NITRATION OF TETRAALKYL-SUBSTITUTED METHYLENEDIAMINE DERIVATIVES WITH NITRONIUM TETRAFLUOBORATE AND NITROGEN PENTOXIDE

O. A. Luk'yanov, N. M. Seregina,
and V. A. Tartakovskii

UDC 542.958.1:547.415.1

Depending on the composition of the nitrating agent and the reaction temperature, the tetraalkyl-substituted derivatives of methylenediamine (TAM) when reacted with HNO_3, with a mixture of HNO_3 and Ac_2O [1,2], or with Ac_2O and NH_4NO_3 [2], form amine nitrates, and secondary nitroso- or nitramines.

We made a study of whether the TAM can be converted to nitramines by treatment with nitronium tetrafluoborate (NTFB), nitrogen pentoxide (NP) or nitroxyl chloride (NC). It was found that TAM in CH_3CN or CH_2Cl_2 is smoothly nitrated by NTFB to the corresponding secondary nitramines (Table 1). The radicals on the nitrogen atoms can be either primary, secondary, cyclic, or unsaturated. The structure of the formed nitramines was established by comparing the IR spectra, refractive indices, and R_f with the analogous characteristics of the authentic compounds.

$$R_2NCH_2NR_2 + NO_2BF_4 \rightarrow R_2N{-}NO_2 + R_2NCH_2^+BF_4^-$$

When the TAM are reacted with NTFB we were able to record, together with the nitramines, a second reaction product and specifically the dialkylimmonium fluoborate salt. Thus, the NMR spectrum of the ether-insoluble product from the reaction of NTFB with methylenebis(dimethylamine) (in CH_3CN) represents a singlet of the CH_2 group at 7.6 ppm (here and subsequently on the δ scale), and a singlet of the two CH_3 groups at 3.5 ppm.

$$(CH_3)_2NCH_2N(CH_3)_2 + NO_2BF_4 \rightarrow (CH_3)_2N{-}NO_2 + (CH_3)_2NCH_2^+BF_4^-$$

The NMR spectra of the saltlike products from the reaction of NTFB with methylenebis(diethylamine), methylenebis(diisobutylamine), and methylenebis(morpholine) also contain, besides the protons of the corresponding alkyl groups, a singlet of the protons of the methyleneimmonium group at 7.9-8.05 ppm.

As can be judged from the NMR spectra, along with the methyleneimmonium salts, dialkylammonium salts are also formed to variable degree, apparently due to the ease with which the former hydrolyze.

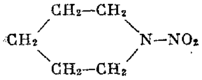
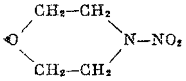
NP also proved to be a quite efficient nitrating agent for the TAM, although the yields of the secondary nitramines under the selected temperature conditions of the reaction proved to be noticeably lower than with NTFB (see Table 1).

It should be mentioned that we were unable to record a narrow singlet in the 7.6-8.1 ppm region in the NMR spectrum of the products from the reaction of NP with methylenebis(dimethylamine). A broad band at 6.8-7.3 ppm was observed in place of it. Attempts to nitrate the TAM with NC proved unsuccessful.

$$R_2NCH_2NR_2 + N_2O_5 \rightarrow R_2N{-}NO_2$$

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.1, pp.225-226, January, 1976. Original article submitted July 9, 1975.

TABLE 1. Yields and Melting Points of the Secondary Nitramines Formed from Tetraalkyl-Substituted Methylenediamine Derivatives and Nitronium Tetrafluoborate or Nitrogen Pentoxide

Nitramine	NO_2BF_4		N_2O_5	
	Yield, %	mp (bp), °C	Yield, %	mp (bp), °C
$(CH_3)_2N-NO_2$ [3]	66	55	54,6	52—53
$(C_2H_5)_2N-NO_2$ [4]	78	—	—	—
$[(CH_3)_2CHCH_2]_2N-NO_2$ [5]	58	76—77	25	75—77
$(CH_2{=}CHCH_2)_2N-NO_2$	65,5	96—97 (9—10 mm)	—	—
 [6]	65	93—95 (8—9 mm)	28	—
 [5]	70	—	36,6	49—50

EXPERIMENTAL METHOD

The substituted methylenediamine derivatives were obtained from the corresponding secondary amines and either formaldehyde or paraform [7-9].

Nitration of Methylenediamines with Nitronium Tetrafluoborate. With stirring, to a solution of 1 g of the substituted methylenediamine in 15 ml of abs. CH_3CN at −25° to −30° was added an equimolar amount of BF_4NO_2, after which the temperature was slowly raised to 20° and kept there for 30-40 min. The CH_3CN was vacuum-distilled, and the secondary N-nitramine was extracted from the residue with ether. The ether-insoluble product represented the crude dialkylmethyleneimmonium tetrafluoborate.

The N,N,N,N-tetraisobutyl- and N,N,N,N-tetraallylmethylenediamines were nitrated under analogous conditions, but in CH_2Cl_2. At the end of nitration the reaction mixture was poured into water, and the N-nitramines were extracted with CH_2Cl_2 and purified by preparative TLC on silica gel. The yields and melting points of the obtained nitramines are given in Table 1.

Diallylnitramine. Found: C 50.69; H 7.33; N 19.86%. $C_6H_{10}N_2O_2$. Calculated: C 50.70; H 7.05; N 19.71%.

Nitration of Methylenediamines with Nitrogen Pentoxide. With stirring, to a solution of 1 g of the substituted methylenediamine in 10 ml of abs. CH_3CN at −25° was added an equimolar amount of N_2O_5 as a chilled solution in CH_2Cl_2. The temperature was slowly raised to 20°, kept there for 20-30 min, the solvent was vacuum-distilled, and the N-nitramines were extracted from the residue with ether. The yields and melting points of the obtained nitramines are given in Table 1.

CONCLUSIONS

Nitronium tetrafluoborate and nitrogen pentoxide nitrate the tetraalkyl derivatives of methylenediamine to the corresponding secondary nitramines. In the case of nitronium tetrafluoborate a second reaction product is the dialkylmethyleneimmonium tetrafluoborate.

LITERATURE CITED

1. H. Boeme and K. Hermann, Ann. Chem., 688, 78 (1965).
2. F. Chapman, J. Chem. Soc., 1631 (1949).
3. A. Franchimont, Rec. Trav. Chim., 2, 123, 343 (1883).
4. A. Franchimont, Rec. Trav. Chim., 6, 149 (1887).
5. D. William, W. Emmons, and J. Freeman, J. Am. Chem. Soc., 77, 4387 (1955).
6. E. Bamberger and M. Kirpal, Ber., 28, 536 (1895).
7. A. I. Kolotov, Zh. Russ. Fiz.-Khim. Obshchestva, 17, 244 (1885).
8. E. Ehrenberg, J. Prakt. Chem., [2], 36, 124 (1887).
9. E. Knoevenagel, Ber., 31, 2586 (1898).