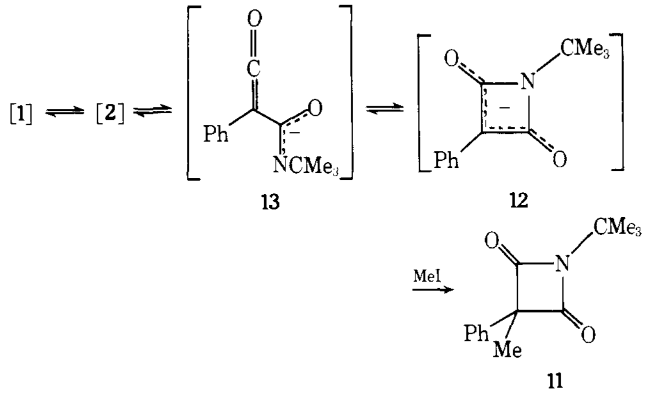
Scheme III



decarboxylation, led to the detection of a second intermediate. Infrared spectral assay of the reaction of **4** (where R′ = Ph or Me) with dimsyl anion in Me_2SO showed new peaks in the carbonyl region,[4] but no cumulene absorption for **1**. The new bands can be assigned to a second anion formed reversibly from **1**, on the basis of the following results with the *N-tert*-butyl substituent. Upon dilution of THF solutions of **1** with HMPA, the ir peak at 4.95 gradually disappeared as absorption for the second anion built up. In accord with a solvent-dependent equilibrium, the spectral change was reversed when more THF was added. In Me_2SO-d_6 concurrent ir and NMR assays indicated an apparent equilibrium mixture (1:1 in **1** and the second anion) was achieved within a few hours.[5] The second anion also formed diamide when solutions were poured into aqueous diethylamine and is more reactive than **1**, as expected for a subsequent intermediate such as **2** of Scheme II. Addition of amine salts to the *N-tert*-butyl anion mixture in Me_2SO resulted in the immediate reaction of the second anion, while consumption of **1** requires a few hours. In the same solvent, the reaction of the starting isoxazolone **4** with amines is on the time scale of weeks.

While decomposition of the second anions has prevented their thorough characterization to date, a trapping experiment has revealed that additional transformations beyond the reversible cyclization of Scheme I are accessible to this reactive system. The second anion, where R′ = CMe_3, in HMPA was converted to a stable derivative by methylation (MeI).[6] The molecular weight of the product ruled out a methylated dimer of **1**, and a high-field *C*-methyl signal in the ^1H NMR spectrum was indicative of a delocalized carbanionic precursor such as **2**. However, the methylation product was not sensitive to moisture or even amines, in contrast to the expectation for the *C*-methyl derivative of **2**. Rearrangement to the relatively stable malonimide system[7] would account for the results, and the presence of a single, low-field, carbonyl carbon signal (173 ppm downfield from Me_4Si) in the ^{13}C NMR spectrum (C_6D_6) confirmed that the methylation product was **11**.

The simplest mechanistic rationale for the formation of **11** would be the reversible anionic rearrangement of Scheme III. The second observed anion may well, then, be **12** rather than **2**, although the present evidence does not permit a rigorous conclusion. The absence of new infrared bands in the cumulene region in the polar solvents used excludes substantial concentrations of the free ketene **13**, but solvent-intercepted derivatives remain an additional possibility. Regardless of the structure of the predominant form of the anion in polar solvents, the rearrangement to the malonimide system in the trapping experiments raises the possibility of the ketene **13** as the actual intermediate leading to products of type **3**.

References and Notes

(1) J. Ficini and J. Pouliquen, *J. Am. Chem. Soc.*, **93**, 3295 (1971); *Tetrahedron Lett.*, 1131 (1972).

(2) D. J. Woodman and P. M. Stonebraker, *Tetrahedron Lett.*, 4473 (1970); D. J. Woodman, C. H. Borman, N. Tontapanish, and P. M. Stonebraker, *J. Org. Chem.*, **34**, 2981 (1969).

(3) The NMR and ir spectra were in accord with all structures shown. For **6–9** the properties also either agreed with reported values for the known compounds or satisfactory elemental analyses were obtained.

(4) In addition to peaks near 6.1 and 6.25 μ where R′ = Ph or Me, both anions show an unexpectedly short wavelength band at about 5.65 μ. In the case of R′ = CMe_3, only the 5.65 μ absorption is not masked by solvent (HMPA) or remaining **1** (in Me_2SO).

(5) The composition was invariant over a ninefold concentration range (keeping total ion concentration constant with added $NaNO_3$), providing possible support for intramolecular cyclization as opposed to an intermolecular reaction.

(6) Mp 46–47°. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.78; H, 7.63; N, 6.03. Molecular weight: theory, 231; Osmometric, 244; CI M S, 231. NMR ($CDCl_3$): 1.50 (s, 9), 1.66 (s, 3), 7.2–7.6 (m, 5).

(7) Infrared carbonyl absorption at 5.75 μ ($CHCl_3$) agrees with values reported for compounds assigned the malonimide structure.[8]

(8) J. A. Moore in "Heterocyclic Compounds", Vol. 19, Part Two, A. Weissberger, Ed., Interscience, New York, N.Y., 1964, p 954, Chapter 7.

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Rearrangements of Free Radicals. 5.[1] Sigmatropic and Electrocyclic Reactions of Bicyclo[3.1.0]hexenyl Radical

Sir:

Rearrangements of free radicals have been observed mainly in reactions with small activation energies.[2] Under these conditions a rearrangement can compete with recombination and disproportionation reactions. Recently[1] we have shown that matrix ESR spectroscopy, which allows the investigation of free radicals as isolated moieties over longer periods of time, provides a tool for studying such reactions even with substantial activation energies. It therefore becomes possible to compare the behavior of analogous closed and open shell molecules and to delineate the special properties of radicals in such reactions. We wish to report a sigmatropic and an electrocyclic reaction of the bicyclo[3.1.0]hexenyl radical (**1**). The properties of **1** in solution were studied previously.[3] **1** was obtained by hydrogen abstraction from bicyclo[3.1.0]hex-2-ene[4] (**2**) with photolytically generated *tert*-butoxy radicals. Its ESR spectrum could be recorded from −100 to +70 °C without appearance of a signal due to a rearranged radical. A thermolysis of **2** in the presence of di-*tert*-butyl peroxide in chlorobenzene at 130 °C yielded 35% benzene as a consequence of an electrocyclic ring opening of **1** to cyclohexadienyl radical.

Bicyclo[3.1.0]hex-2-ene in adamantane as matrix was x-ray irradiated at −196 °C.[5] At temperatures below −60 °C one observes the ESR spectrum of **1**. Heating the sample in the cavity of the ESR spectrometer above −60 °C produces gradually the spectrum of the cyclohexadienyl radical which had been generated by x-ray irradiation of benzene in adamantane.[6] The free energy of activation for the rearrangement which could be determined by recording the growth of the signal for the cyclohexadienyl radical as a function of time and temperature amounts to $\Delta G^{\ddagger} = 14.5$ kcal/mol at −50 °C. Because of competing reactions with very small activation energies it was not possible to observe this rearrangement in solution. The concentration of cyclohexadienyl radical never becomes sufficient for detection by ESR. As a consequence one should be cautious to conclude that the nonobservance of a rearrangement in solution is a sufficient proof against its occurrence.

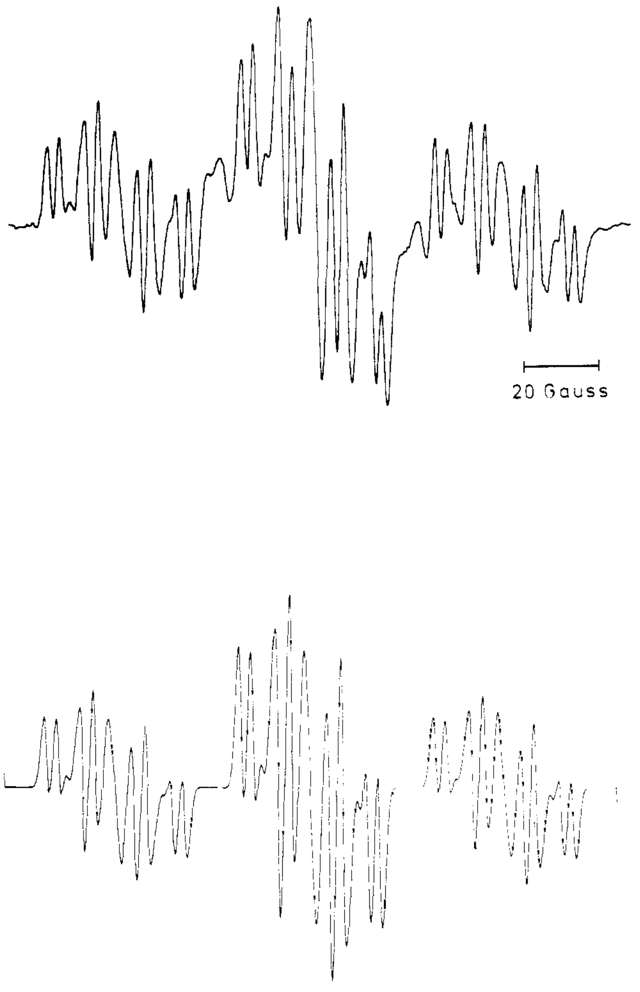
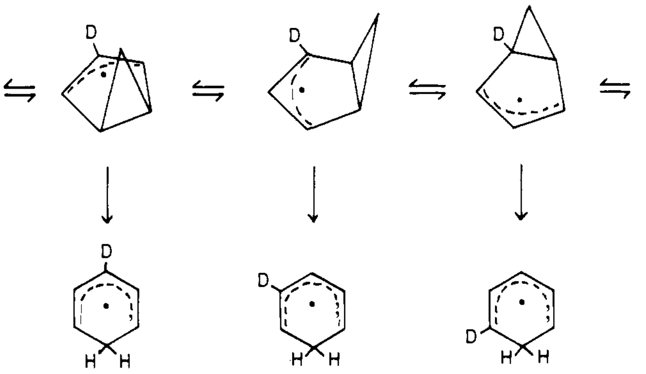


Figure 1. ESR spectrum (above) of x-ray irradiated [2-^{2}H]bicyclo[3.1.0]hex-2-ene in adamantane at +18°. Simulated spectrum (below) for a mixture of monodeuterated cyclohexadienyl radicals with a ratio of deuterium in 1-:2-:3-position of 2:2:1.

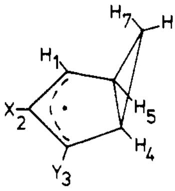
Table I. Coupling Constants for Bicyclo[3.1.0]hexenyl Radicals (Gauss)

	T, °C	a_{H_1/H_3}	a_{H_2}	a_{H_4/H_5}	a_{H_6}	a_{H_7}	a_D
1	−78	13.66	2.54	12.60	3.75	3.55	
5	−62	13.62		12.60	3.77	3.52	0.39
6	−60	13.70	2.56	12.60	3.77	3.56	2.10

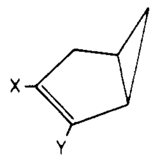
Scheme I



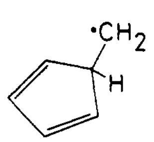
It was found earlier[3] that 6-*endo*-carboxybicyclo[3.1.0]hexenyl radical isomerizes to the corresponding exo radical. In the course of elucidating the mechanism of this reaction we prepared monodeuterated derivatives of **2** (**3** and **4**). Both compounds were synthesized from bicyclo[3.1.0]hexan-2-one which in turn was obtained in 79% yield from the corresponding alcohol by oxidation with chromic acid anhydride in acetone. Reduction of the ketone with lithium aluminum deuteride in diethyl ether leads to the deuterated alcohol (87%) which can be converted to **3** by preparing the xanthate of the bicyclic alcohol and pyrolizing it at 120 °C. This is similar to the preparation of **2**.[4] The deuterium in 3-position was introduced by repeatedly refluxing bicyclo[3.1.0]hexan-2-one in deuterium oxide containing 7% sodium deuterioxide. In this way a sample with ≥90% deuterium in 3-position was obtained. Reduction with lithium aluminum hydride led to the bicyclic alcohol which was transformed in **4** by the xanthate procedure.



1 X = Y = H
5 X = H, Y = D
6 X = D, Y = H



2 X = Y = H
3 X = H, Y = D
4 X = D, Y = H



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The solution ESR spectra of the corresponding radicals **5** and **6** generated by hydrogen abstraction in allylic position exhibit the coupling parameters shown in Table I. They conform with expectation based upon the coupling constants for **1**. The solution ESR spectra gave no indication for rearrangement of **5** or **6**. Producing **5** or **6** by x-ray irradiation in adamantane at −196 °C and recording the ESR spectra above −60 °C has the result shown in Figure 1. The superposition of three different deuterated cyclohexadienyl radicals is observed. The computer simulation of the spectrum was based on the coupling constants for cyclohexadienyl radical[5,7] using Gaussian line shapes and a line width of 1.25 G. The deuterium couplings were evaluated from the a_D/a_H ratio. The ratio in which 1-, 2-, and 3-deuterated cyclohexadienyl radicals appear is 2:2:1 with a maximum error of ±10%; i.e., within the limits of error it corresponds to a statistical distribution of deuterium over the atoms of the pentadienyl unit. Furthermore this ratio is independent of **3** or **4** being the starting material. This result implies the sigmatropic reaction sequence shown in Scheme I. The rearrangements take place below −60 °C and must have a barrier of activation which is smaller than that for the ring opening reaction, i.e., $\Delta G^{\ddagger}$ must be <14 kcal/mol.

Sigmatropic and electrocyclic reactions of bicyclo[3.1.0]hexenyl cations have been studied experimentally[8-18] and theoretically.[19] The rearrangement of deuterated bicyclo[3.1.0]hexenyl cations[15] is of relevance to our work. The free energy of activation for ring opening at −20 °C is 19.8 kcal/mol; the circumambulation which takes place with inversion of configuration at the migrating carbon atom requires an activation energy of $\Delta G^{\ddagger} = 15 \pm 1$ kcal/mol at −90 °C. Compared to the corresponding cation the electrocyclic reaction of **1** needs a smaller activation energy, that also means the sigmatropic process requires less activation. The circumambulation in **1** has been deduced indirectly from deuterium labeling in the cyclohexadienyl radical. Because the line width in the low temperature ESR spectrum of **1** in matrix does not permit a detailed analysis there is no possibility to study the stereochemistry of the migrating carbon directly. However, the observed endo/exo isomerization of the *endo*-6-carboxybicyclo[3.1.0]hexenyl radical[3] and other derivatives[20] points to a difference in behavior of radical and cation. If endo/exo isomerization and sigmatropic rearrangement occur through the same transition state or intermediate then the migration of the methylene bridge in the radical could take place with retention of configuration. This problem as well as the possible intermediacy of 7 during the rearrangement are presently under investigation.

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References and Notes

(1) Part IV: R. Sustmann and D. Brandes, *Tetrahedron Lett.*, 1791 (1976).
(2) J. W. Wilt in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973.
(3) R. Sustmann and F. Lübbe, *Tetrahedron Lett.*, 2831 (1974).
(4) P. K. Freeman, M. F. Gostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 772 (1965).
(5) M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, **97**, 1004 (1975), and references therein.
(6) S. DiGregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.*, **95**, 8455 (1973).
(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).
(8) D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967).
(9) R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968).
(10) R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968).
(11) H. Hart, T. R. Rodgers, and J. Griffiths, *J. Am. Chem. Soc.*, **91**, 754 (1969).
(12) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969).
(13) I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova, and V. A. Koptyug, *Zh. Org. Khim.*, **6**, 2493 (1970).
(14) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970).
(15) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Am. Chem. Soc.*, **93**, 1551 (1971).
(16) R. F. Childs, M. Sakai, B. Parrington, and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6403 (1974).
(17) R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6409 (1974).
(18) G. A. Olah, G. Liang, and S. P. Jndal, *J. Org. Chem.*, **40**, 3259 (1975).
(19) W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).
(20) F. Lübbe, unpublished results.

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A Novel Intramolecular Exchange Reaction between Coordinated NO and NO$_2$ Groups in *cis*-[Fe(NO)(NO$_2$)(S$_2$CN(CH$_3$)$_2$)$_2$]

Sir:

We wish to report a novel exchange reaction between coordinated NO and NO$_2$ groups. Although it is well known that a coordinated NO$_2$ group can be chemically converted to coordinated NO by treatment with acids or reducing agents,[1,2] to our knowledge, the direct interchange of coordinated NO$_2$ and NO has not heretofore been demonstrated. In our previous studies of the dithiocarbamate derivatives of the $\{FeNO\}^6$ and $\{FeNO\}^7$ groups,[3] we reported the preparation of Fe(NO)(NO$_2$)(S$_2$CN(C$_2$H$_5$)$_2$)$_2$ and demonstrated by proton NMR spectroscopy that it has cis geometry.[4] A subsequent structure determination by x-ray crystallography[5] has confirmed its cis geometry and has shown that the NO$_2$ group is attached to iron through the nitrogen atom.

The cis and trans isomers of the analogous complex, Fe(NO)(NO$_2$)(S$_2$CN(CH$_3$)$_2$)$_2$, have now been prepared and their coordination geometries established by infrared and proton NMR spectroscopy. Isotopic substitution with ^{15}N shows that the NO$_2$ ligand is attached to iron through nitrogen in both cis and trans isomers (Table I). The trans isomer labeled with ^{15}NO (95%) is stable to isomerization below 5 °C and is readily prepared by reaction 1:

$$\mathrm{Fe(^{15}NO)(S_2CN(CH_3)_2)_2} + {}^{14}\mathrm{NO_2} \xrightarrow[\mathrm{CHCl_3}]{-60\ ^\circ\mathrm{C}} trans\text{-}[\mathrm{Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2}] \quad (1)$$

Above 5 °C the trans isomer is converted to the cis isomer *with retention of the* ^{15}NO label (reaction 2):

$$trans\text{-}[\mathrm{Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2}] \xrightarrow[\mathrm{CHCl_3}]{>5\ ^\circ\mathrm{C}} cis\text{-}[\mathrm{Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2}] \quad (2)$$

The isomerization of trans to cis (reaction 2) is then succeeded by a slow exchange between the coordinated ^{15}NO and ^{14}NO$_2$ groups of the cis isomer:

$$cis\text{-}[\mathrm{Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2} \rightleftharpoons cis\text{-}[\mathrm{Fe(^{14}NO)(^{15}NO_2)(S_2CN(CH_3)_2)_2}] \quad (3)$$

To establish the course of this unusual exchange reaction between coordinated NO and NO$_2$, reaction 3 has been studied at different concentrations in several solvents by monitoring the nitrosyl region of the infrared spectrum (Table II). The results of these kinetic studies show that the exchange of coordinated NO and NO$_2$ is first order in the cis isomer, is independent of solvent, and is independent of the concentration of either NO, NO$_2$, or NO$_2^-$ for the range of concentrations studied. The fact that the rate of eq 3 is independent of the concentration of NO$_2^-$ and of the donor properties of the solvent indicates that dissociative mechanisms in which iron–nitrogen bonds are cleaved heterolytically are not important. The requirement of cis geometry for exchange of the coordinated NO and NO$_2$ groups strongly suggests that an intramolecular process is responsible for reaction 3.

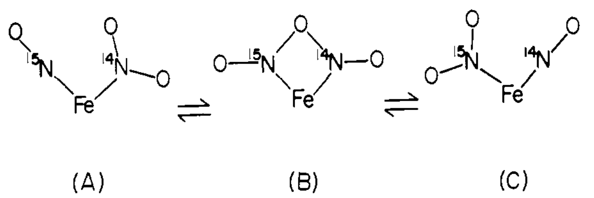

Figure 1. Proposed rate determining step for the exchange reaction between the NO and NO$_2$ groups of *cis*-[Fe(NO)(NO$_2$)(S$_2$CN(CH$_3$)$_2$)$_2$].

One intramolecular pathway that can be envisaged for the exchange of adjacent NO and NO$_2$ groups is shown in Figure 1. The rate determining step depicted in Figure 1 requires that there be no direct reaction of *cis*-[Fe(NO)(NO$_2$)(S$_2$CN(CH$_3$)$_2$)$_2$] with either free NO or free NO$_2$ which is faster than the reaction shown in Figure 1, in agreement with the observations that eq 3 is independent of the pressure of NO and NO$_2$ (Table II). However, to explore the possible exchange reactions of coordinated NO and NO$_2$ with free NO and NO$_2$, the rates of reactions 4–7 were also studied (Table II).

Table I. NO and NO$_2$ Vibrational Frequencies of *cis*- and *trans*-Fe(NO)(NO$_2$)(S$_2$CN(CH$_3$)$_2$)$_2$ and Their ^{15}N Derivatives

Compound	ν_{NO} (CHCl$_3$)	ν_{NO} (KBr)	ν_{NO_2} (KBr)	ν_{NO_2} (KBr)	δ_{NO_2} (KBr)
cis-Fe^{14}NO(S$_2$CNMe$_2$)$_2$^{14}NO$_2$	1857	1835	1382	1305	812
cis-Fe^{15}NO(S$_2$CNMe$_2$)$_2$^{15}NO$_2$	1821	1802	1352	1282	804
trans-Fe^{14}NO(S$_2$CNMe$_2$)$_2$^{14}NO$_2$	1866	1840	1386	1275	760
trans-Fe^{14}NO(S$_2$CNMe$_2$)$_2$^{15}NO$_2$	1866	1840	1355	1255	754
trans-Fe^{15}NO(S$_2$CNMe$_2$)$_2$^{14}NO$_2$	1829	1804	1385	1275	760