may be calculated using Burnside's Lemma[25]

$$D_{V'W'} = \frac{1}{|\Pi'(\bar{V}, \bar{W})|} \sum_{\Pi'(\bar{v}_i, \bar{w}_j) \in \Pi'(\bar{V}, \bar{W})} \chi(\bar{v}_i, \bar{w}_j) \quad \text{(A2)}$$

where $\chi(\bar{v}_i, \bar{w}_j)$ is the number of h_k in H which $\Pi'(\bar{v}_i, \bar{w}_j)$ leaves fixed, *i.e.*, the number of h_k in H for which

$$h_k = \Pi'(\bar{v}_i, \bar{w}_j)h_k \equiv \bar{v}_i \cdot h_k \cdot \bar{w}_j^{-1}$$

or equivalently

$$v_i = h_k \cdot \overline{w}_j \cdot h_k^{-1}$$

Accordingly, $\chi(\bar{v}_i, \bar{w}_j) = 0$ unless $\bar{v}_i$ and $\bar{w}_j$ have identical generalized cyclic type, and if $\bar{v}_i$ and $\bar{w}_j$ both have generalized cyclic type $(i_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2};\ l_1, l_2, \ldots, l_{n_3})$, then

$$\chi(\bar{v}_i, \bar{w}_j) = \prod_{p=1}^{n_1} (j_p!p^{j_p}) \prod_{q=1}^{n_2} (k_q!q^{k_q}) \prod_{r=1}^{n_3} (l_r!r^{l_r}) \quad \text{(A3)}$$

Since $\chi(\bar{v}_i, \bar{w}_j)$ is dependent only on the generalized cyclic type of $\bar{v}_i$ and $\bar{w}_j$, and $\chi(\bar{v}_i, \bar{w}_j) \neq 0$ if and only if $\bar{v}_i$ and $\bar{w}_j$ have identical generalized cyclic type, the summation in eq A2 may be changed to one over the generalized cyclic types of the operations in V, W, V', and W'. Let $h^{\mathrm{V}}{}_{j_1j_2\ldots j_{n_1}, k_1k_2\ldots k_{n_2}, l_1l_2\ldots l_{n_3}}$, $h^{\mathrm{V}\prime}{}_{j_1j_2\ldots j_{n_1}, k_1k_2\ldots k_{n_2}, l_1l_2\ldots l_{n_3}}$, $h^{\mathrm{W}}{}_{j_1j_2\ldots j_{n_1}, k_1k_2\ldots k_{n_2}, l_1l_2\ldots l_{n_3}}$, and $h^{\mathrm{W}\prime}{}_{j_1j_2\ldots j_{n_1}, k_1k_2\ldots k_{n_2}, l_1l_2\ldots l_{n_3}}$ be the number of operations in V, V', W, and W', respectively, having generalized cyclic type $(i_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2};\ l_1, l_2, \ldots, l_{n_3})$. Then by substituting eq A1 and A3 into eq A2 and using the new summation extending over all generalized cyclic types of permutations in V, W, V', and W', we obtain eq 22.

During the course of this derivation we have assumed that all elements in H^{VW} represent reactions. For the case V = W, some elements in H^{WW} do not represent reactions but represent rotation of configuration, and therefore the number of diastereomeric reactions is $D_{W'W'} - 1$.

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(25) F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, p 181.

Effects of Additional Ring Fusions and Binding to Metal Atoms upon the Cyclooctatriene–Bicyclooctadiene Equilibrium[1]

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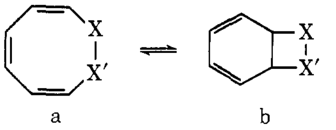
Abstract: The hydrocarbons bicyclo[6.3.0]undeca-2,4,6-triene (**1**) and bicyclo[6.4.0]dodeca-2,4,6-triene (**3**) have been prepared by reaction of dilithiocyclooctatetraene with 1,3-dibromopropane and 1,4-dibromobutane, respectively. **1** and **3** could not be isolated pure, but instead **1** was obtained mixed with its tautomer tricyclo[6.3.0.0^{2,7}]undeca-3,5-diene (**2**) and **3** was obtained mixed with its tautomer tricyclo[6.4.0.0^{2,7}]dodeca-3,5-diene (**4**). The kinetics and equilibrium of the **1** → **2** conversion have been studied. The rate constant at 20° (extrapolated from measurements at 34 and 58°) is 1.6×10^{-5} sec^{-1}. Assuming a frequency factor of 10^{13} the Arrhenius activation energy is 24 ± 1 kcal/mol. At 58° the equilibrium constant, K = [**2**]/[**1**], is ~33. The equilibrium molar ratio **3**:**4** at 114° is approximately unity. From pmr spectra and other considerations the probable molecular structures and ring conformations are deduced. The systems **1**–**2** and **3**–**4** react with $Fe_2(CO)_9$ and $Mo(CO)_3(NCCH_3)_3$ to form a variety of crystalline derivatives, all of which have been characterized as to gross structure (*i.e.*, connexity of bonds but not conformational details) by ir and pmr spectra. These derivatives, which will be suitable for X-ray crystallographic studies of structural details, are the following: (**2**)$Fe(CO)_3$, (**2**)$_2Mo(CO)_2$, (**1**)$Mo(CO)_3$, (**4**)$Fe(CO)_3$, (**4**)$_2Mo(CO)_2$, (**3**)$Fe_2(CO)_6$, (**3**)$Mo(CO)_3$. Yields of the various derivatives run parallel to the intrinsic relative stabilities of the tautomers in each of the pairs, **1**–**2** and **3**–**4**.

It was nearly 20 years ago that Cope and coworkers[4] first studied an equilibrium of the type



a b

for the case where X = X' = CH_2, *i.e.*, for cyclooctatriene and its tautomer bicyclooctadiene. They reported that the equilibrium ratio a/b is ~6 at 80–100°. More recently, Huisgen and coworkers[5] reinvestigated this system (for which they found a ratio of ~8 at 60°) and 11 others with a variety of X and X' groups. Variations in X and X' were found to influence the ratio greatly, changing it over a range of ~10^4. Huisgen and coworkers considered several factors which might be expected to influence the position of equilibrium, but concluded that no entirely satisfactory explanation for the observed facts could be found within the framework of their considerations.

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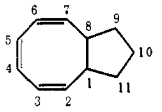
(4) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 74, 4876 (1952).

(5) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

Several previous experiences in these laboratories led us to undertake the investigation reported here. One was the observation that for 1,3,5,7-tetramethylcyclooctatetraene, attachment of $Fe(CO)_3$ apparently causes the bicyclo tautomer to become stable,[6] whereas with $Mo(CO)_3$ the monocyclic[7] tautomer is isolated as its metal complex. Second, we have recently studied[8] the reaction of $Fe_2(CO)_9$ with bicyclo[6.2.0]deca-2,4,6-triene (X–X′ in a = $\overline{\mathrm{CHCH_2CH_2CH}}$). We observed, not at all unexpectedly, that fusing the cyclobutane ring to the 7,8 positions of the cyclooctatriene ring stabilized a relative to b. We were somewhat surprised to observe, however, that the dienophilicity of the $Fe(CO)_3$ group was great enough to stabilize the tricyclo[6.2.0.0^{2,7}]deca-3,5-diene form of the olefin in $C_{10}H_{12}Fe(CO)_3$.

On the basis of the prior information summarized above, we considered it of interest to prepare the systems **1**–**2** and **3**–**4**, investigate the equilibria and kinetics of the tautomer interconversions in each case, and, particularly, to isolate and study complexes of these tautomers using $Mo(CO)_3$ and $Fe(CO)_3$ to sequester selectively the triene and diene tautomers, respectively, in each case. The detailed stereochemistry of the ring fusions should be little disturbed by appending the $M(CO)_3$ moieties to the olefinic systems, and thus a series of derivatives eminently suitable for X-ray crystallographic study of stereochemistry of the ring systems was anticipated.



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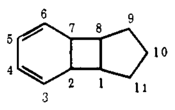

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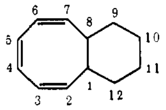

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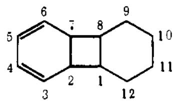

4

Experimental Section

The preparation and handling of all compounds were routinely carried out in an atmosphere of nitrogen. The pmr spectra were recorded with Hitachi-Perkin-Elmer R-20B, Varian HA-100, and Varian T-60 spectrometers. Infrared spectra were measured with a Perkin-Elmer Model 337 spectrometer. Melting points are uncorrected. Elemental analyses were carried out by Meade Microanalytical Laboratories, Amherst, Mass., and Spang Microanalytical Laboratories, Ann Arbor, Mich.

Bicyclo[6.3.0]undeca-2,4,6-triene (1) and Tricyclo[6.3.0.0^{2,7}]undeca-3,5-diene (2). Lithium wire (1.98 g, 0.28 g-atom) was added in small pieces to liquid ammonia (250 ml) at −70°. To the blue solution, freshly distilled cyclooctatetraene (14.7 g, 0.14 mol) was added dropwise during 15 min. A yellow-brown precipitate was formed immediately. After stirring the mixture for 20 min at about −50° a solution of 1,3-dibromopropane (28.48 g, 0.28 mol) in anhydrous ether (15 ml) was added dropwise over a period of 30 min. The mixture was stirred for 5 additional hr at −33° so as to maintain a gentle reflux of the ammonia. At the end of this period the color of the mixture became pale yellow. Anhydrous ether (30 ml) was first added, followed by 20 ml of a saturated aqueous ammonium chloride solution, and then 100 ml of water. The two layers were separated and the aqueous one was extracted with ether (3 × 50 ml). The combined ether layers were dried overnight over anhydrous magnesium sulfate at −5°. The ether was then evaporated at reduced pressure and the orange residue pumped under high vacuum until no more unreacted cyclooctatetraene was left. Distillation of the residue was performed with a warm bath at 35° and a colorless liquid (bp 31° (0.03 mm)) was obtained. This was found to be an approximately 3:7 mixture of the bicyclotriene (**1**) and tricyclodiene (**2**) compounds (10 g, 0.068 mol, yield 48.5%). The pmr spectrum of this mixture is reported in Figure 1 together with the pmr spectrum of almost pure tricyclodiene obtained by heating the mixture for 20 min at 80° and then distilling at 74° (6 mm). The sample of **2** so obtained solidifies between 0 and −5°. *Anal.* Calcd for $C_{11}H_{14}$: C, 90.41; H, 9.59. Found: C, 90.3; H, 9.41.

Kinetics of 1 to 2 Conversion. Beginning with the mixture of **1** and **2** as obtained above, the conversion of **1** to **2** was followed as a function of time at two temperatures, 34 ± 1° and 58 ± 1°, by recording the areas of the olefinic protons of each tautomer. The area of the peak assigned to **1** (see Discussion) was divided by six and that for **2** by four; the sum of these quotients was constant within experimental error. Least-squares fitting of straight lines to plots of $\ln\{[\mathbf{1}]^0/[\mathbf{1}]^t\}$ *vs.* time yielded $k = (4.2 \pm 0.1) \times 10^{-5}\ \mathrm{sec}^{-1}$ at 34°, and at $t = \infty$ the concentration of **1** is 0.4%. At 58° $k = (3.4 \pm 0.1) \times 10^{-3}\ \mathrm{sec}^{-1}$ and the concentration of **1** at $t = \infty$ is 3%. At the higher temperature the straight line begins to bend after about 25 min because the system is approaching equilibrium composition. The results are displayed in Figure 2.

Bicyclo[6.4.0]dodeca-2,4,6-triene (3) and Tricyclo[6.4.0.0^{2,7}]dodeca-3,5-diene (4). The preparation of an approximately 7:3 mixture of **3** and **4** was carried out in a manner similar to the preparation of **1** and **2**. To lithium wire (2.8 g, 0.40 g-atom) dissolved in liquid ammonia (300 ml) was added cyclooctatetraene (20.8 g, 0.2 mol) and then 1,4-dibromobutane (43.2 g, 0.2 mol). After a similar work-up procedure, distillation under vacuum gave an approximately 7:3 mixture of **3** and **4** (bp 32° (0.3 mm)) as a colorless liquid (16.6 g, 0.098 mol, yield 35%). The pmr spectrum is shown in Figure 4. *Anal.* Calcd for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.7; H, 9.79.

Complexes Derived from 1 and 2. $C_{11}H_{14}Fe(CO)_3$ (5). To a solution of **2** (1.64 g, 11.3 mmol) in hexane (60 ml) was added diiron enneacarbonyl (7.2 g, 19.8 mmol). The mixture was stirred for 12 hr at 50°. After filtration the green solution was evaporated under vacuum, extracted with petroleum ether (3 × 5 ml), and the extracts chromatographed on a 2 × 20 cm alumina column (Woelm, activity 2). Elution with petroleum ether gave only a yellow band, while a brown band due to decomposition of $Fe_3(CO)_{12}$ remained at the top of the column. Evaporation of the yellow band gave yellow needles. Crystallization from petroleum ether gave the pure complex, mp 94–95° (2.24 g, 8.19 mmol, yield 72%).

The ir spectrum of a cyclohexane solution has strong CO stretching bands at 2047, 1985, and 1977 cm^{-1} (each ±5 cm^{-1}). The pmr spectrum in C_6D_6 (Figure 5a) has multiplets centered at τ 5.18 (2 H), 7.09 (2 H), 8.37 (4 H), and 8.77 (6 H). *Anal.* Calcd for $C_{14}H_{14}FeO_3$: C, 58.74; H, 4.89; Fe, 19.54. Found: C, 58.6; H, 4.83; Fe, 19.6.

The approximately 3:7 mixture of **1**–**2** was allowed to react with $Fe_2(CO)_9$ at room temperature for 32 hr. The only product which could be isolated was **5**, in 75% yield.

$C_{22}H_{28}Mo(CO)_2$ (6). To a solution of $Mo(CO)_3(CH_3CN)_3$ (1.5 g, 5 mmol) in anhydrous tetrahydrofuran (200 ml) was added **2** (0.730 g, 5 mmol). The solution was stirred for 24 hr at 60°; some decomposition occurred. The mixture was filtered and the filtrate evaporated to dryness to give a pale yellow oily solid which was then dissolved in the minimum volume of benzene and chromatographed on a Florisil (Fischer, 100–200 mesh) column (2 × 20 cm). Elution with petroleum either gave a pale yellow band with some decomposition. The solution of the pale yellow band was evaporated and the residue dried under high vacuum to remove some ligand and some $Mo(CO)_6$ (probably from decomposition of excess of $Mo(CO)_3(CH_3CN)_3$). The residue was dissolved in petroleum ether, filtered, and crystallized to give a pale yellow compound which starts to decompose at 155° (0.526 g, 1.18 mmol, yield 44%).

The ir spectrum (cyclohexane) has two strong CO stretching bands at 1985 and 1942 cm^{-1} (±5 cm^{-1}). The pmr spectrum in C_6D_6 (Figure 6a) has multiplets centered at τ 5.45 (4 H), 6.88 (4 H), 8.02 (4 H) doublet, 8.24 (4 H), 8.54 (12 H). *Anal.* Calcd for $C_{24}H_{28}MoO_2$: C, 64.86; H, 6.30. Found: C, 64.8; H, 6.31.

$C_{11}H_{14}Mo(CO)_3$ (7). To a solution of $Mo(CO)_3(CH_3CN)_3$ (0.660 g, 2.5 mmol) in 250 ml of anhydrous THF was added $C_{11}H_{14}$ (1.0 g,

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[6] F. A. Cotton and A. Musco, *J. Amer. Chem. Soc.*, 90, 1444 (1968).

[7] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, 90, 1438 (1968).

[8] F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, 38, 147 (1972).

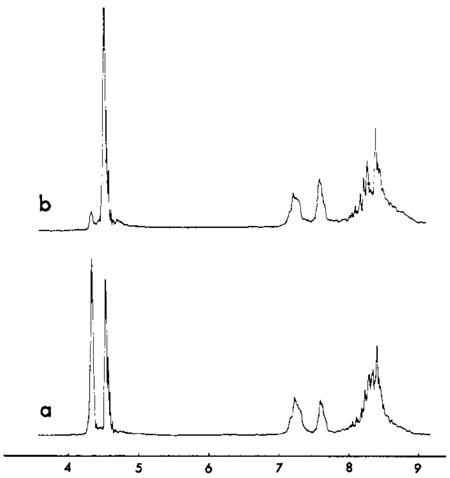


Figure 1. The pmr spectra (τ values at 60 MHz) in CCl_4 solution of: (a) a mixture of **1** and **2** (in ~3:7 ratio), (b) the same sample after heating for sufficient time (~20 min) at 80° to be considered in equilibrium.

6.85 mmol), which was a mixture of about 25% of **1** and 75% of **2**. The solution was stirred for 3 days at room temperature; some decomposition was evident. The solvent was evaporated leaving an oily brown solid which was extracted with three 20-ml portions of anhydrous benzene and filtered on Florisil (Fisher, 100-200 mesh) to remove solid material. The resulting orange filtrate was evaporated and the excess of ligand pumped off under high vacuum at 40°. The orange-yellow solid was extracted with petroleum ether (5 × 3 ml) to give an orange solution and a yellow solid (A). The orange solution was concentrated and chromatographed on a Florisil (Fisher, 100–200 mesh) column (2 × 10 cm) prepared in petroleum ether. Elution with petroleum ether–benzene (1:1) gave a small yellow band (B) followed by an orange band. The solution of the orange band was evaporated to give orange crystals (0.053 g, 0.16 mmol, yield 6.4%). The substance has no sharp melting or decomposition point; using a normal procedure for taking a melting point, decomposition first becomes evident at about 85°. The infrared spectrum (cyclohexane) has three strong CO stretching bands at 1993, 1929, and 1909 cm^{-1} (± 5 cm^{-1}). The pmr spectrum in C_6D_6 has multiplets at τ 4.86 (2 H), 5.35 (2 H), 5.94 (2 H), and 8.54 (8 H).

This compound is rather unstable. The quantity of pure product was too small for an elemental analysis.

The yellow solid (A) and the small yellow band (B) from the chromatography column were combined and dissolved in benzene. The solution was filtered on Florisil and the yellow filtrate was then evaporated to give pale yellow crystals (0.354 g, 0.82 mmol, yield 33%) of **6**.

Complexes Derived from 3 and 4. $C_{12}H_{16}Fe(CO)_3$ (8). To a solution of **3** and **4** in 7:3 molar ratio (1.0 g, 6.25 mmol) in hexane (30 ml) was added diiron enneacarbonyl (2.98 g, 8.2 mmol). The mixture was stirred at 50° for 12 hr. After filtration the green-brown solution was evaporated under vacuum to give an oily solid which was extracted with petroleum ether (3 × 5 ml) and chromatographed on an alumina (Woelm activity 2) column (2 × 20 cm). Elution with petroleum ether developed a yellow band while a brown-orange band remained at the top of the column. The yellow solution from the yellow band was evaporated under vacuum to give a yellow solid and an oil. The oil was distilled off at high vacuum giving ligands **3** and **4** (0.528 g, 3.3 mmol) in the same ratio as in the starting mixture (by pmr). The dry yellow solid was then crystallized from petroleum ether to give yellow needles, mp 93° (0.622 g, 2.08 mmol, yield 30%, or 70.5% based on only the reacted ligand). The ir spectrum in cyclohexane shows strong bands ν-(CO) at 2043, 1980, and 1973 cm^{-1} (± 5 cm^{-1}). The pmr spectrum in C_6D_6 (Figure 5b) has the following multiplets: τ 5.2 (2 H), 6.96 (2 H), 7.98 (2 H), 8.76 (10 H). *Anal.* Calcd for $C_{15}H_{16}FeO_3$: C, 60.05; H, 5.33; Fe, 18.62. Found: C, 60.1; H, 5.41; Fe, 18.6.

$C_{12}H_{16}Fe_2(CO)_6$ (9). The brown-orange band, remaining at the top of the column after elution of **8**, was eluted with a 2/1 mixture of petroleum ether and diethyl ether as an orange band. A brown residue remained at the top of the column. Evaporation of the solvent gave a red-orange crystalline solid which was dissolved in petroleum ether and recrystallized, mp 105° (0.018 g, 0.04 mmol, yield 0.6 or 1.4% based on reacted ligand). The ir spectrum (cyclohexane) has five strong bands in the CO stretching region: 2059, 2012, 1996, 1977, 1959 cm^{-1} (all ± 5 cm^{-1}). The pmr spectrum (CS_2 solution) shows (Figure 7) multiplets at τ 5.5 (2 H), 6.35 (2 H), 8.17 (2 H), and 8.51 (8 H) and a broad doublet at τ 7.7 (2 H). The quantity of product was too small for an elemental analysis.

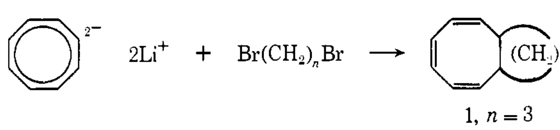
If the reaction time of $Fe_2(CO)_9$ with the mixture of **3** and **4** is increased, the yield of **8** is raised while the yield of **9** is reduced.

$C_{24}H_{32}Mo(CO)_2$ (10). To a solution of $Mo(CO)_3(CH_3CN)_3$(2.0 g, 6.3 mmol) in anhydrous tetrahydrofuran (350 ml) was added an approximately 7:3 mixture of **3** and **4** (1.12 g, 7.0 mmol). After about 15 min the mixture turned orange. The reaction mixture was stirred at 60° for 16 hr and then filtered. The orange filtrate was evaporated to dryness. The dark brown residue was extracted with a minimal volume of benzene and chromatographed on a Florisil (Fisher 100-200 mesh) column (2 × 20 cm). Elution with petroleum ether gave a yellow band (A) followed by an orange band (B) which moved very slowly. The solution from the yellow band (A) was evaporated under vacuum to give a yellow solid with some oil (ligand). The oil was distilled off at 0.03 mm to give about 200 mg of a mixture of **3** and **4** (same pmr spectrum as the starting mixture). The residue was crystallized from petroleum ether to give the product as pale yellow needles (0.151 g, 0.32 mmol, yield 9.1 or 11% based on the reached ligand) which starts to decompose at 145°. The ir spectrum (cyclohexane) shows two sharp CO stretching bands at 1986 and 1941 cm^{-1} (± 5 cm^{-1}). The pmr spectrum in C_6D_6 (Figure 6b) has multiplets at τ 5.4 (4 H), 6.8 (4 H), 7.65 (4 H), and 8.63 (20 H). *Anal.* Calcd for $C_{26}H_{32}MoO_2$: C, 65.82; H, 6.75. Found: C, 65.6; H, 6.82.

$C_{12}H_{16}Mo(CO)_3$ (11). The orange band (B) was eluted with a mixture of petroleum ether and diethyl ether (2:1) to give an orange solution which was evaporated to dryness and crystallized from petroleum ether. The product was obtained as orange crystals, mp 102–103° (0.845 g, 2.48 mmol, yield 35 or 43% based on the reacted ligand). The ir spectrum (cyclohexane) shows three strong CO stretching bands at 1988, 1928, and 1910 cm^{-1} (± 5 cm^{-1}). The pmr spectrum in C_6D_6 (Figure 8b) has multiplets at τ 4.93 (2 H), 5.38 (2 H), 5.91 (2 H), and 8.86 (10 H). *Anal.* Calcd for $C_{15}H_{16}MoO_3$: C, 52.94; H, 4.70; Mo, 28.24. Found: C, 53.0; H, 4.60; Mo. 28.1.

Discussion

The preparative method previously used[8,9] for bicyclo[6.2.0]deca-2,4,6-triene has been extended to obtain **1** and **3**, *viz.*



1, $n = 3$

3, $n = 4$

Compounds 1 and 2. Although **1** is presumably the initial product of the preparative reaction, it has not been possible to obtain it pure. Even under the mildest conditions for work-up and product isolation, appreciable isomerization of **1** to **2** occurs and the highest molar ratio of **1**:**2** which we have obtained is about 3:7. This reflects the fact that **1** is very unstable relative to **2**, as discussed later. The rate constants (*vide infra*) for the **1** → **2** transformation are great enough to account for substantial transformation of **1** into **2** over the time–temperature regime involved in the procedure for preparation and isolation of products.

The pmr spectra of **1** and **2** have been assigned rather straightforwardly on general criteria concerning chemical shifts, relative intensities, and spin–spin coupling constants together with constraints imposed by a comparison of the a and b spectra of Figure 1. The relative intensities in the spectrum of essentially pure **2**, Figure 1b, require assigning the peak at τ 4.5 to the four ole-

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[9] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, 92, 7612 (1970).

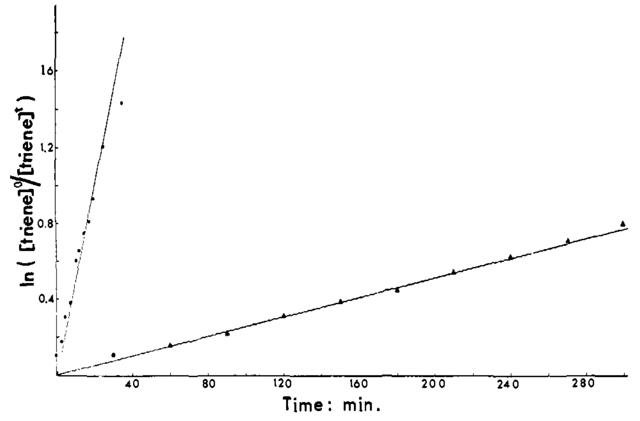


Figure 2. Plots of kinetic data for the transformation of **1** → **2**: ● at 58°, ▲ at 34°.

finic protons, the complex multiplet at τ 8.0–8.7 to the six methylene protons of the 5-ring, and the remaining two peaks to the two sets of bridgehead protons. While no conclusive deductions can be drawn, the appearance of the latter peaks suggests that the fused 5- and 6-rings have a trans relationship with reference to the plane of the central 4-ring. The peak at τ 7.65 is relatively narrow and is thus consistent with its being due to the 2,7 bridgehead protons which, in the postulated conformation, should not be strongly coupled either to the 3,6 protons (which is confirmed by the narrowness of the peak at τ 4.5) nor to the protons at the other bridgeheads.

The spectrum of Figure 1a can be assigned by using the ratio of the intensities at τ 4.35 and 4.5 to find the **1**/**2** molar ratio. With this ratio known the relative intensities in the remainder of the spectrum can be quantitatively accounted for by assigning the bridgehead protons of **1** a chemical shift of about τ 7.3 and the methylene protons an average shift of τ 8.3.

The olefinic proton resonances were used to follow the kinetics of conversion of **1** to **2** at two temperatures (Figure 2). Using each of the first-order rate constants together with an assumed frequency factor of 10^{13} an Arrhenius activation energy of 24 ± 1 kcal/mol is obtained. From this E_a value and a frequency factor of 10^{13}, the rate constant at 20° can be extrapolated to be 1.6×10^{-5} sec^{-1}.

These results are all similar to and consistent with those obtained by Huisgen, *et al.*,[5] for various cyclooctatrienes and their bicyclodiene tautomers. For the cyclooctatriene system itself they report $k_1(20°) = 5.3 \times 10^{-7}$ sec^{-1}, the diene/triene ratio (60°) = 0.12, and $\Delta H°$ for the triene → diene conversion = +1.1 kcal/mol. In the case of the **1**–**2** system the rate constant is higher, 160×10^{-7} sec^{-1}, and the $\Delta H°$ is more favorable by ~3 kcal/mol. The activation energy is lower by ~3 kcal/mol. Huisgen, *et al.*,[5] found general trends of this sort over a series of nine of their systems, but with many individual irregularities.

The main qualitative result to be emphasized is that fusion of the five-membered ring has a marked stabilizing effect upon the diene tautomer relative to the triene tautomer. The effect is very large in terms of the change in ratios (by a factor of ~300), although the change in $\Delta G°$ is only 3–4 kcal/mol. Any attempt to account for this result quantitatively would be premature in the absence of detailed structural data. However, the qualitative effect may be rationalized by invoking the well-known fact that the most stable conformation of a cyclopentane ring causes C–H bonds from two adjacent carbon atoms to be coplanar. Presumably the cyclohexadiene ring in any bicyclo structure of type b will impose planarity upon the 4-ring. Thus any additional factor which also favors planarity of the 4-ring will enhance the stability of the diene tautomer relative to the triene tautomer.

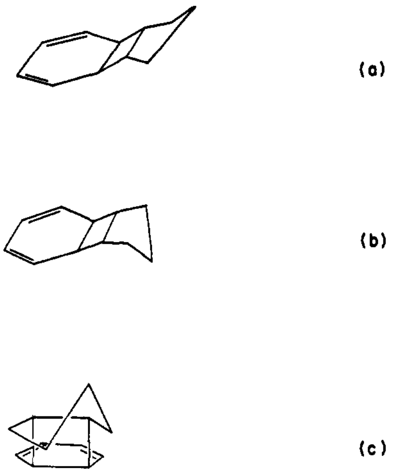


Figure 3. (a, b) Inferred structures and conformations for compound **2**. The bend in the 5-ring is deliberately exaggerated for clarity. (c) The structure considered most likely for compound **4**.

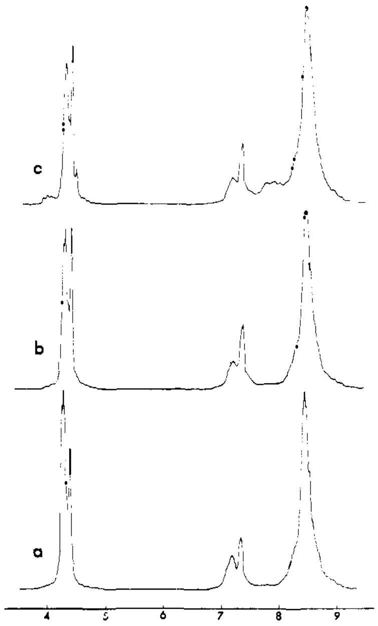


Figure 4. The pmr spectra (τ values at 60 MHz) of mixtures of **3** and **4** (neat sample with 5 drops of benzene as internal reference): (a) before heating, (b) after 1 hr at 114°, (c) after 17 hr at 114°.

It follows from all of the above considerations that the most probable structure of **2** is that shown in Figure 3a or 3b. The direction in which the unique methylene group will deviate from coplanarity with the remainder of the 5-ring is not predictable.

Compounds 3 and 4. For this system we have at present only qualitative information on the kinetics and equilibrium of interconversion. The pmr spectra shown in Figure 4 are interpreted in the following way.

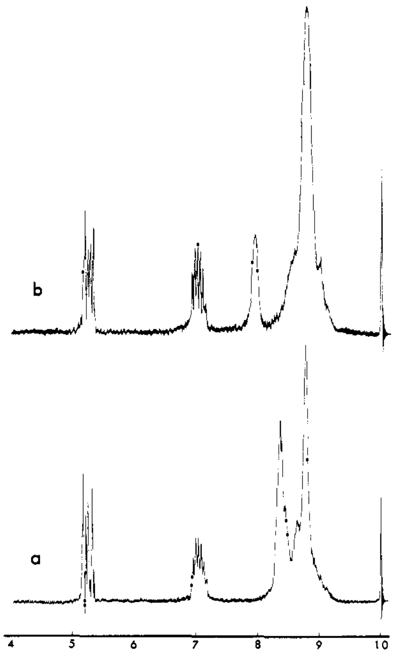


Figure 5. The pmr spectra (τ values at 60 MHz) in C_6D_6 solution of: (a) $C_{11}H_{14}Fe(CO)_3$ (**5**), (b) $C_{12}H_{16}Fe(CO)_3$ (**8**).

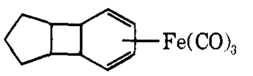
The product obtained directly from the preparative procedure is clearly a mixture of both tautomers and they are present in approximately 7:3 molar ratio of **3** to **4**. Only at temperatures above 100° could significant changes in the relative amounts be observed as a function of time. Results obtained at 114° are shown in Figure 4. The broad peak at τ 4.27 is assigned to the olefinic protons of the triene tautomer **3** while the singlet at τ 4.36 is due to the olefinic protons of the diene tautomer **4**. Since the broad peak at τ 7.2 decreases on heating along with the τ 4.27 peak, it is assigned to the bridgehead protons of **3**. The peak at τ 7.37 has a relative intensity approximately equal to that of the peak at τ 4.36 and must therefore be assigned to both sets of bridgehead protons in **4**. This is in contrast to the situation in **2** where the signals from the two sets were separated. Finally, the broad, complex band centered at about τ 8.5 is composed of all the signals from the methylene protons of both tautomers. The total intensity of this broad absorption is equal to the total intensity in the remainder of the spectrum, regardless of how the latter redistributes itself among the several different peaks.

The growth of additional absorption at τ 8.0 after 45 hr at 114° signifies either slow decomposition or perhaps transformation to another species by means of a hydrogen shift, which further complicates the problem of quantifying the kinetics and equilibrium of the **3** → **4** interconversions.

Qualitatively, it appears that fusing the 6-ring to the cyclooctatriene system slightly enhances the relative stability of the diene. The equilibrium ratio of **4**:**3** at 114° is approximately 1:1. However, the effect of the fused 6-ring is very slight compared to that of the fused 5-ring in favoring **2** over **1**. This may be due to the fact that a 6-ring cannot assume its most favorable conformation, the chair, when fused to the 4-ring in this case. The latter tends to constrain the 6-ring to have three consecutive C–C bonds coplanar, or nearly so. Strict coplanarity would require that the 6-ring adopt a tub or a half-chair conformation. The latter (structure c or its enantiomorph in Figure 3) is preferable with respect to H···H repulsions. However, if the 4-ring folds a little along one of its diagonals (as the free cyclobutane ring does), the 6-ring could have a conformation intermediate between the half chair and the full chair.

Metal Carbonyl Derivatives of 1 and 2. The preparation and study of these complexes has two purposes. First, the ease of preparation of complexes of the triene and diene tautomers gives further indication of the relative stabilities of the two tauomers in each system. Second, and more important, these complexes provide, in general, stable, isolable, crystalline derivatives which can be used to study in detail the structures, especially the stereochemistry of ring fusions and conformations. Such studies are already in progress on several of the derivatives reported here.

Pure **2** reacts with $Fe_2(CO)_9$ to give a high yield of **5** and no other isolated product. Similarly a 3:7 mixture of **1** and **2** also gave only **5** in good yield. Unlike the reactions of bicyclo[6.2.0]deca-2,4,6-triene[8] and the mixture of **3** and **4** with $Fe_2(CO)_9$, no $Fe_2(CO)_6$ derivative of the triene was detected among the products. This is consistent with the uniquely great relative stability of the tricyclodiene **2** which combines with the markedly dienophilic $Fe(CO)_3$ group.[10]



5

Compound **5** has an nmr spectrum (Figure 5a) which fully supports the proposed structure. The chemical shifts, hyperfine structure, and relative intensities of the two multiplets with the lowest τ values are conclusively diagnostic[8] of a coordinated 1,3-butadiene group. Although the resonances of the two pairs of bridgehead protons in **2** were separated, it appears probable that a small upfield shift of the 1,8 protons and a larger upfield shift of the 2,7 protons have resulted in a superposition of the two, giving a complex multiplet of relative intensity 4 at τ 8.37. The methylene protons are then assumed to have remained as a complex multiplet, shifted slightly upfield from τ 8.35 to 8.77. Although we believe that the foregoing assignment of the two upfield resonances is the more probable, it is not possible, on the data available, to exclude an alternative assignment in which the τ 8.37 multiplet is attributed to overlapping peaks from one set of bridgehead protons (probably 1 and 8) and from the endo 9 and 11 protons. In either of the conformations, Figure 3a or 3b, the 2,7 protons might be shifted upfield while the 1 and 8 protons might retain approximately the same position they have in **2**. Then a downfield shift of the endo 9 and 11 proton signals might bring them into coincidence with the 1 and 8 proton signals.

Reaction of the mixture of **1** and **2** with $Mo(CO)_3(NCCH_3)_3$ produced not only the expected complex of the triene $C_{11}H_{14}Mo(CO)_3$, **7**, but also the rather uncommon type of complex $(dien)_2Mo(CO)_2$, **6**. This reflects the considerably greater intrinsic stability of the diene ligand **2** over the triene ligand **1**. In fact, **6** was

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(10) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).

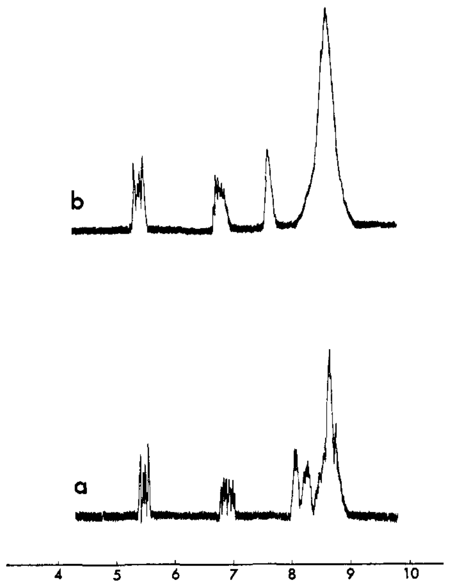
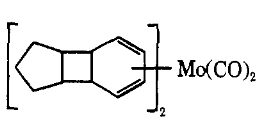


Figure 6. The pmr spectra (τ values at 60 MHz) in C_6D_6 solution of: (a) $C_{22}H_{28}Mo(CO)_2$ (**6**), (b) $C_{24}H_{32}Mo(CO)_2$ (**10**).



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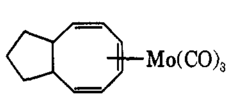


7

produced in high yield (44%) and **7** in only small yield (~6%).

Compound **6** is well characterized as to gross structure by its ir and pmr spectra (Figure 6a). The presence of two strong CO stretching bands in the ir spectrum is consistent with a pair of cis CO groups, and the pmr spectrum, especially the two low-field multiplets, leaves no doubt that two pmr equivalent 1,3-diene moieties are bound to the $Mo(CO)_2$ group. Detailed assignment of the upfield resonances is subject to the same ambivalence mentioned for **5**, but the spectrum is, in any event, fully consistent with the proposed structure. Few complexes of the $(diene)_2Mo(CO)_2$ type have previously been reported. Examples are $(Ph_4C_4)_2Mo(CO)_2$,[11a] a complex of cyclobutadiene (ν_{CO} = 2004, 1961 cm^{-1}), and (1,3-cyclohexadiene)$_2$Mo(CO)$_2$.[11b,c]

For **7** the pattern of the CO stretching bands in the ir region is indicative of a trigonal $Mo(CO)_3$ group. The pmr spectrum, Figure 8a, has a pattern of low-field multiplets very similar to that observed[12] in (h^5-1,3,5-C_8H_{10})$Mo(CO)_3$, and it thus strongly supports the assigned structure.

Metal Carbonyl Derivatives of 3 and 4. A mixture of **3** and **4** (7:3 molar ratio) reacts with $Fe_2(CO)_9$ to give a good yield (~70%) of the diene complex of $Fe(CO)_3$, **8**. It is also possible to isolate a tiny amount (~1% yield) of the $Fe_2(CO)_6$ adduct **9** of the bicyclotriene **3**.

The pmr spectrum of **8** (Figure 5b), like that of **5**, gives clear evidence for a coordinated 1,3-diene moiety in the low-field region. It is interesting that only one of the pairs of bridgehead protons now gives a resonance which is distinct from the strong upfield band. These are probably the 1,8 protons.

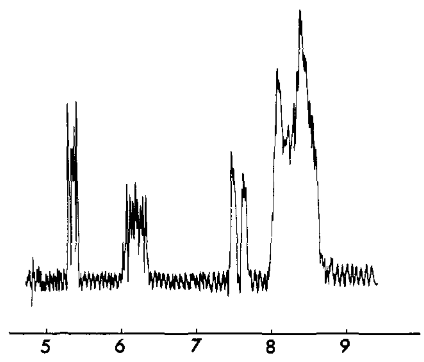


Figure 7. The pmr spectrum (τ values at 60 MHz) of $C_{12}H_{16}Fe_2(CO)_6$ (**9**) in CS_2 solution.

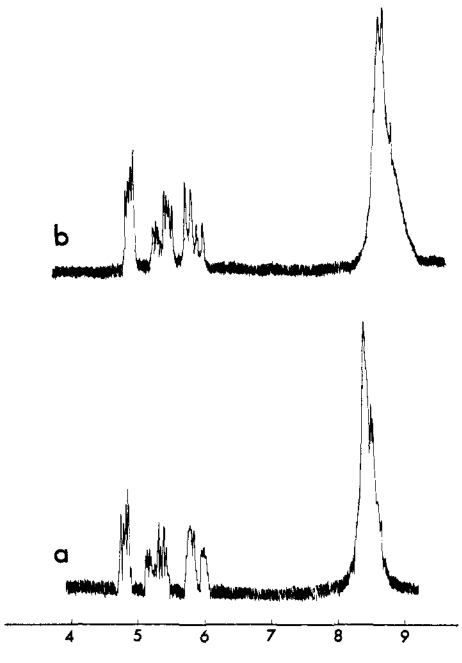
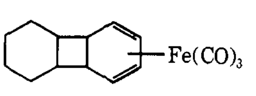


Figure 8. The pmr spectra (τ values at 60 MHz) in C_6D_6 solution of: (a) $C_{11}H_{14}Mo(CO)_3$ (**7**), (b) $C_{12}H_{16}Mo(CO)_3$ (**11**).



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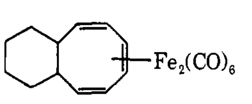

9

The pmr spectrum of **9** is shown in Figure 7. This spectrum closely resembles that of the $Fe_2(CO)_6$ complex of bicyclo[6.2.0]deca-2,4,6-triene reported earlier,[8] and thus implies that the two complexes have similar structures. X-Ray crystallographic and pmr studies of the latter[13] have shown that it has the same sort of skewed structure[14] as does (cyclooctatriene)$Fe_2(CO)_6$ and that its pmr spectrum is similarly temperature dependent.[15] Compound **9** should behave similarly.

The reaction of the 7:3 mixture of **3** and **4** with $Mo(CO)_3(NCCH_3)_3$ again led to two products, **10** and **11**,

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[11] (a) W. Hübel and R. Merenyi, *J. Organometal. Chem.*, 2, 213 (1964); (b) H. P. Fritz, H. Keller, and E. O. Fischer, *Naturwissenshaften*, 48, 518 (1961); (c) R. B. King, *J. Organometal. Chem.*, 8, 139 (1967).

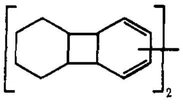
[12] R. B. King, *Inorg. Chem.*, 2, 807 (1963).

[13] F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, in press.

[14] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, **91**, 843 (1969).

[15] F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, **19**, 237 (1969).

analogous to those previously described (**6** and **7**)



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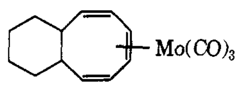

11

in the **1–2** system. The major difference is that now the yield of the $(diene)_2Mo(CO)_2$ complex **10** is small (~10%) while the yield of the triene complex **11** is much greater (~40%). This is consistent with the much higher relative stability of the triene **3** relative to the diene **4** as compared to the situation in the **1–2** system.

The two molybdenum carbonyl complexes have been structurally characterized by ir and pmr in much the same way as were the analogous compounds **6** and **7**. The $(diene)_2Mo(CO)_2$ complex has a pmr spectrum (Figure 6b) with the characteristic features of a coordinated 1,3-diene, and the triene complex **11** has a spectrum (Figure 8b) in the olefinic region very similar to that of cyclooctatrienemolybdenum tricarbonyl[12] and that of compound **7**.[16]

(16) NOTE ADDED IN PROOF. The crystal structures of **5** and **8** have been determined. The trans relationship of the fused rings postulated here for these compounds and their free olefin precursors, **2** and **4**, is thus confirmed. The conformation of the saturated 6-ring in **8** is intermediate between a chair and a half chair. Detailed reports on these structures are in preparation.

Solvation of Ions. XVII.[1] Free Energies, Heats, and Entropies of Transfer of Single Ions from Protic to Dipolar Aprotic Solvents

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Abstract: The results of applying several extrathermodynamic assumptions for estimating heats and entropies of transfer at 25° and free energies of transfer at 100° of single ions, when transferred from propylene carbonate to seven other solvents, are examined. With some exceptions, agreement between the assumptions is acceptable. We recommend that chemists adopt the assumptions that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$, and $\Delta S_{tr}(PhAs^+) = \Delta S_{tr}(Ph_4B^-)$.

The results of applying several extrathermodynamic assumptions, which are currently popular with chemists, for estimating single-ion free energies of transfer, ΔG_{tr}, from one solvent to another were compared in part XVI.[1] The comparisons were made in terms of solvent activity coefficients for transfer of a species i between a reference solvent 0 and another solvent S at 25°, and the thermodynamic relationships are as in eq 1.

$$\Delta G_{tr}(i) = 298R \ln {}^{0}\gamma_{i}{}^{S} \qquad (1)$$

Agreement between six quite different sets of assumptions was remarkably good, with a few reservations about one assumption when water was solvent. Thus we were able to recommend the assumption that there was negligible liquid junction potential in a cell composed of silver electrodes immersed in solutions of 0.01 *M* $AgClO_4$ in two solvents linked by a salt bridge of 0.1 *M* tetraethylammonium picrate in either solvent at 25°.

In this paper we examine the same extrathermodynamic assumptions, when applied to solutions at temperatures other than 25°, and also examine the results of applying these extrathermodynamic assumptions to enthalpies and entropies of transfer of single ions. Previous workers who have studied single ion enthalpies of transfer[3-6] have been almost unanimous in their choice of the assumption that $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$. Recent papers by Coetzee and Sharpe[7] and by Krishnan and Friedman[4] have shaken the confidence of those who favor this assumption. It is hoped that this paper will restore some of that confidence, at least when ΔH_{tr} is >5 kcal mol^{-1}.

We were by no means confident that the agreement noted in part XVI would extend from free energies to heats of transfer, because it is commonplace in chemistry to find that similar values of free energy result from widely differing but compensatory values of enthalpies and entropies. Clearly if chemists have confidence in values of ΔG_{tr}, ΔH_{tr}, and ΔS_{tr} for single ions, then they can obtain a much better understanding of ion–solvent interactions, within the framework of the assumption.

In this paper ΔG_{tr}, ΔH_{tr}, and ΔS_{tr} for transfer of both silver and bromide ions between eight solvents at 25 and 100° are estimated from four types of assumptions,[1] *i.e.*, the anion–molecule, the cation–molecule, the anion–cation, and the assumption of negligible liquid

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(1) Part XVI: R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1148 (1972).

(2) Author to whom enquiries should be addressed.

(3) G. Choux and R. L. Benoit, *J. Amer. Chem. Soc.*, **91**, 6221 (1969).

(4) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **75**, 3606 (1971).

(5) R. P. Held and C. M. Criss, *ibid.*, **71**, 2487 (1967).

(6) E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, **88**, 2598 (1966).

(7) J. F. Coetzee and W. R. Sharp, *J. Phys. Chem.*, **75**, 3141 (1971).