Interaction of the trimethylsilyl cation with molecules of aliphatic nitro compounds in the gas phase

V. I. Kadentsev, N. G. Kolotyrkina, A. A. Stomakhin, O. S. Chizhov, and S. A. Shevelev*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: 007 (095) 135 5328

Interaction of mononitroalkanes with the trimethylsilyl cation in the gas phase under chemical ionization (CI) conditions results in the formation of $[M+SiMe_3]^+$ ions, which are more stable than the corresponding protonated molecular ions. In the case of 2-nitro-2-methylpropane and 2-nitropentane, fragmentation of the $[M+SiMe_3]^+$ ions occurs with the formation of $C_4H_9^+$ and $C_5H_{11}^+$ carbocations, respectively. In the case of 1,1-dinitroethane and 1-halo-1,1-dinitroethane, fragmentation of the $[M+SiMe_3]^+$ ions occurs with splitting off of a $NO_2^{\cdot}$ radical or an XNO_2 molecule (X = H, F, or Cl).

Key words: mass spectrometry, chemical ionization, trimethylsilyl cation, aliphatic nitro compounds.

In a continuation of our studies[1] of reactions of the trimethylsilyl cation with organic molecules in the gas phase,[2] in this work we studied the chemical ionization (CI) mass spectra of aliphatic nitro compounds using tetramethylsilane as the reagent gas.

Experimental

Mass spectra were recorded on a Kratos MS-30 mass spectrometer (energy of ionizing electrons 200 eV, temperature of the ion source 150 °C). The reagent gas pressure (0.2 Torr) was kept constant with the use of an external manometer mounted on the inlet system. Tetramethylsilane (Merck) of 99.7% purity was used in the experiments. The samples were introduced through a heated direct inlet system. Nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane were commercial reagents of analytical grade. 2-Nitro-2-methylpropane, 2-nitropentane, 1,1-dinitroethane, 1-fluoro-1,1-dinitroethane-, and 1-chloro-1,1-dinitroethane were obtained using previously described procedures (see Refs. 3—7, respectively). According to GLC data, none of the samples contained impurities.

Results and Discussion

The CI mass spectra of mononitroalkanes with tetramethylsilane as the reagent gas contain ions of two types (ion-adducts and fragment ions). No appreciable quantity of fragment ions is formed in the case of lower members of the homologous series (Table 1). As is known, tetramethylsilane plasma contains more than 10 types of secondary ions,[8,9] among which the adducts with organic molecules are the most efficient in producing the main component of the plasma, the trimethylsilyl cation Me_3Si^+ (*m/z* 73), as well as the $Me_5Si_2^+$ (*m/z* 131) and $Me_3SiCH_2SiMe_2^+$ (*m/z* 145) ions.[7] In this regard, nitroalkanes do not differ from other organic compounds, and all possible ion-adducts are present in their CI mass spectra. The $[M+SiMe_3]^+$ ions formed from mononitroalkanes are somewhat more stable than the corresponding protonated molecular ions (*cf.* Ref. 1). The only direction of the fragmentation of ion-adducts is formation of the R^+ carbocation (see Table 1).

Table 1. CI mass spectra of mononitroalkanes RNO_2 (with tetramethylsilane as the reagent gas)

Compound	*m/z* (I_{rel} (%))			
	$[M+SiMe_3]^+$	$[M+Si_2Me_5]^+$	$[M+Me_5Si_2CH_2]^+$	R^+
Nitromethane	134 (100)	192 (9.8)	206 (14.4)	—
Nitroethane	148 (100)	206 (14.3)	220 (17.5)	—
1-Nitropropane	162 (100)	220 (10.4)	234 (5.7)	—
2-Nitropropane	162 (100)	220 (20.9)	234 (15.1)	—
2-Nitro-2-methylpropane	176 (15.7)	234 (4.3)	248 (2.0)	57 (100)
2-Nitropentane	(25.7	248 (0.4)	262 (0.4)	71 (100)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1232—1234, June, 1997.

1066-5285/97/4606-1184 $18.00

Table 2. CI mass spectra of 1,1-dinitroethane and 1-halo-1,1-dinitroethanes $MeCX(NO_2)_2$ (with tetramethylsilane as the reagent gas)

Compound	*m/z* (I_{rel} (%))		
	$[M+SiMe_3]^+$	$[M+SiMe_3-NO_2]^+$	$[M+SiMe_3-XNO_2]^+$
1,1-Dinitroethane	193 (45.5)	147 (40.5)	146 (100)
1-Fluoro-1,1-dinitroethane	211 (99.5)	165 (61.8)	146 (100)
1-Chloro-1,1-dinitroethane	227 (67.9)	181 (100)	146 (67.5)
	229 (24.4)	183 (42.7)	—

Other routes of fragmentation, analogous to the reactions of decomposition of the protonated molecular ions of nitroalkanes (elimination of H_2O and HNO),[2] were not observed in the case of ion-adducts of mononitroalkanes with the trimethylsilyl cation.

Unlike those of mononitroalkanes, the CI mass spectra of dinitroethanes contain ion-adducts of only one type, $[M+SiMe_3]^+$ (Table 2), which decompose with the loss of a stable $NO_2^{\cdot}$ radical similarly to the corresponding protonated molecular ions (*cf.* Ref. 1). By analogy with the $[M+H-NO_2]^+$ ions, the structure of $MeC^{\cdot}XN^+O_2 \cdot SiMe_3$ can be ascribed to the $[M+SiMe_3-NO_2]^+$ ions.

The another reaction path of fragmentation of the $[M+SiMe_3]^+$ ions of dinitroethanes, with the loss of an XNO_2 (X = H, F, or Cl) molecule, has no analogs among the fragmentation processes of their protonated molecular ions.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33398).

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Received January 9, 1997

Synthesis of 6α-methyl-16α,17α-cyclohexanoprogesterone *via* γ-methylenation of 16α,17α-cyclohexanopregn-4-ene-3,20-dione

I. S. Levina* and A. V. Kamernitskii

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: 007 (095) 135 5328

6-Methylene-16α,17α-cyclohexanopregn-4-ene-3,20-dione **2** has been synthesized by the reaction of Δ^4-3-ketone **1** with $CH_2(OEt)_2$ and $POCl_3$ in the presence of AcONa in 55% yield. Reduction of the product **2** in the presence of 5% Pd/C gives 6α-methyl-16α,17α-cyclohexanoprogesterone **3** in a yield exceeding 70%.

Key words: methylenation, pentarane, progestin.

6α-Methyl-16α,17α-cyclohexanoprogesterone (6α-methyl-D'_6-pentarane) (**3**) (Scheme 1) is a synthetic progestin that exhibits high progestational and contraceptive activities.[1] Earlier for the synthesis of compound **3**, the succession of transformations **4** → **5** → **6** → **3** (see Scheme 1) was used,[2,3] in which the key step was the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1234—1236, June, 1997.