organic compounds [6]. The first member of the series, as in other instances, is an exception to the rule. The observed dependence confirms the purity of the compounds.

As shown in Table 2, as the size of the cation in the nitramine salt increases, the yield of the N,N-dinitramine improves. This behavior appears to be general for the nitration of nitramine salts with nitryl fluoride. On the other hand, nitration with nitronium tetra-fluoroborate affords predominantly the alkyl nitrate, in low yields. Thus, treatment of the tetramethylammonium salt of methylnitramine with nitronium tetrafluoroborate in MeCN afforded 27% of methyl nitrate and only 7% of methyl-N,N-dinitramine. A similar reaction with the te-traethylammonium salt of methylnitramine gave methyl nitrate only, in 21% yield.

Thus, the nitronium cation, being bonded to the hard, anionoid F atom, brings about O-nitration of anions of the alkali-metal salts of nitramines. This cation, however, when paired with anions such as tetrafluoroborate, hexafluorosilicate, heptafluorophosphate, bisulfate, or perchlorate, effects N-nitration of the anions of these salts.

When salts of nitramines with bulky tetraalkylammonium cations are nitrated, the reverse is the case, i.e., nitryl fluoride yields N-nitrated products, and nitronium salts give Onitration products. Consequently, both the cationoid moiety of the substrate and the anionoid portion of the molecule of the nitrating agent have a marked influence on the course of the reaction.

EXPERIMENTAL

<u>Tetramethylammonium Salt of Methylnitramine</u>. To a solution of 5 g of methylnitramine in 15 ml of methanol at 0°C was added over 12 min 60 g of 10% tetramethylammonium hydroxide. The solution was stirred for 30 min at 18-20°, and the solvent removed *in vacuo*. The residue was recrystallized from a mixture of anhydrous isobutanol and anhydrous ether to give 7.94 g (81%) of colorless crystals, mp 62-64°. Found: C 40.1; H 9.9; N 28.0%. $C_5H_{15}N_3O_2$. Calculated: C 40.27; H 10.07; N 28.18%.

<u>Tetraethylammonium Salt of Methylnitramine</u>. To a solution of 5.5 g of methylnitramine in 30 ml of ethanol at 0° was added over 5 min a solution of 15.8 g of tetraethylammonium hydroxide in 45 ml of EtOH. The solution was stirred for 20 min at 20°, the alcohol distilled off, and the residual oil dried *in vacuo* (0.1 mm) for 16 h; yield 14.01 g (94.6%).



Fig. 1. Dependence of density on refractive index in a homologous series of alkyl-N,Ndinitramines of general formula $RN(NO_2)_2$.

Found: C 52.6; H 11.0; N 20.4%. C₉H₂₃N₃O₂. Calculated: C 52.68; H 11.21; N 20.48%.

The tetraalkylammonium salts of the other nitramines were obtained similarly. Typical methods of nitration are given below.

<u>Ethyl-N,N-dinitramine.</u> a) Into a suspension of 4 g of the tetramethylammonium salt of ethylnitramine in 30 ml of anhydrous MeCN at -30° was passed with vigorous stirring 1.9 g of FNO₂, over 15 min. The mixture was stirred for 20 min at -20 to -10° , then allowed to warm to 0° and poured into 250 ml of ice water. The oil which separated was extracted with ether (2 × 50 ml), and the combined extracts were washed with a 5% solution of Na₂CO₃ (2 × 75 ml) and water (2 × 100 ml), and dried over MgSO₄. After removal of the ether, and distillation under reduced pressure, there was obtained 1.92 g (54.7%) of ethyl-N,N-dinitramine, bp 40-41° (13.5 torr); n_D° 1.4399; d_4° 1.296. Found: C 20.6; H 3.7; N 31.0%. C₂H₅N₃O₄. Calculated: C 20.74; H 3.73; N 31.1%.

b) Into a mixture of 3 g of the tetraethylammonium salt of ethylnitramine in 55 ml of anhydrous MeCN was passed at -30 to -25° with stirring over 15 min 1.1 g of FNO₂, and stirring was continued for a further 15 min at -10 to -5° . The mixture was poured into 250 ml of ice water, and extracted with CH₂Cl₂ (2 × 30 ml). The product was isolated in the usual way to give 0.94 g (68.3%) of ethyl-N,N-dinitramine.

Nitration of the other tetralkylammonium salts was carried out in a similar way.

<u>Nitration of the Tetramethylammonium Salt of Methylnitramine by Nitronium Tetrafluoro-borate</u>. To a solution of 3.57 g of $NO_2^{\oplus}BF_4^{\odot}$ in 55 ml of anhydrous MeCN at -10° was added with stirring over 5 min 4 g of methylnitramine, tetramethylammonium salt. The reaction mixture was stirred at 0° for 2.5 h, and poured into 200 ml of ice water. The oil which separated was extracted with CH_2Cl_2 (2 × 40 ml), and the combined extracts were washed with water (2 × 100 ml) and dried over MgSO₄. Removal of the solvent and distillation afforded 0.63 g (27%) of methyl nitrate, bp 64-65° (760 torr); $n_D^{2°}$ 1.3754, cf. [7]. The residual oil was distilled *in vacuo* to give 0.22 g (7%) of methyl-N,N-dinitramine, bp 33° (14 torr); $n_D^{2°}$ 1.4470, cf. [8].

Nitration of the Tetraethylammonium Salt of Methylnitramine with Nitronium Tetrafluoroborate. To a solution of 1.9 g of $NO_2^{\oplus}BF_4^{\odot}$ in 45 ml of anhydrous MeCN at -10° was added with stirring 3 g of methylnitramine tetraethylammonium salt. The reaction mixture was stirred at 0-10° for 3 h, and poured into 200 ml of ice water. Extraction with CH_2Cl_2 (2 × 40 ml) followed by the usual workup afforded 0.26 g (20.7%) of methyl nitrate, bp 64° (760 torr); n_D^{20} 1.3760.

CONCLUSIONS

1. A method has been developed for the N-nitration of the anions of primary nitramines with nitryl fluoride to N,N-dinitramines.

2. Bulky tetraalkylammonium cations in nitramine salts direct the attack of nitryl fluoride on the nucleophilic amine center of the ion, whereas the harder metal cations favor O-nitration.

3. In the nitration of nitramine anions by nitronium tetrafluoroborate, the opposite effect is observed with respect to the influence of the salt cation on the outcome of the reaction, i.e., bulky, soft cations favor 0-nitration.

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RADICAL REACTION OF ACETONE WITH AROMATIC COMPOUNDS

R. S. Min, V. S. Aksenov, UDC 541.515:542.91:547.284.3:547.562.4'261:547.73 M. G. Vinogradov, and G. I. Nikishin

Substitution of the aromatic nucleus by alkyl radicals has been extensively investigated [1-3]. The reaction of aromatic compounds with functionally substituted alkyl radicals has been investigated only in the cases of CH_2COMe [4], CH_2COOH [5-8], CH_2COOEt [9], CH_2NO [10], and the isomeric composition of the products has been examined quantitatively only in the carboxymethylation of toluene [5, 6] and anisole [7, 8].

We have examined the reaction of anisole, toluene, chlorobenzene, ethyl benzoate, benzonitrile, and thiophene with CH_2COMe radicals, generated in the redox system acetone-Mn(OAc)₃-AcOH at 70°:

 $MeCOMe + Mn(OAc)_3 \rightarrow MeCOCH_2 + Mn(OAc)_2 + AcOH$

Reaction of CH_2COMe with benzene derivatives affords benzyl ketones (I) in yields of 30-80% based on Mn(III).



 $X = CH_3O$ (a), CH_3 (b), Cl (c), COOEt (d), CN (e)

2,5-Hexanedione, formed by the recombination of CH_2COMe radicals, is obtained in yields of only 3-4% based on Mn(III). The yield of (I) decreases regularly with decreasing electronegativity of the substituents in the benzene ring (Table 1) owing to the electrophilic character of the CH_2COCH_3 radical. Similar behavior has been observed in the radical carboxymethylation and nitromethylation of monosubstituted benzenes [7, 10].

The benzyl ketones (I) are thermally stable except for the o isomer (Id), which under GLC conditions undergoes partial conversion to 3-methylisocoumarin. This was allowed for in

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Institute of Petroleum Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Tomsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2292-2295, October, 1979. Original article submitted July 1, 1978.