LITERATURE CITED

1. M. Jacobson, K. Ohinata, D. L. Chambers, W. A. Jones, and M. S. Ejiumoto, J. Med. Chem., 16, 248 (1973).
2. M. Jacobson, I. Keiser, D. L. Chambers, D. Miyashita, and C. Hardig, J. Med. Chem., 14, 236 (1971).
3. G. Jones, M. A. Acquadro, and M. A. Carmody, J. Chem. Soc. Chem. Commun., 1975, 206.
4. R. Rossi, Chim. Ind. (Milan), 59, 591 (1977).
5. A. Martinez, M. O. Euis, and A. T. Avello, Spanish Patent 485357; C. A., 94, 83599 (1981).
6. E. J. Smutny, J. Am. Chem. Soc., 89, 6793 (1967).
7. L. I. Zakharkin and T. B. Agakhanova, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 1400.

NITRATION OF N-CHLOROMETHYL-SUBSTITUTED SECONDARY AMIDES BY NITRONIUM TETRAFLUOBORATE

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In the nitration of a number of secondary amide derivatives the role of the leaving group is played by either an alkoxymethyl or an amidomethyl cation [1, 2], whose relative thermodynamic stability is determined by the delocalization of the charge involving the unshared electron pair (UEP) of the adjacent heteroatom (N, O)

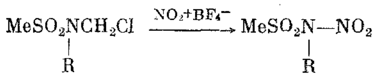
$$RN(Y)CH_2X \xrightarrow{NO_2^+BF_4^-} RN(Y)NO_2 + (\overset{+}{C}H_2X \leftrightarrow CH_2{=}\overset{+}{X})BF_4^-$$

$$X = MeO,\ RN(Y);\ Y = MeSO_2,\ MeO_2C.$$

It seemed of interest to ascertain the behavior of similar compounds, which contain the Cl atom as the heteroatom with an UEP, which atom is less capable of polar conjugation [3] and, consequently, stabilization of the carbcation.

In this connection we studied the nitration of the N-chloromethyl-substituted secondary amides of the acetic, carbonic, nitric, and sulfonic acids using nitronium tetrafluoborate (NTFB). It was established that the character of the thus formed nitration products is quite dependent on the nature of the acid moiety and the nitration conditions (Table 1).

When N-chloromethyl-N-methylmethanesulfamide (I) is nitrated in MeCN the main reaction product is N-nitro-N-methylmethanesulfamide. Replacing the MeN group in (I) by the more bulky Me_2CHN leads to a decrease in the yield of the corresponding nitrosulfamide due to a decrease in the steric accessibility of the amide N atom. Nevertheless, it remains the main nitration product.



$$MeSO_2\underset{\displaystyle R}{\underset{|}{N}}CH_2Cl \xrightarrow{NO_2^+BF_4^-} MeSO_2\underset{\displaystyle R}{\underset{|}{N}}{-}NO_2$$

R = Me, *i*-Pr.

As a result, in these cases the amide N atom is attacked by the nitronium cation, while the role of the leaving group is formally fulfilled by the chloromethyl cation. This tendency is also partially retained when going from the chloromethyl-substituted secondary amides of sulfonic acids to the corresponding urethane derivative.

$$(III) \xrightarrow{NO_2^+BF_4} (VIII)$$

However, the main attack here is not on the amide N atom; the nitronium cation attacks mainly the Cl atom. Among other things, the fate of the charged particle that is formed here is determined by the character of the employed solvent. In CH_2Cl_2 the main product is methylenebis-N-methylurethane (IX). In MeCN, together with

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TABLE 1. Nitration Conditions and Reaction Products of N-Alkyl-N-chloromethylamides with NTFB

Nitrated compound	Solvent	Reaction time at 20°C, h	Products	Separation method	Yield, %	Yield when based on PMR spectrum, %
$\mathrm{MeSO_2\underset{Me}{N}CH_2Cl}$ (I)	MeCN	1	$\mathrm{MeSO_2\underset{Me}{N}NO_2}$ (VI)	TLC	72	
$\mathrm{MeSO_2\underset{CHMe_2}{N}CH_2Cl}$ (II)	MeCN	3	$\mathrm{MeSO_2\underset{CHMe_2}{N}NO_2}$ (VII)	TLC	30	
$\mathrm{MeO_2C\underset{Me}{N}CH_2Cl}$ (III)	MeCN	1	$\mathrm{MeO_2C\underset{Me}{N}NO_2}$ (VIII)	Vacuum-distillation	36	36
			$\mathrm{MeO_2C\underset{Me}{N}CH_2\underset{Me}{N}CO_2Me}$ (IX)		20	28
			$\mathrm{MeO_2C\underset{Me}{N}CH_2NHCOMe}$ (X)		6*	25
	$\mathrm{CH_2Cl_2}$	1	(VIII) (IX)			14 58
$\mathrm{O_2N\underset{Me}{N}CH_2Cl}$ (IV)	MeCN	1	$\mathrm{O_2N\underset{Me}{N}CH_2\underset{Me}{N}NO_2}$ (XI)	TLC	54	
$\mathrm{MeCO\underset{Me}{N}CH_2Cl}$ (V)	MeCN	0,5	Complex mixture			

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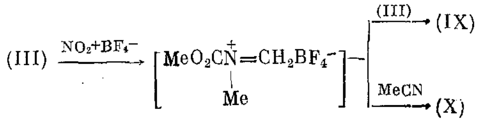
* It was shown that (X) is converted to (IX) at ~ 100°.

(IX), the N-acetamidomethyl derivative of the urethane (X) is formed in nearly the same amount of (IX), apparently by the following scheme:



Replacing the acid moiety in the N-chloromethyl derivatives of the carbonic and sulfonic acids by a stronger electron acceptor, like the nitro group, lowers the nucleophilicity of the amide N atom to such a degree that attack on the latter, in general, evidently becomes impossible. The main reaction product here is the corresponding methylenebis-N-alkylamide.

$$(IV) \xrightarrow{NO_2^+BF_4} (XI)$$

As a result, when the behavior of alkylamides of general formula $RN(Y)CH_2X$ (Y = acid moieties; X = Cl, OR, N(Y)R) in nitration reactions using nitronium salts is compared it can be seen that in all cases the amide N atom, the heteroatom of fragment X, or both of these centers, undergoes electrophilic attack. The ratio of the formed products is determined by the character of the acid moiety and the heteroatom containing the UEP.

EXPERIMENTAL

General Procedure for Nitrating N-Alkyl-N-chloromethylamides. With vigorous stirring and cooling to −25 to −30°C, 5 mmoles of NO_2BF_4 was added in small portions to a solution of 5 mmoles of the nitrated compounds in 15 ml of abs. MeCN (or CH_2Cl_2), after which the mixture was allowed to warm up to ~20° and stirred at ~ 20° for a definite time (see Table 1). The reaction mixture was poured into 20 ml of ice water, extracted with CH_2Cl_2 (5 × 15 ml), washed with water, and dried over Na_2SO_4. The solvent was evaporated in vacuo. The mixture of products was separated either by fractional distillation or by TLC on silica gel. The structure of the products was confirmed via the IR and PMR spectra by comparing with authentic specimens [1, 4-7].

N-Isopropyl-N-chloromethylmethanesulfamide (II) was obtained the same as (I) [8]. With vigorous stirring, 6.9 g (50 mmoles) of $MeSO_2NH(i\text{-}Pr)$ was added in small portions to a suspension of 2.25 g (75 mmoles) of paraform in 10 ml of $SOCl_2$. Stirring at ~ 20° was continued until the gas evolution ceased. The excess paraform was filtered and the $SOCl_2$ was evaporated in vacuo. The oily residue was distilled to give 7.5 g (82%) of (II), bp 96-97° (1 mm). PMR spectrum ($CDCl_3$, δ, ppm): 1.35 s (2 MeCH), 3.05 s ($MeSO_2$), 4.16 m (CHN), 5.45 s (CH_2). Infrared spectrum (ν, cm^{-1}): 1350, 1165 (S =O), 847 (CCl).

N-Methyl-N-acetamidomethylurethane (X) was isolated from the reaction mixture, bp 90° (1 mm). PMR spectrum ($CDCl_3$, δ, ppm): 1.97 s (MeCO), 2.82 s (MeN), 3.53 s (MeO), 4.61 d (CH_2). Infrared spectrum (ν, cm^{-1}): 3330 (NH), 1724 (CO_2), 1680 (C =O), 1550, 1280 (NH), 1215 (COC).

CONCLUSIONS

When treated with nitronium tetrafluoborate the N-chloromethyl derivatives of the secondary amides of the carbonic, sulfonic, and nitric acids form either the corresponding N-alkyl-N-nitramides, methylenebis-N-alkylamides, or their mixture.

LITERATURE CITED

1. O. A. Luk'yanov, T. G. Mel'nikova, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 2335.
2. O. A. Luk'yanov, T. G. Mel'nikova, E. G. Kashirskaya, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 2610.
3. V. A. Pal'm, Principles of Quantitive Theory of Organic Reactions [in Russian], Khimiya, Moscow (1977), p. 204.
4. E. H. White, M. C. Chen, and L. A. Dolak, J. Org. Chem., 31, 3038 (1966).
5. O. A. Luk'yanov, V. P. Gorelik, V. A. Tartakovskii, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 1804.
6. R. C. Brain and A. H. Lamberton, J. Chem. Soc., 1949, 1633.
7. L. Goodman, J. Am. Chem. Soc., 75, 319 (1953).
8. C. Beerman and H. Ramloch, German Patent 1915898 (1970); C. A., 74, 13741v (1971).

ACETYLENIC DERIVATIVES OF ANILINE

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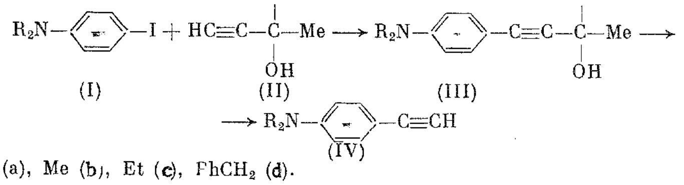
In planning a search for new light-sensitive systems it was proposed to develop a scheme for the synthesis of acetylenic aniline derivatives, general methods for whose preparation remain practically undeveloped. The syntheses of the individual acetyleneanilines are characterized by being either multistep, as in the case of obtaining p-ethynyl-N,N-dimethylaniline from p-bromo-N,N-dimethylaniline [1], or restricted, as in the synthesis of ethynyl-N,N-dialkylanilines from phenylacetylene and dialkylamines, or by the inavailability of the starting aminoacetophenones, as in the case of going from the acetyl group to the ethynyl group [2].

We used the method of direct condensation of terminal acetylenes with iodoaryls (I) in the presence of $Pd(PPh_3)_2Cl_2-CuI$ in amines as the medium [3], which leads to the acetylenic carbinols (III) in 70-85% yield, which are cleaved by the reverse Favorskii reaction to give the ethynylanilines (IV) in 70-85% yield.



R = H (a), Me (b), Et (c), $PhCH_2$ (d).

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