Experimental

All the reactions were carried out under argon and monitored by TLC on Silufol UV-254 plates; preparative column chromatography was performed using SiO_2 Silpearl UV-254. NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 instrument operating at 400.13 MHz (^1H) and 100.61 MHz (^{13}C). The chemical shifts were referenced to the signal of the residual $CHCl_3$. EI mass spectra (70 eV) were run on an MS-890 spectrometer.

All solvents were thoroughly purified by known procedures. Complexes **2** [3] and **4** [4] were prepared by previously reported procedures.

(η^5-Cyclopentadienyl)(η^4-4-chloro-5-methylcyclohepta-2,4,6-trien-1-one)rhodium (5). A solution of a mixture of complex **4** (0.05 g, 0.127 mmol) and **2** (0.16 g, 0.140 mmol) in 8 mL of C_6H_6 was stirred for 72 h at 20 °C and concentrated on a rotary evaporator. The dry residue was chromatographed on SiO_2 (using a 3 : 1 C_6H_6—EtOH mixture as the eluent); the fraction with $R_f = 0.5$ was isolated. Evaporation of the solvent and crystallization of the residue from a C_6H_6—hexane (1 : 1) mixture gave 0.014 g of **5** (34%). Found (%): C, 48.44; H, 3.82. $C_{13}H_{12}ClORh$. Calculated (%): C, 48.40; H, 3.75. ^1H NMR, δ: 1.53 (s, 3 H, Me); 4.06 (d, 1 H, CH, $^2J_{H-H} = 7.8$ Hz); 4.20 (d, 1 H, $^3J_{H-H} = 7.8$ Hz); 4.92 (m, 2 H, 2 CH); 5.47 (d, 5 H, Cp, $^2J_{H-Rh} = 0.7$ Hz). ^{13}C NMR, δ: 18.4 (s, Me); 64.9 (d, CH, $^1J_{C-Rh} = 15.1$ Hz); 66.8 (d, CH, $^1J_{C-Rh} = 15.1$ Hz); 72.9 (d, CH, $^1J_{C-Rh} = 7.0$ Hz); 73.46 (d, CH, $^1J_{C-Rh} = 6.0$ Hz); 87.3 (d, Cp, $^1J_{C-Rh} = 5.0$ Hz). MS *m/z* (I_{rel}, (%)): 322 $[M]^+$ (18), 294 $[M-C=O]^+$ (16), 168 $[RhCp]^+$ (93), 154 $[M-RhCp]^+$ (6), 91 (100).

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Tetramethylsilane as reagent gas: mass spectra of nitrocarboxylic acid esters and nitroalcohols

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Nitrocarboxylic acid esters and nitroalcohols react with trimethylsilyl cation in the gas phase under conditions of chemical ionization to form stable $[M+SiMe_3]^+$ ions. The pathways of their fragmentation were established and characteristic distinctions in the mass spectra caused by mutual arrangement of functional groups were found.

Key words: mass-spectrometry, chemical ionization, trimethylsilyl cation, nitrocarboxylic acid esters, nitroalcohols.

In a continuation of our studies of reactions between the trimethylsilyl cation and nitroalkanes and halonitroalkanes in the gas phase,[1] in this work the chemical ionization (CI) mass spectra of nitroalcohols and carboxylic acid esters were studied using tetramethylsilane as the reagent gas.

Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz (^1H), 75.47 MHz (^{13}C), 59.63 MHz (^{29}Si, INEPT) (with tetramethylsilane as internal standard), and 21.69 MHz (^{14}N) (with $MeNO_2$ as external standard).

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Mass spectra were recorded on a Kratos MS-30 mass spectrometer at an energy of ionizing electrons of 200 eV and a temperature of the ion source of 150 °C. The reagent gas pressure was kept constant (0.2 Torr) using 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 direct inlet system. Methyl nitroacetate[2] (**1**), methyl 3-nitropropionate[3] (**2**), methyl 3-nitrobutyrate[4] (**3**), methyl 4-nitrobutyrate[5] (**4**), methyl 4-nitrovalerate[6] (**5**), ethyl 2-methyl-4-nitrobutyrate[7] (**6**), and 2-methyl-4-nitropentan-3-ol[8] (**7**) were obtained using previously described procedures, and the synthesis of 4-nitrohexan-2-ol (**8**) will be reported later. 4-Nitro-2-trimethylsiloxyiminohexane was obtained following the procedure reported in Ref. 9.

4-Nitrohexan-2-one. Water (250 mL) and conc. hydrochloric acid (50 mL) were added to 4-nitro-2-trimethylsiloxyiminohexane (5.68 g, 24 mmol), and the mixture was stirred at ~20 °C for 4 h. The mixture was diluted with water (500 mL) and extracted with ether (4×100 mL), and the combined ethereal layer was washed with water (2×40 mL) and dried with sodium sulfate. Evaporation *in vacuo* afforded 4-nitrohexan-2-one (3.10 g, yield 89%), b.p. 60—62 °C (0.2 Torr), n_D^{20} = 1.4433, ^{1}H NMR: 0.98 (t, 3 H, $^3J_{H(6)H(5)}$ = 7.4 Hz, C(6)H$_3$), 1.92 (m, 2 H, C(5)H$_2$), 2.21 (s, 3 H, C(1)H$_3$), 2.74 (dd, 1 H, $^2J_{H_AH_B}$ = 18.1 Hz, $^3J_{H_AH(4)}$ = 4.0 Hz, CH$_A$H$_B$), 3.32 (dd, 1 H, $^2J_{H_BH_A}$ = 18.1 Hz, $^3J_{H_BH(4)}$ = 8.7 Hz, CH$_A$H$_B$), 4.87 (m, 1 H, CH); ^{13}C NMR: 9.63 (C(6)H$_3$), 26.79 (C(5)H$_2$), 29.65 (C(1)H$_3$), 44.66 (C(3)H$_2$), 83.43 (CH), 203.66 (C=O); ^{14}N NMR: 10.76 (NO$_2$).

4-Nitrohexan-2-ol: ratio of isomers **8a** : **8b** 1 : 3. A solution of 4-nitrohexan-2-one (150 mg, 1 mmol) in 1 mL of anhydrous THF was added to 0.63 mL of a BH$_3$—THF solution (B—H concentration 6.69 mol L^{-1}) at 5 °C and kept at this temperature for 1.5 h. Then methanol (1 mL) was added dropwise and the mixture was poured into 7 mL of 2.5% HCl and extracted with ether (5×4 mL); the combined ethereal layer was washed with a saturated solution of NaCl (2×2 mL), and dried with sodium sulfate. Evaporation *in vacuo* afforded **8a,b** (140 mg, yield 95%), b.p 71—72 °C (0.3 Torr), ^{1}H NMR: 0.96 (**8a**) and 0.97 (**8b**) (t, 3 H, $^3J_{H(6)H(5)}$ = 7.4 Hz, C(6)H$_3$), 1.23 (**8a,b**) (d, 3 H, $^3J_{H(1)H(2)}$ = 6.7 Hz, C(1)H(3)), 1.65—2.28 (m, 4 H, CH$_2$), 2.40—2.85 (br, 1 H, OH), 3.77 (**8b**) and 3.89 (**8a**) (m, 1 H, CHOH), 4.57 (**8a**,**8b**) and 4.75 (**8b**) (m, 1 H, CHNO$_2$); ^{13}C NMR: **8a**: 10.06 (C(6)H$_3$), 23.60 (C(1)H$_3$), 27.29 (C(5)H$_2$), 42.07 (C(3)H$_2$), 65.32 (CHOH), 87.76 (CHNO$_2$), **8b**: 10.20 (C(6)H$_3$), 23.84 (C(1)H$_3$), 27.76 (C(5)H$_2$), 42.21 (C(3)H$_2$), 64.19 (CHOH), and 87.21 (CHNO$_2$). ^{14}N NMR: 14.88 (NO$_2$).

Results and Discussion

Polyfunctional organic compounds can be divided into two classes differing in reactivity toward the trimethylsilyl cation under conditions of chemical ionization,[10—12] namely, compounds containing and not containing mobile hydrogen atom. The addition of a Me$_3$Si$^+$ ion to a group carrying a mobile hydrogen atom results in the formation of a Brønsted acid of the Y—R—X$^+$(H)—SiMe$_3$ type capable of protonating YRXH molecules (XH is a functional group containing a mobile hydrogen atom, R is the hydrocarbon skeleton, and Y is a heteroatom or functional group) to form protonated molecular ions HY$^+$RXH and YRX$^+$H$_2$ and undergoing an intramolecular prototropic shift to give ions of the HY$^+$RXSiMe$_3$ type. In this case, the composition of fragment ions in the CI mass spectrum is determined by the structure and relative stability of [M+SiMe$_3$]$^+$ and [M+H]$^+$ ions. The behavior of compounds belonging to the second class depends entirely on the relative efficiency of trimethylsilylation of functional groups constituting their molecules.

The CI mass spectra (with SiMe$_4$ as the reagent gas) of nitrocarboxylic acid esters (**1**—**6**) contain intense peaks of adduct-ions [M+SiMe$_3$]$^+$, in which the SiMe$_3$ group can be bonded to either the nitro or ester group (Table 1, Scheme 1). Fragmentation of adduct-ions is determined by mutual arrangement of the two functional groups. The mass spectrum of methyl nitroacetate (**1**) contains no fragment ion peaks at all. The splitting of a nitrous acid molecule from [M+SiMe$_3$]$^+$ ions is characteristic of β-nitrocarboxylic esters **2** and **3**. This reaction, similar to elimination of a substituent from β-substituted carbonyl compounds, can occur only in those adduct-ions, in which the SiMe$_3$ group is bonded to the ester group. The mass spectra of γ-nitrocarboxylic esters **4**—**6** contain no peaks of [M+SiMe$_3$—HNO$_2$]$^+$

Scheme 1

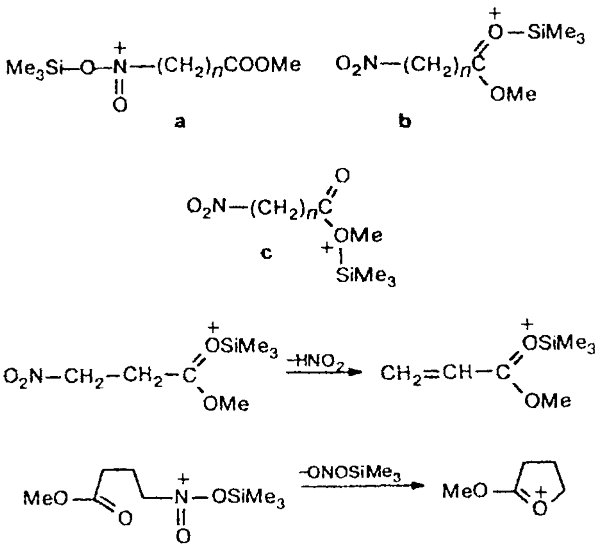
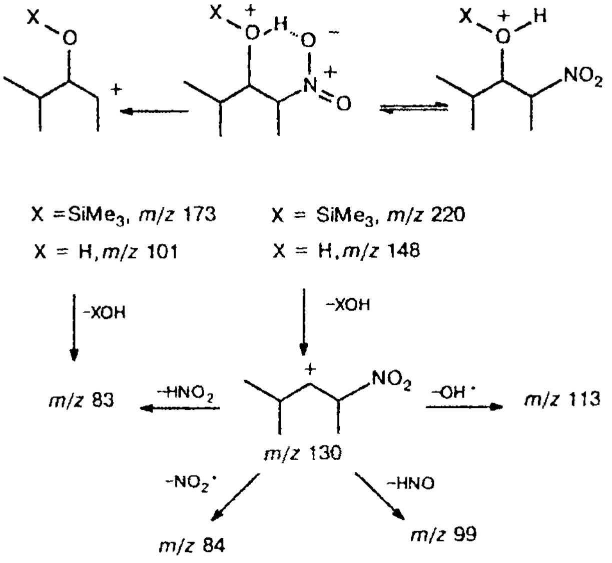


Table 1. Mass spectra of nitrocarboxylic acid esters (with tetramethylsilane as the reagent gas), *m/z* (intensity (%))

Ion	**1**	**2**	**3**	**4**	**5**	**6**
[M+SiMe$_3$]$^+$	192 (100)	206 (100)	220 (100)	220 (81)	234 (31)	248 (100)
[M+SiMe$_3$—HNO$_2$]$^+$	—	159 —	173 (92)	— (30)	— —	—
[M—OH]$^+$	— —	116 (16)	130 (13)	130 (20)	144 (11)	158 (21)
[M—NO$_2$]$^+$	— —	87 (12)	101 (28)	101 (100)	115 (100)	129 (80)

ions while those of $[M-NO_2]^+$ ions are the most intense; the latter can be due to merely those adduct-ions in which the $SiMe_3$ group is bonded to the nitro group. In this case, elimination of Me_3SiNO_2 can be accompanied by participation of the alkoxycarbonyl group, which results in the formation of a cyclic product and is the reason for increasing the probability of formation of $[M-NO_2]^+$ ions in the mass spectra of γ-nitrocarboxylic esters (Scheme 1).

Scheme 2



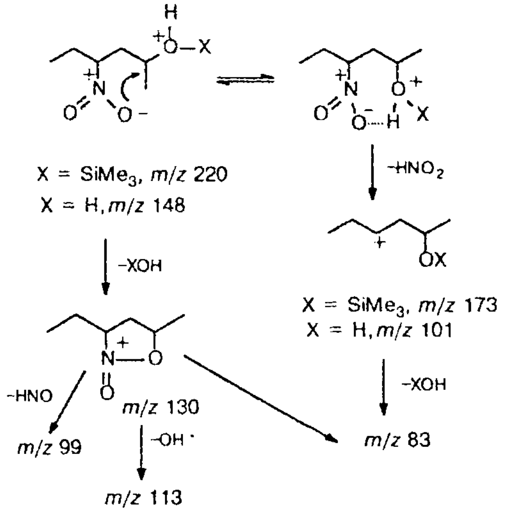
The CI mass spectra of nitroalcohols (**7** and **8**) also contain intense peaks of adduct-ions $[M+SiMe_3]^+$ (Table 2). The presence of trimethylsilyloxonium ions $Me_3SiO^+H_2$ (*m/z* 91) and $(Me_3Si)_2O^+H$ (*m/z* 163), which are rather strong acids in the gas phase, in the $SiMe_4$ plasma leads to protonation of molecules **7** and **8** with the formation of $[M+H]^+$.

The degree of fragmentation of $[M+SiMe_3]^+$ and $[M+H]^+$ ions depends strongly on the structure of starting compounds. In this case, the probability of formation of an intramolecular hydrogen bond between the hydroxyl and nitro groups plays a decisive role. This probability is rather high for compound **7**, where the formation of a six-membered ring is possible, and is much lower for nitroalcohol **8**, where a seven-membered cycle should be formed. That is why the intensity of the peak of the $[M+H]^+$ ion, additionally stabilized by intramolecular hydrogen bond, is considerably higher for nitroalcohol **7** than for compound **8**. On the contrary, elimination of Me_3SiOH and H_2O molecules from the $[M+SiMe_3]^+$ and $[M+H]^+$ ions (formed from compound **8** and having mainly an open structure), respectively, can occur with the participation of the nitro group, which results in the formation of an ion with *m/z* 130 that presumably has a cyclic structure (Scheme 3). This is likely the reason for the increased probability of formation of a cyclic ion as compared to that of an isomeric ion with *m/z* 130 (Scheme 2) and, as a consequence, for the higher intensity of the corresponding peak. The further fragmentation of ions with *m/z* 130 occurs with splitting off of HNO and HNO_2 (Table 2, Scheme 3).

Table 2. CI mass spectra of nitroalcohols **7** and **8** (with tetramethylsilane as the reagent gas)

Ion	*m/z*	*I*(%)	
		7	8
$[M+SiMe_3]^+$	220	100	100
$[M+SiMe_3-HNO_2]^+$	173	12	5
$[M+H]^+$	148	60	13
$[M-OH]^+$	130	13	51
$[M-2\,OH]^{+\cdot}$	113	17	12
$[M-NO_2]^+$	101	12	7
$[M-OH-HNO]^+$	99	17	48
$[M-OH-NO_2]^{+\cdot}$	84	30	6
$[M-OH-HNO_2]^+$	83	18	34

Scheme 3



Thus, the CI mass spectra (with tetramethylsilane as the reagent gas) of nitrocarboxylic acid esters and nitroalcohols make it possible to determine the molecular masses of these compounds owing to the presence of the intense peaks of $[M+SiMe_3]^+$ ions. The specific features of fragmentation help in determining the position of the nitro group relative to the second functional group of the molecule. The branching of the hydrocarbon skeleton has little effect on the character of fragmentation of nitrocarboxylic acid and nitroalcohol ions $[M+SiMe_3]^+$ and $[M+H]^+$.

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Reactivity of molecules with nitrogen-containing functional groups toward H^+ and $SiMe_3{}^+$ ions

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The equilibrium constants of trimethylsilyl cation transfer reactions differ from those of proton transfer reactions by many orders of magnitude. The basicity of MeCN (**1**), $MeNO_2$ (**2**), and Et_2NH (**3**) in the gas phase decreases in the series **3** >> **1** > **2**, whereas the affinity of the same compounds for trimethylsilyl cation decreases in the series **1** >> **3** ≈ **2**. Semiempirical quantum-chemical MNDO calculations indicate that the formation of $MeCN{\cdot}SiMe_3{}^+$ ions is thermodynamically more favorable than that of $MeNH_2{\cdot}SiMe_3{}^+$ ions.

Key words: mass spectrometry, chemical ionization, trimethylsilyl cation, basicity, acetonitrile, nitromethane, diethylamine.

The interaction of trimethylsilyl ion with substrate molecules under conditions of chemical ionization (CI) using $SiMe_4$ as the reagent gas results in the formation of weakly excited adducts $[M+SiMe_3]^+$, and the intensities of their peaks can serve as a measure of basicity of the molecules.[1,2] Being a bulkier analog of a proton, the Me_3Si^+ ion is incapable of either migration between functional groups or chelation with them.[3] In this work, the reactivity of MeCN, $MeNO_2$, and Et_2NH molecules in the reactions of H^+ (and $SiMe_3{}^+$) ion transfer was studied.

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. Equimolar mixtures were introduced through a heated direct inlet system.

Results and Discussion

The CI mass spectra of acetonitrile (**1**), nitromethane (**2**), and diethylamine (**3**) with tetramethylsilane as the reagent gas contain only peaks of ion-adducts $[M+SiMe_3]^+$. If a mixture of compounds M^1 and M^2 is introduced simultaneously, then thermodynamically controlled reactions (1) and (2) occur in the ionization chamber of the mass spectrometer.

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