CONCLUSIONS

1. The insertion of a gem-dichlorocyclopropyl group in the β-position of vinyl ethers makes it possible to use them as reactants for lengthening the carbon chain by two C atoms in the case of the acetate of gem-dichlorocyclopropane and acetylenic aldehydes.

2. Depending on the ratio of the reactants, when trans-β-gem-dichlorocyclopropylvinyl ethyl ether is reacted with the diacetal of malonic dialdehyde the chain can be lengthened by either two or four C atoms.

3. trans-β-gem-Dichlorocyclopropylvinyl methyl ether reacts selectively with the bis(dimethyl acetal) of glutaconic dialdehyde at the acetal group that is activated by the double bond.

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NITRATION OF N-ALKYLIMIDES

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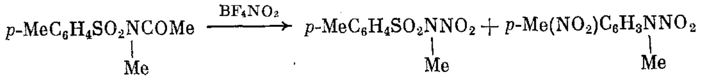
UDC 542.958.1:547.298

The reaction for the substitutive nitration of the N-acyl derivatives of amines, where the role of the leaving group is fulfilled by the acid moiety, has a general character. It was described on the examples of using various nitrating agents to nitrate the N,N-dialkylamides of aliphatic [1-3] and aromatic [4] carboxylic, sulfuric [5], alkyl- [6, 7] and arylsulfonic acids [7, 8], and the alkylnitroamides of carboxylic acids [9].

In order to ascertain the possibility and direction of the substitutive nitration reaction in the series of N-alkylimides (AI), and also the comparative activity of the acid moieties as leaving groups, we studied the nitration of some symmetrical and unsymmetrical, both linear and cyclic, AI of carboxylic, carbonic, and sulfonic acids. As the nitrating agents we used nitronium tetrafluoborate (NTFB), concentrated HNO_3, and its mixture with H_2SO_4 or trifluoroacetic anhydride.

The results of nitrating the AI are given in Table 1. From the data in Table 1 it can be seen that the possibility and direction of reacting the N-methylimides (MI) with NTFB are determined by the nature of the acid moieties and the structure of the MI. The acetyl group is replaced the easiest. Reaction in this case is quite rapid and the corresponding N-methyl-N-nitroamides are formed in high yields. The methylsulfonyl group can also be replaced by the nitro group, but it is much less reactive, which is easily seen on the example of nitrating (IV). Cases of replacing the carbomethoxyl group by the NO_2 group were not observed. If the MI molecule contains groups that are easily nitrated, they are also involved in the nitration.



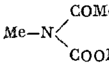
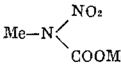
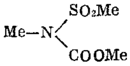
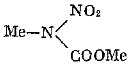
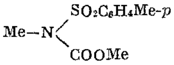
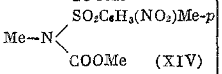
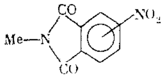
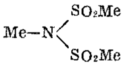
$$p\text{-MeC}_6\text{H}_4\text{SO}_2\underset{\substack{|\\ \text{Me}}}{\text{N}}\text{COMe} \xrightarrow{\text{BF}_4\text{NO}_2} p\text{-MeC}_6\text{H}_4\text{SO}_2\underset{\substack{|\\ \text{Me}}}{\text{N}}\text{NO}_2 + p\text{-Me(NO}_2\text{)C}_6\text{H}_3\underset{\substack{|\\ \text{Me}}}{\text{N}}\text{NO}_2$$

(II) (XI) (XII)

The absence of substitutive nitration at the nitrogen atom in (V) can be explained by the fact that a strong electron-acceptor substituent is inserted as the result of C-nitration in the ring, which substituent lowers the electron density on the N atom and hinders its further attack by the nitronium cation. Together with this, the ability of the p-toluenesulfonyl moiety to function as a leaving group is apparently lowered due to a decrease in the thermodynamic stability.

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. 2138-2141, September, 1981. Original article submitted December 19, 1980.

TABLE 1. Reaction Products of N-Alkylimides with NTFB

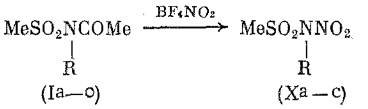
N-Alkylimide	AI:NTFB (mole)	Reaction time at 20°C, h	Reaction products	Yield,* %
(Ia)	1 : 1	0,5	(Xa)	83
(Ib)	1 : 1	0,5	(Xb)	71 (79)
(Ic)	1 : 1	0,5	(Xc)	76 (81)
(II)	1 : 1	0,5	(XI)	24
			(XII)	37
 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{COMe}\\ \mathrm{COOMe}\end{smallmatrix}$ (III)	1 : 1	0,5	 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{NO_2}\\ \mathrm{COOMe}\end{smallmatrix}$ (XIII)	63
 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{SO_2Me}\\ \mathrm{COOMe}\end{smallmatrix}$ (IV)	1 : 1	15	 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{NO_2}\\ \mathrm{COOMe}\end{smallmatrix}$ (XIII)	33 (73)
 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{SO_2C_6H_4Me\text{-}}p\\ \mathrm{COOMe}\end{smallmatrix}$ (V)	1 : 1	15	 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{SO_2C_6H_3(NO_2)Me\text{-}}p\\ \mathrm{COOMe}\end{smallmatrix}$ (XIV)	45 (62)
	2 : 1	15		68
(VI)	1 : 1	1	(XV)	26 (40)
			(XVI)	15 (23)
	2 : 1	1	(XVI)	75 (75)
(VII)	1 : 1	15	None	0
(VIII)	1 : 1	15	 (XVII)	36 (66)
	2 : 1			75 (90)
 $\mathrm{Me{-}N}{<}\begin{smallmatrix}\mathrm{SO_2Me}\\ \mathrm{SO_2Me}\end{smallmatrix}$ (IX)	1 : 1	15	None	0

* The yield when based on reacted AI is given in parentheses.

It was found that, depending on the ratio of the reactants, the nitration of N-methylacetimide (VI) with NTFB leads to a mixture of N-methyl-N-nitroacetamide (XV) and methyldinitroamine (XVI) or to methyldinitroamine (XVI). It proved that the structure of the MI exerts a substantial effect on the possibility of the substitutive nitration reaction. In contrast to (VI), its closest cyclic analogs, namely N-methylsuccinimide (VII) and N-methylphthalimide (VIII), do not enter into the substitutive nitration reaction at the nitrogen atom; (VIII) is nitrated only in the aromatic ring.

According to the literature data on the nitration of dialkylamides [2, 5, 7], when going from the dimethylamides to the higher homologs the yield of the dialkylnitroamines decreases sharply, and in some cases the direction of the reaction changes. In this connection it seemed of interest to ascertain the effect of the alkyl substituent at the nitrogen atom on the direction and ease of reaction progress in the AI series.

We studied the nitration of N-alkyl-N-acetylmethanesulfamides (Ia, b, c) with various alkyl substituents. It was shown that the reaction of (I) with NTFB leads in all cases to obtaining the N-alkyl-N-nitromethanesulfamides in high yields, while here the acetal group functions as the leaving group. As a result, as a first approximation the character of the alkyl substituent does not affect the direction of the substitutive nitration reaction in the AI series.



$$\underset{\text{(Ia—c)}}{\mathrm{MeSO_2\underset{\underset{R}{|}}{N}COMe}} \xrightarrow{\mathrm{BF_4NO_2}} \underset{\text{(Xa—c)}}{\mathrm{MeSO_2\underset{\underset{R}{|}}{N}NO_2}}$$

R = Me (a), Et (b), *i*-Pr (c).

We also studied whether acid nitrating agents could be used to nitrate the AI. Compound (Ia) is smoothly nitrated using conc. HNO_3 to give N-methyl-N-nitromethanesulfamide (Xa) in 77% yield. The same direction of the reaction is retained if the nitrating agents are a mixture of HNO_3 with H_2SO_4 or trifluoroacetic anhydride. Attempts to nitrate (VI) with acid mixtures proved unsuccessful, apparently due to the instability of this compound or its nitration products in strongly acid medium.

EXPERIMENTAL

General Method for Nitration of N-Alkylimides with Nitronium Tetrafluoborate.* With vigorous stirring,

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* When nitrating methylacetimide the order of mixing the reactants was the reverse, and the yields of the reaction products were determined via the PMR spectra.

to a suspension of 0.005 mole* of BF_4NO_2 in 20 ml of abs. MeCN was added at −25°, in small portions, 0.005 mole of the AI. The reaction mixture was allowed to spontaneously warm up to ~20° and then kept for a definite time period (see Table 1). The mixture was poured into 20 ml of ice water, extracted with CH_2Cl_2 (5 × 20 ml), washed with water, and dried over $MgSO_4$. The solvent was evaporated in vacuo. In the case of several products they were separated by TLC on silica gel, in which connection the composition and structure were determined via the IR and PMR spectra, and also the elemental analysis data.

Nitration of N-Methyl-N-acetylmethanesulfamide (Ia) with HNO_3. With stirring and cooling to −25°, to HNO_3 (d 1.51) was added in small portions 1 g (0.0066 mole) of (Ia). The mixture was allowed to spontaneously warm up to ~ 20°. Then it was poured on 30 g of ice, extracted with CH_2Cl_2 (4 × 20 ml), and dried over $MgSO_4$. The solvent was evaporated and we obtained 0.78 g (77%) of $CH_3SO_2N(CH_3)NO_2$ (Xa), mp 41-43°.

Nitration of N-Methyl-N-acetylmethanesulfamide (Ia) with Mixed Acid. To 1.25 g of HNO_3 (d 1.51) at 0° was added 3.18 ml of H_2SO_4. The mixture was cooled to −25° and, with stirring, 1 g (0.0066 mole) of (Ia) was added in portions. The mixture was allowed to warm up to ~ 20°, poured into ice water, extracted with CH_2Cl_2 (4 × 20 ml), washed with water, and dried over $MgSO_4$. The solvent was evaporated in vacuo. We obtained 0.52 g (51%) of (Xa), mp 41-43°.

Preparation of N-Isopropyl-N-acetylmethanesulfamide (Ic). To a solution of 8 g (0.058 mole) of N-isopropylmethanesulfamide in 20 ml of freshly distilled Ac_2O was added 0.68 ml (0.006 mole) of $SnCl_4$ and the mixture was refluxed for 30 min. Then the mixture was cooled, 100 ml of CH_2Cl_2 was added, and the mixture was washed several times with water and dried over $MgSO_4$. After evaporating the solvent the residue was vacuum-distilled. We obtained 7.2 g (69%) of (Ic), bp 98°/1 mm. PMR spectrum ($CDCl_3$, δ, ppm): 1.45 d (2MeCH), 2.33 s (MeCO) 3.13 s (MeSO$_2$), 4.45 m (CH−N). IR spectrum (ν, cm^{-1}): 1705 (C=O), 1350, 1170 (S=O). Found: C 40.46; H 7.48; S 17.53%. $C_6H_{13}O_3NS$. Calculated: C 40.2; H 7.26; S 17.88%.

Preparation of N-Methyl-N-carbomethoxymethanesulfamide (IV). With stirring, to a suspension of 10 g (0.076 mole) of $CH_3SO_2N(CH_3)Na$ in 50 ml of abs. ether was added in drops a solution of 7.2 g (0.076 mole) of MeOCOCl in 10 ml of abs. ether. The mixture was stirred for 2.5 h at ~ 20°. The precipitate was filtered and the solvent was evaporated in vacuo. We obtained 9.9 g (78%) of (IV), mp 65.5-66° (from EtOH). PMR spectrum (C_2D_6CO, δ, ppm): 3.11 s (MeSO$_2$), 3.2 (MeOCO), 3.72 s (MeN). IR spectrum (KBr, ν, cm^{-1}): 1745 (C=O); 1355, 1155 (S = O). Found: C 28.72; H 5.42%. $C_4H_9O_4NS$. Calculated: C 28.70; H 5.39%.

Preparation of N-Methyl-N-carbomethoxy-p-toluenesulfamide (V). With stirring and cooling with water, to a suspension of 3.11 g (0.015 mole) of p-$MeC_6H_4SO_2N(Me)Na$ in 30 ml of abs. MeCN was added in drops 1.42 g (0.015 mole) of $MeOCH_2Cl$. The mixture was stirred for 5 h at ~ 20°. The precipitate was filtered and the solution was evaporated in vacuo to give 3.1 g (85%) of (V), mp 75-76° (from i-PrOH). PMR spectrum (acetone-d$_6$, δ, ppm): 2.38 s (p-MeC_6H_4), 3.29 s (MeOCO), 3.60 s (MeN), 7.6 q (aromatic H). IR spectrum (KBr, ν, cm^{-1}): 1735 (C=O); 1595 (C=C); 1360; 1165 (S=O). Found: C 49.33; H 5.59, S. 13.26%. $C_{10}H_{13}O_4NS$. Calculated: C 49.45; H 5.35; S 13.28%.

N-Ethyl-N-nitromethanesulfamide (Xb). bp 82-83°/1 mm, n_D^{25} 1.4711. PMR spectrum ($CDCl_3$, δ, ppm): 1.3 t (MeCH$_2$); 3.45 s (MeSO$_2$); 4.15 q (CH$_2$N). IR spectrum (ν, cm^{-1}): 1573, 1285 (N−NO$_2$), 1370, 1175 (S=O).

N-Isopropyl-N-nitromethanesulfamide (Xc), bp 88-89°/1 mm, mp 33-35°. PMR spectrum (acetone d$_6$, δ, ppm): 1.45 d (MeCH); 3.55 s (MeSO$_2$); 4.85 m (CHN). IR spectrum (ν, cm^{-1}): 1585, 1270 (N−NO$_2$); 1370, 1180 (S=O). Found: C 26.40; H 5.68%. $C_6H_{18}O_3NS$. Calculated: C 26.39; H 5.54%.

N-Methyl-N-carbomethoxy-4-methylnitrobenzenesulfamide (XIV). mp 91-91.5° (from EtOH). PMR spectrum (acetone d$_6$, δ, ppm): 2.63 s (p-MeC_6H_4); 3.35 s (MeCO$_2$); 3.67 s (MeN); 8.1 m (aromatic H). IR spectrum (KBr, ν, cm^{-1}): 1740 (C=O); 1605 (C=C); 1533, 1290 (C−NO$_2$); 1368, 1175 (S=O). Found: C 41.21; H 4.09, N 9.97%. $C_{10}H_{12}O_6N_2S_1$. Calculated: C 41.60; H 4.17; N 9.73%.

N-Methylnitrophthalimide (XVII), mp 178-179° (from CCl_4: $CHCl_3$ − 3:1), PMR spectrum (acetone-d$_6$, δ, ppm): 3.1 s (MeN); 8.35 m (aromatic H). IR spectrum (KBr; ν, cm^{-1}): 1730, 1615 (C=O); 1620 (C=C); 1535, 1250 (C−NO$_2$). Found: C 52.01; H 2.84%. $C_8H_6O_4N_2$. Calculated: C 52.40; H 2.91%.

CONCLUSIONS

1. We effected the substitutive nitration of some linear N-alkylimides of carboxylic and sulfonic acids to N-alkyl-N-nitroamides, and also of N-methylacetamide to N-methyl-N,N-dinitroamine.

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* In some cases (see Table 1) the amount of BF_4NO_2 was 0.01 mole.

2. The activity of the acid moieties of the studied N-alkylimides in this reaction decreases in the order: MeCO > $MeSO_2 \gg p\text{-}Me(NO_2)C_6H_3SO_2$, COOMe.

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REACTION OF HYDRIDE COMPLEXES OF PLATINUM AND IRIDIUM WITH TRIARYLMETHYL CATIONS

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Z. N. Parnes, and D. N. Kursanov

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Recently it was shown that the phosphine complexes of Pt and IR are catalysts for the ionic hydrogenation of olefins and carbonyl compounds [1]. During reaction the hydride complex of the metal transfers the hydrogen as hydride ion* to the intermediately formed carbenium or carboxonium ion.

The ability of the hydrides of the transition metals to be hydride-ion donors toward carbenium ions has received little study. It was shown that the dihydrides of ruthenium reduce the triphenylcarbenium ion to give triphenylmethane and the ruthenium cationic complex [2]. The reduction of the diphenyl- and triphenylcarbocations with a large excess of the hydride complexes of Pt and Ir in the presence of H_2SO_4 was described in [3].

We studied the reduction of some substituted trityl cations by the hydride complexes of Pt and IR in the absence of an acid. When the triphenyl and tri-p-tolycarbenium perchlorates are reacted with trans-$(Ph_3P)_2Tp(H)Cl$ in $CHCl_3$ at ~ 20°C for 140 h we isolated the corresponding triarylmethanes in close to 100% yields. With the other conditions constant, the yield of the triarylmethane depends on the pK_{R^+} of the ion and decreases in the order: Ph_3C^+ (pK_{R^+} −6.6) > $(p\text{-}CH_3C_6H_4)_3C^+$ (−3.5) > $(p\text{-}CH_3OC_6H_4)_3C^+$ (+0.8).

The reaction of trityl chloride with trans-$(Ph_3P)_2Pt(H)Cl$ is slower. In the IR spectrum of the mixture of reactants in $CHCl_3$ at 20° the intensity of the band of the Pt−H bond at 2225 cm^{-1} decreases in half after 240 h. At the same time the band of the C−H bond at 2855 cm^{-1}, which is characteristic for triphenylmethane and is absent in the IR spectrum of the starting trityl chloride, appears and increases in intensity. The IR spectrum of the reaction mixture is completely identical with the spectrum of the specially prepared mixture of trityl chloride, triphenylmethane, $(Ph_3P)_2Pt(H)Cl$ and $(Ph_3P)_2PtCl_2$. After running the experiment all of the indicated compounds were isolated from the reaction mixture. The platinum cis-dichloride and trans-chlorohydride do not depress the mixed melting point with authentic specimens.

It is interesting to mention that when the hydride complex of Pt is added to a solution of trityl chloride in DCE, where the degree of ionization of trityl chloride is very slight, the λ_{max} at 430 nm, which corresponds to the trityl cation, disappears in the UV spectrum of the solution in several seconds. However, triphenylmethane is not formed here, since the addition of CF_3COOH to the obtained solution leads to the quanti-

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*The total transfer of a proton and two electrons from one molecule to another is considered to be the process for the transfer of hydride ion.

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