The First Long-Lived Olefinic π-Complex of Nitrosonium Cation: Structure and Degenerate Rearrangement of the NO^+–Octamethyl-1,4-cyclohexadiene π-Complex

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Although quantum-chemical calculations indicate olefin–NO^+ π-complexes to be rather stable,[1,2] to the best of our knowledge there have been no reliable data yet on their preparation (*cf.* ref 3).

We have prepared the π-complex **2a** (as the tetrachloroaluminate) by reaction of $NO^+AlCl_4^-$ with 1,2,3,3,4,5,6,6-octamethyl-1,4-cyclohexadiene (**1a**)[4] in SO_2/CD_2Cl_2 or $SO_2/SO_2ClF/CD_2Cl_2$ at −90 °C.

Complex **2a** undergoes a degenerate π,π-rearrangement by Scheme 1 (pathways i and ii).[7] This is confirmed by the NMR data, particularly by rather small downfield shifts of the pairwise averaged signal of methyl groups (1-CH_3 and 5-CH_3 as well as 2-CH_3 and 4-CH_3) in the ^1H NMR spectrum and those of the olefinic carbon atoms (C^1 and C^5 as well as C^2 and C^4) in the ^{13}C NMR spectrum relative to the corresponding signals of olefin **1a** (Table 1, Figure 1) (*cf.* refs 8–10). The difference value in chemical shifts for the olefinic carbon atoms of **2a** and the precursor **1a** ($C_{1,2,4,5}$) ($\Delta\delta = 30$ ppm) is much greater than that for the $C_{3,6}$ atoms ($\Delta\delta = 6$ ppm). This seems to be due to a considerable transfer of positive charge from the NO^+ group to the olefinic carbon atoms in **2a** (*cf.* refs 2, 8–10).

An alternative variant which forms "fluxional" σ-complexes **3** rather than π-complexes **2** (Scheme 2) (*cf.* ref 9) is rejected on the basis of the data which we have obtained by the isotope perturbation method.[11]

Complexes **2b,c** (as tetrachloroaluminates) have been prepared from the corresponding deuterated precursors **1b,c**[12] and $NO^+AlCl_4^-$ in SO_2/CD_2Cl_2. The ^{13}C NMR spectrum of **2b** shows "isotope splitting" of $C_{1,2,4,5}$ signals (at −80 °C, $\delta = 0.23$ ppm). The ^{13}C NMR spectrum of a mixture of complexes **2a,c** at −80 °C showed shifts of −1.18, −0.91, and 1.02 ppm for the atoms C_1, C_2, and $C_{4,5}$, respectively,[15] relative to the averaged signal of the atoms C_1, C_2, C_4, and C_5 of the non-deuterated π-complex **2a**. The small values of the "isotope splitting" correspond to the rearrangement of **2a** according to Scheme 1 (*cf.* refs 10, 11).

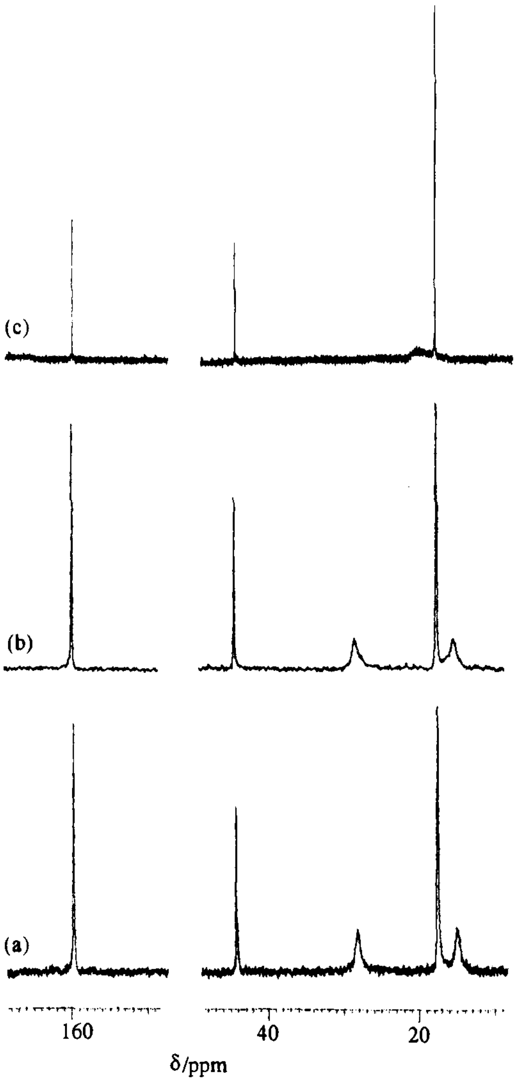
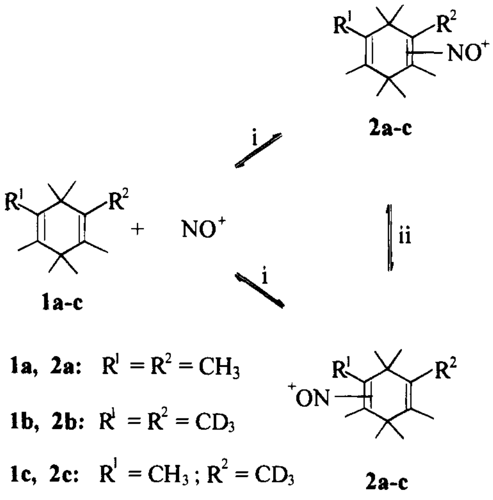


Figure 1. Variable-temperature ^{13}C NMR spectra (50.3 MHz) of the π-complex **2a** in $SO_2/SO_2ClF/CD_2Cl_2$ (~2:2:1) at −100 °C (a) and at −80 °C (b) and in SO_2/CD_2Cl_2 (~1:1) at −85 °C (c).

Scheme 1



1a, 2a: $R^1 = R^2 = CH_3$
1b, 2b: $R^1 = R^2 = CD_3$
1c, 2c: $R^1 = CH_3$; $R^2 = CD_3$

An equilibrium between nitrosonium cation, olefin **1a**, and π-complex **2a** is virtually completely shifted toward the latter. This is indicated by the low sensitivity of the ^1H and ^{13}C NMR

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[4] Compound **1a** was synthesized similarly to the literature procedure[5] by reaction of heptamethylbenzenium tetrachloroaluminate[6] with CH_3MgI. Satisfactory analytical and spectral data were obtained for this compound.

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[7] Upon "quenching" of the SO_2/CD_2Cl_2 solution of **2a** with methanol, the starting diene **1a** was recovered in 42% yield.

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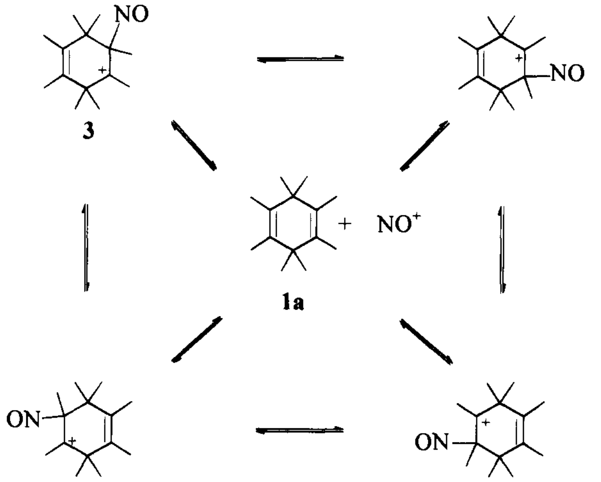
Table 1. ^{1}H and ^{13}C Chemical Shifts[a] for **1a** and **2a**

	solvent[b]	olefin/ $NO^+AlCl_4^-$ ratio	*T*, °C	δ (^{1}H) 3,3,6,6-CH_3	δ (^{1}H) 1,2,4,5-CH_3	δ (^{13}C) 1,2,4,5-CH_3	δ (^{13}C) 3,3,6,6-CH_3	$C_{1,2,4,5}$	$C_{3,6}$
1a	CD_2Cl_2		−80	0.96	1.53	14.4	25.0	129.7	38.5
2a	$SO_2/SO_2ClF/CD_2Cl_2$	1:1	−100	1.2 (br)[c]	1.90	17.6	15.1 (br), 28.3 (br)	159.7	44.4
	$SO_2/SO_2ClF/CD_2Cl_2$	1:1	−80	1.2 (br)	1.91	17.7	15.4 (br), 28.5 (br)	159.9	44.6
	SO_2/CD_2Cl_2	1:1	−85	1.19	1.89	17.5	21.9 (br)	159.6	44.2
	SO_2/CD_2Cl_2	1:4	−85	1.16	1.86	17.6	21.6 (br)	159.5	44.1

[a] In ppm relative to Me_4Si with CH_2Cl_2 (^{1}H, δ = 5.33 ppm) and CD_2Cl_2 (^{13}C, δ = 53.6 ppm) as internal standards. [b] Volume ratios $SO_2/SO_2ClF/CD_2Cl_2$ and SO_2/CD_2Cl_2 are ~2:2:1 and ~1:1, respectively. [c] br, broad.

Scheme 2



spectra of **2a** to variation of solvent, temperature, and the olefin/$NO^+AlCl_4^-$ ratio (Table 1).

It is interesting to note that the ^{13}C NMR spectrum of **2a** in $SO_2/SO_2ClF/CD_2Cl_2$ at −100 °C shows two slightly broadened signals of the 3,3,6,6-CH_3 groups, which at −80 °C[16] become still broader, while the ^{13}C NMR spectrum of this complex in SO_2/CD_2Cl_2 at −85 °C shows a coalesced signal of these groups (Figure 1). This may be due to the greater rate of the intramolecular migration of the NO group (Scheme 1, pathway ii) compared to the intermolecular migration (Scheme 1, pathway i). The rate of the latter in SO_2/CD_2Cl_2 is higher than that in $SO_2/SO_2ClF/CD_2Cl_2$, possibly because of the more efficient solvation of the NO^+ cation in the former case (*cf.* refs 17−19). The intramolecular π,π-rearrangement (Scheme 1, pathway ii) obviously proceeds via the structure of type **4**, which is energetically less favorable than the π-complex **2** because it does not satisfy the 8 electron rule.[20] This is confirmed by MINDO/3 calculations[21] (Figure 2). The structure **5** is 271 and 111 kJ/mol more favorable than the isomeric structures **4** and **6**, respectively. The geometry (Figure 2) and calculated charge distribution in the fragment C_1C_2N are close to those in the complex of NO^+ with ethylene.[2]

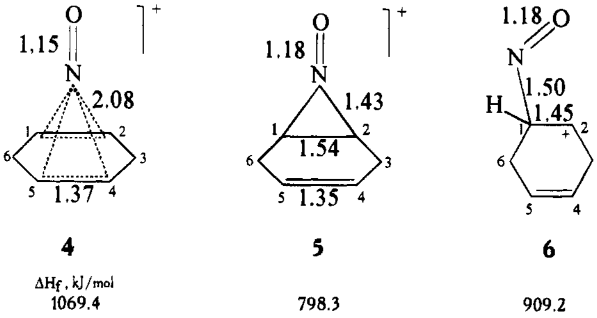


Figure 2. Key geometrical features of complexes **4**−**6** calculated by MINDO/3 (all bond distances in angstroms).

Using the MNDO/PM3 method[22] leads to the same relative stabilities of structures **4**−**6**, structure **4** not being a minimum on the potential energy surface.

The results obtained demonstrate that diolefins can form "fluxional" π-complexes with NO^+.

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(12) Compounds **1b**,**c** were synthesized similarly to the preparation of the non-deuterated analog **1a** by the reaction of the respective 2-R^1,6-R^2-1,1,3,4,5-pentamethylbenzenium tetrachloroaluminates ($R^1 = R^2 = CD_3$; $R^1 = CH_3$, $R^2 = CD_3$) with CH_3MgI. The salts were prepared from 3-methylene-1-R^1,5-R^2-2,4,6,6-tetramethyl-1,4-cyclohexadienes ($R^1 = R^2 = CD_3$; $R^1 = CH_3$, $R^2 = CD_3$, respectively) as described by Doering et al.[6] for the non-deuterated analog. The deuterated dienes were synthesized by the action of CH_3MgI on 3,5-di(trideuteriomethyl)-2,4,4,6-tetramethyl-2,5-cyclohexadien-1-one[13] or that of CD_3MgI on 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadien-1-one.[14]

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(15) Negative values are upfield from the signal of C_1,C_2, C_4, and C_5 atoms of the π-complex **2a**.

(16) At higher temperatures, **2a** is unstable.

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