the same way as the Wittig reaction progresses, a titanaceous intermediate of type **A** may form and then ring open with retention of titanium–oxygen and carbon–nitrogen bonds (**B**). Since, as discussed elsewhere,[4] one titanocene hydrogen seems to be available at the termination of a nitrogen fixation–reduction reaction, it is possible that such hydrogen may be transferred (possibly *via* nitrogen) to α carbon in the amine, as shown. The role of titanium in this overall process may be crucial, as intimated by the above, since other metal nitrides apparently do not undergo C-amination reactions of any kind. Investigations into the scope and mechanism of the above reaction type are being pursued in this laboratory.

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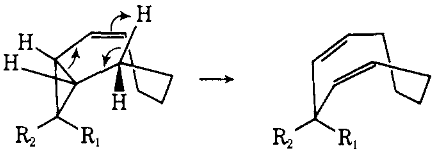
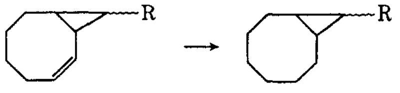
Stereoselective 1,5-Hydrogen Migration in 9-Hydroxymethylbicyclo[6.1.0]non-2-ene[1]

Sir:

The 1,5-hydrogen migration of bicyclo[6.1.0]non-2-ene (**1**, R_1, R_2 = H) to give *cis,cis*-1,4-cyclononadiene (**2**, R_1, R_2 = H) has been suggested to proceed through the unfavorable "saddle" conformation.[2] Where this conformation is not possible due to steric hindrance, the rearrangement is not expected to occur; *e.g.*, where R_1, R_2 = Br a complicated reaction ensues and the 1,5-hydrogen migration product is not observed, although it could be an intermediate.[3] In the corresponding monosubstituted compounds, the conformation necessary for rearrangement is possible where R_1 = H but not where R_1 = a bulky substituent. In support of this theory we have observed the selective rearrangement of the exo isomer of 9-hydroxymethylbicyclo[6.1.0]non-2-ene (**1**, R_1 = H, R_2 = CH_2OH) to 3-hydroxymethyl-*cis,cis*-1,4-cyclononadiene (**2**, R_1, R_2 = H, CH_2OH) under conditions that do not affect the corresponding endo isomer (**1**, R_1 = CH_2OH, R_2 = H).



1 **2**



3 **4**

We attempted to synthesize the exo and endo isomers of 9-hydroxymethylbicyclo[6.1.0]non-2-ene (**3**, R = CH_2OH) *via* the addition of ethyl diazoacetate to 1,3-cyclooctadiene followed by lithium aluminum hydride reduction. Injection of the alcohol product mixture into a vapor-phase chromatograph at 200° with the injection port and detector heated to 230 and 240°, respectively, gave a chromatogram showing two peaks in the ratio of *ca.* 4:1. Samples of each product were collected from the vpc.[4] The nmr spectrum ($CDCl_3$) of the minor component, compatible with the expected endo isomer of **3**, R = CH_2OH, displays a hydroxymethylene doublet (J = 7 Hz) at τ 6.45 (2 H), two olefinic multiplets centered at 4.3 and 4.6, and absorptions to 9.0 ppm. The nmr spectrum of the major product consists of a four-proton multiplet extending from τ 4.1 to 4.9 and a multiplet at 6.35 that integrates for three protons suggesting that a rearrangement had occurred and 3-hydorxymethyl-1,4-cyclononadiene as a possible structure. The rearranged product analyzed for an isomeric structure. *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.84; H, 10.85. The gross structure was confirmed by hydrogenation followed by chromic acid oxidation to cyclononanecarboxylic acid identified as its carboxyanilide; mp 139–140.2°, lit.[5] mp 140–141°. A mixture melting point gave no depression. The position of the double bonds was confirmed by ozonolysis followed by hydrogen peroxide oxidation to give adipic acid.

The infrared spectrum of **2** displayed bands at 1637 (w), 1070 (s), 1060 (s), 1020 (s), 813 (m), 743 (s) cm^{-1}, a *cis*-olefinic C–H out-of-plane deformation band at 705 (s) cm^{-1}, and no bands corresponding to the C–H out-of-plane and in-plane deformation bands characteristic of *trans*-olefins, supporting the assigned cis,cis stereochemistry. Repeating the synthesis of **2** but reducing the ester with lithium aluminum deuteride followed by vpc collection gives the deuterated compound ($-CD_2OH$) whose nmr spectrum now clearly shows the bisallylic H_3 as a triplet (J = 7.5 Hz) at τ 6.1. The nmr spectrum of the liquid acetate of **2** (R_1 = CH_2OAc) gives a two-proton doublet (J = 2 Hz) at τ 5.9.

In order to confirm the identity of the starting alcohols (**3**, R = CH_2OH), exo and endo isomers of 9-carboethoxybicyclo[6.1.0]non-2-ene (**3**, R = CO_2Et) were separated and collected by preparative vpc.[4] Hydrogenation gave the corresponding dihydro exo and endo isomers (**4**, R = CO_2Et) which were, respectively, identical with the major and minor products from the copper-catalyzed addition of ethyl diazoacetate to cyclooctene,[6] a reaction which is expected to give a

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[1] Presented in part at the Midwest Regional American Chemical Society Meeting, Kansas City, Mo., Oct 1969.

[2] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966). This article contains an excellent discussion and leading references. A heteroatom analog, 3,4-epoxycyclooctene, undergoes thermal rearrangement to *cis,cis*-3-oxa-1,4-cyclononadiene among other products (J. K. Crandall and R. J. Watkins, *ibid.*, 1717 (1967)).

[3] M. S. Baird, D. G. Lindsay, and C. B. Reese, *Chem. Commun.*, 784 (1968).

[4] Wilkens A-700 (Autoprep) instruments were used for vpc analyses and separations utilizing fluorosilicone (QF-1) as stationary-phase material. Typical retention times (minutes) for a 20 ft × 3/8 in. 30% QF-1 column under a helium gas flow rate of 100 cc/min at 200° were: **1**, R_1 = CH_2OH, R_2 = H (19); **2**, R_1, R_2 = CH_2OH (15); *endo*-**3**, R = CO_2Et (22.5); *exo*-**3**, R = CO_2Et (25); *endo*-**4**, R = CO_2Et (22); *exo*-**4**, R = CO_2Et (30).

[5] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960). We are indebted to Professor Gutsche for an authentic sample of the derivative.

[6] S. Akiyoshi and T. Matsuda, *ibid.*, 77, 2476 (1955). The formation of isomers is not discussed and the reported melting point of the hydrolysis product is probably that of an isomeric mixture of carboxylic acids.

predominance of the exo isomer.[7] The assigned endo isomer of **4**, R = CO_2Et, could be epimerized to the exo isomer using lithium *tert*-butoxide in DMSO at room temperature[8] demonstrating that the two compounds are epimeric and confirming the assignments of the exo and endo isomers of **3**, R = CO_2Et. Lithium aluminum hydride reduction of the *endo*-**3** ester (**1**, R_1 = CO_2Et) gives the corresponding *endo*-hydroxymethyl compound (**1**, R_1 = CH_2OH) shown to be identical with the minor product obtained by vpc collection of the original alcohol mixture. Similar reduction of the *exo*-**3** ester (**1**, R_2 = CO_2Et) gives *exo*-9-hydroymethylbicyclo[6.1.0]non-2-ene (**1**, R_2 = CH_2OH) whose nmr spectrum ($CDCl_3$) displays a hydroxymethylene doublet (J = 7 Hz) at τ 6.5 (2 H), an olefinic multiplet centered at 4.5 (2 H), and absorptions extending to 9.5 ppm. Injection of this compound into the vpc gives a single peak whose retention time is identical with the rearranged major product. Preparative collection of a sample from the vpc and spectral comparison confirmed the rearrangement to **2** (R_1, R_2 = H, CH_2OH) on the vpc column. Identical results can be obtained by injecting **3**, R = CH_2OH, onto a column filled with glass beads at 340°[9] under helium gas flow, limiting pyrolysis time to seconds instead of 15 min by vpc injection. The stereoselective pyrolytic rearrangement constitutes a facile synthesis of a 3-substituted 1,4-cyclononadiene in good yield from readily available starting material.

Acknowledgment. The financial support of the Petroleum Research Fund administered by the American Chemical Society (1207-G1), the Research Corporation (Frederick Gardner Cottrell Grant), and the Research Committee—UMSL is gratefully acknowledged.

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(7) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

(8) Attempted epimerizations by standard techniques were surprisingly futile.

(9) Conversion was incomplete at lower temperatures with less than 10% conversion at 240°, the maximum temperature in the vpc system. Thus, the rearrangement in the vpc does not occur specifically in the injection port or detector.

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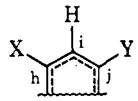
Nuclear Magnetic Resonance Spectroscopy. Studies of Carbon-13 Spectra of *n*-Alkyl Nickel(II) Aminotroponiminates[1]

Sir:

In a previous communication from these laboratories[2] we reported the ^{13}C nmr spectrum of nickel(II) *N,N'*-di(*p*-tolyl)aminotroponiminate and proposed that, at least qualitatively, the ^{13}C isotropic shifts were consistent with the propagation of unpaired spin density by way of both the π and σ electrons of the ligand. This analysis assumed that the π contribution to the ^{13}C hyperfine coupling constant, a^{C_i}, could be approximated by the Karplus–Fraenkel equation[3] (eq 1),

$$a^{C_i} = (S^C + Q_{C_iH}{}^C + Q_{C_iC_h}{}^C + Q_{C_iC_j}{}^C)\rho_{C_i}{}^\pi + Q_{C_hC_i}{}^C\rho_{C_h}{}^\pi + Q_{C_jC_i}{}^C\rho_{C_j}{}^\pi \quad (1)$$

where S^C is the proportionality factor for the polarization of the 1s electrons and the Q's are the proportionality factors for the 2s electrons.[4] The spin density in the p_π orbital centered at C_i of the molecular fragment **1** is $\rho_{C_i}{}^\pi$, while $\rho_{C_h}{}^\pi$ and $\rho_{C_j}{}^\pi$ are for the adjacent atoms h and j. We have now extended our studies to include the *N*-alkyl-substituted aminotroponiminates **2a** and **2b** and the results provide further evidence for the propagation of unpaired spin density through the σ electronic framework of the ligand.



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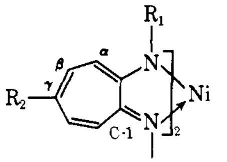

2a, $R_1 = CH_3$; $R_2 = H$
2b, $R_1 = CH_2CH_3$; $R_2 = CHO$
2c, R_1 = *p*-tolyl; $R_2 = H$

The spectral data for the complexes **2a** and **2b** are summarized in Table I. Observation and assignment of the ^{13}C spectrum of **2a** was straightforward, consistent with the known, large (square planar)/tetrahedral ratio of the forms of the complex.[5a,b] However, **2b** is largely in the paramagnetic tetrahedral form[6] with concurrent difficulties in observing and assigning its ^{13}C resonances. For this complex, only the carbon resonances corresponding to the β-C and the CH_2 and CH_3 groups could be assigned with certainty by single-frequency proton-decoupling experiments.[2] The carbon resonances, tentatively assigned to the α-C and CHO group, were observed with proton noise decoupling in the appropriate proton region of the spectrum. As with **2c**, no resonances assignable to the γ-C or C-1 were observed. Normally, 1000 scans of a $\approx$0.4 M sample were required to give satisfactory resonance peaks.

Previously,[2] eq 2 was used to predict ratios of the ^{13}C and ^1H isotropic shifts for the ring positions of the cycloheptatriene moiety, using the spin densities $\rho_{C_i}{}^\pi$ of the paramagnetic form of the complex computed from the proton isotropic shifts,[5,6] the equilibrium for the paramagnetic ⇄ diamagnetic interconversion, and the McConnell equation.[7] The results of the same procedure for **2a** and **2b** are given in Table II which also includes the experimental values determined from the shifts in Table I. Values for **2c** are included for comparison.[2]

$$\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i} \approx -6.2 + 2.5(\rho_{C_h}{}^\pi + \rho_{C_j}{}^\pi)/\rho_{C_i}{}^\pi \quad (2)$$

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(1) Supported by the National Science Foundation, and by the Public Health Service, Grant No. 11072, from the Division of General Medical Services.

(2) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 4484 (1970).

(3) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(4) We have taken the Q's to be independent of the nature of the complex, although they are in fact expected to be sensitive to structural parameters.[3]

(5) (a) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963); (b) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(6) D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Amer. Chem. Soc.*, **89**, 4040 (1967).

(7) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).