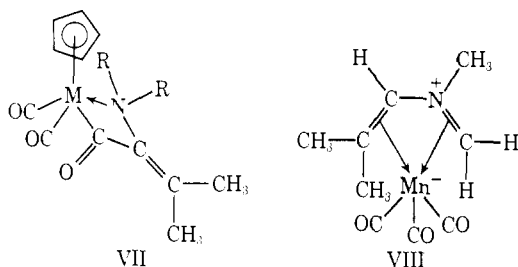


hexane 2071 (m), 1980 (s), 1964 (vs), 1953 (vs), and 1663 (m)  $\text{cm}^{-1}$ ; infrared  $\nu(\text{C}=\text{C})$  in KBr 1607  $\text{cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  [ $[\text{N}(\text{CH}_3)_2]$   $\tau$  6.85 and  $[\text{C}(\text{CH}_3)_2]$  8.09 and 8.33. These spectroscopic properties, particularly the observation of a *cis*- $\text{L}_2\text{M}(\text{CO})_4$  rather than an  $\text{LM}(\text{CO})_5$  pattern of terminal  $\nu(\text{CO})$  frequencies<sup>11</sup> and the presence of an acyl  $\nu(\text{CO})$  frequency (1663  $\text{cm}^{-1}$ ), preclude formulation of this manganese derivative as II ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) analogous to the rhenium compound discussed above but instead require formulation as a cyclic acyl derivative such as VI ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ). Similarly, reaction<sup>7</sup> of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{Cl}$  with  $\text{NaW}(\text{CO})_5\text{C}_5\text{H}_5$  gives a low yield of yellow crystalline<sup>8</sup>  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  (VII;  $\text{M} = \text{W}$ ,  $\text{R} = \text{CH}_3$ ): mp 106–112° dec; infrared  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$  1938 (s), 1913 (w), 1856 (s), 1822 (w), and 1617 (m)  $\text{cm}^{-1}$ ; proton nmr<sup>9</sup> in  $\text{CDCl}_3$  ( $\text{C}_5\text{H}_5$ )  $\tau$  4.80, [ $[\text{N}(\text{CH}_3)_2]$  6.44 and 6.76, and  $[\text{C}(\text{CH}_3)_2]$  8.96. The nmr equivalence of the two *N*-methyl groups ( $\text{R} = \text{CH}_3$ ) in  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{Mn}(\text{CO})_4$  (VI) but their nonequivalence in  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  (VII;  $\text{M} = \text{W}$ ) arises from the symmetry of the *cis*- $\text{Mn}(\text{CO})_4$  unit and the asymmetry of the  $\text{W}(\text{CO})_2\text{C}_5\text{H}_5$  unit.



Ultraviolet irradiation of  $(\text{CH}_3)_2\text{C}=\text{C}[\text{N}(\text{CH}_3)_2]\text{C}(\text{O})\text{Mn}(\text{CO})_4$  (VI;  $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) in hexane solution<sup>12</sup> results in the loss of two carbonyl groups to give a 28% yield of a yellow crystalline tricarbonyl:<sup>7,9</sup> mp 36–37°; infrared  $\nu(\text{CO})$  in hexane 2018 (s), 1927 (s), and 1906 (s)  $\text{cm}^{-1}$ . The proton nmr spectrum of this tricarbonyl indicates migration of one of the *N*-methyl protons to the carbon atom not bearing the methyl groups, resulting in the complex VIII with the five-electron donor 2-azabutadiene ligand. Thus, this proton nmr spectrum exhibits resonances at  $\tau$  4.66 (singlet), 7.40 (singlet), 8.01 (doublet,  $J = 5$  Hz), 8.16 (singlet), 8.27 (singlet), and 8.56 (broadened doublet,

(11) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(12) This double decarbonylation reaction also proceeds without ultraviolet irradiation in boiling heptane or hexane; 13 days are required for completion in the latter solvent.

$J = 5$  Hz) of approximate relative intensities 1:3:1:3:3:1, respectively, which may be assigned to the  $-\text{CH}=\text{C}$  proton, the *N*-methyl group, one  $=\text{CH}_2$  proton, the two nonequivalent *C*-methyl groups, and the other  $=\text{CH}_2$  proton, respectively. The hydrogen migration necessary to convert the manganese carbonyl derivative VI ( $\text{M} = \text{Mn}$ ,  $\text{R} = \text{CH}_3$ ) to the 2-azabutadiene manganese tricarbonyl derivative is somewhat similar to hydrogen migrations which occur upon heating iron carbonyls with nonconjugated diolefins<sup>13</sup> to give iron tricarbonyl complexes of conjugated diolefins.

Implicit in some of the above structural deductions through proton nmr spectroscopy is the assumption that the lower field methyl resonances arise from the *N*-methyl groups and the higher field methyl resonances arise from the *C*-methyl groups. This assumption has been verified by preparation, characterization, and taking the nmr spectra of the piperidino analogs of the key compounds IV, V, VI, and VIII (*i.e.*,  $2\text{R} = -(\text{CH}_2)_5-$ ) by reaction of the  $\alpha$ -chloroamine I ( $2\text{R} = -(\text{CH}_2)_5-$ ) with the corresponding metal carbonyl anion under conditions essentially identical with those used for the preparations of the dimethylamino analog (*i.e.*,  $\text{R} = \text{CH}_3$ ) discussed above.

This work indicates that reactions of  $\alpha$ -chloroamines with transition metal compounds can be used to prepare organometallic derivatives of novel types not yet obtainable by other methods. Further work on these interesting compounds is currently in progress.

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(13) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961); J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, **83**, 2954 (1961); G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

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### Cationic Studies on the 9-Bicyclo[4.2.1]nona-2,4,7-trienyl System<sup>1,2</sup>

Sir:

An area of considerable research interest involves the nature of homoaromaticity<sup>3</sup> and bicycloaromaticity,<sup>4</sup> where the importance of these concepts was made evident by the chemical behavior of the 7-norbornadienyl and 7-norbornenyl cations.<sup>5</sup> The concept of bicyclo-

(1) This research was supported in part by the National Science Foundation, Cottrell Research Foundation, and USPHS 2-T01-GM-01045.

(2) Presented in part at the 8th Regional Meeting of the American Chemical Society, San Francisco, Calif., Oct 1972.

(3) See S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967); *Quart. Rev., Chem. Soc.*, **22** (2), 141 (1969).

(4) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2200 (1972); **92**, 3186 (1970); P. Alberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *ibid.*, **92**, 3478 (1970).

(5) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); (b) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133, 3135 (1966); (c) R. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350, 6352 (1967); (d) J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969).

Table I. Acetolysis  $k$ 's for a Variety of Alkyl Toluenesulfonates

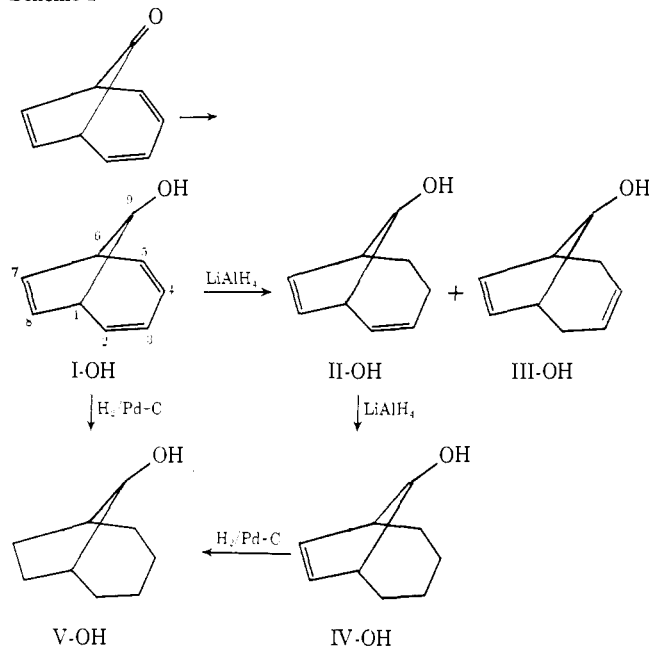
ROTs (0.01 $M$ )	Mp, °C	Temp, °C	$10^6k$ , sec $^{-1}$	Rel $k$	$\Delta H^\ddagger$ , kcal	$\Delta S^\ddagger$ , eu
I-OTs	85.0–85.5	25.0 (ext)	2.88	20,300	23.0	–6.7
		50.0	$63.7 \pm 0.8$			
		75.0	$901 \pm 12$			
		125.0 (ext)	68,000			
IV-OTs	49–52	125.0	$7.5 \pm 0.3$	2.2	28.5	–12.7
V-OTs	76.0–76.5	125.0	$3.35 \pm 0.11$	(1.0)		
		148.8	$27.0 \pm 0.2$			
<i>anti</i> -7-Norbornenyl-OTs		25.0 <sup>6a</sup>	904			
7-Norbornyl-OTs		125.0 <sup>a</sup> (ext)	0.33	0.1	35.7	–3.5

<sup>a</sup> A. Diaz, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970).

aromaticity was invoked by Goldstein and Hoffmann<sup>6</sup> in a series of papers where they attempt to clarify the nature of the interaction between  $\pi$ -systems in bicyclic ions and classify a variety of ionic structures. We now wish to present the results of a study on the solvolysis of *endo*-9-bicyclo[4.2.1]nona-2,4,7-trienyl toluenesulfonate, I-OTs, precursor for a potential bicycloaromatic cation with six  $\pi$ -electrons delocalized over seven carbon atoms.

The *endo*-9-bicyclo[4.2.1]nona-2,4,7-trienyl alcohol, I-OH, was prepared using the synthesis recently published.<sup>7</sup> The *endo* configuration of the carbinol was previously established.<sup>7</sup> The carbinol (mp 51.0–51.5°) was converted to its toluenesulfonate ester (I-OTs) with toluenesulfonyl chloride in pyridine. Reaction of I-OH with  $\text{LiAlH}_4$  produced a mixture of II-OH and III-OH, mp 80.0–80.5 and 51.0–51.5°, respectively. Further reaction of II-OH with  $\text{LiAlH}_4$  yielded IV-OH in 95% yield, mp 115–117° (Scheme I). The carbinol V-OH

Scheme I



is produced in high yields from the above carbinols by catalytic hydrogenation, mp 116–117°. The corresponding toluenesulfonate esters were prepared as usual.

The rates of acetolysis of the various toluenesulfonate esters were followed by titration of the produced tolu-

enesulfonic acid.<sup>8</sup> Good first-order kinetics were observed in every case except with IV-OTs which showed a slight downward drift during the run. Inspection of Table I shows the enhanced reactivity of I-OTs over the other more saturated compounds in the series. Comparison of similar compounds of this series with the [2.2.1]alkyl-OTs ester series<sup>5</sup> shows that V-OTs is ten times more reactive than 7-norbornyl-OTs while I-OTs is 300 times less reactive than *anti*-7-norbornenyl-OTs and therefore  $3 \times 10^5$  times less reactive than the norbornadienyl vinyllog.<sup>5</sup> Overall, in the [4.2.1] system the reactivity difference between the fully unsaturated and the saturated compounds is  $2 \times 10^4$  compared to  $10^{14}$  for a similar comparison in the [2.2.1] system.<sup>5</sup> The difference in the amount of  $\pi$  participation between the two series may be due to the difference in geometry.<sup>9</sup>

The products from the NaOAc buffered acetolysis of I-OTs were recovered in 99% yield after ten reaction half-lives at 50° and consisted of a 99 to 1 mixture of *exo*-dihydroindenyl acetate (VI-OAc)<sup>10</sup> and indene, respectively. This same product mixture was found even in reaction conditions where the intermediate cations are shorter lived. In 67% aqueous diglyme containing 4  $M$   $\text{NaBH}_4$  plus 1  $M$   $\text{NaOH}$ , the product mixture contained 98% *cis*-dihydroindene and 2% indene. Therefore, the products from I-OTs arise primarily from chemical capture of a rearranged cation.

Product analysis was also performed on 9-deuterated I-OTs (mp 89.5–90.5°) prepared from the carbinol available from the  $\text{NaBD}_4$  (99% D) reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one.  $\alpha$ -D-I-OTs was solvolyzed in NaOAc-buffered AcOH for one half-life. The recovered ROTs contained less than 2%  $\alpha$ -H as determined by nmr. Therefore no significant deuterium scrambling involving the 9 position occurs in the starting material.

The 220-MHz nmr spectrum for VI-OAc shows signals at  $\delta$  1.92 (s, 2.95 H), 2.89 (d, 1.02 H), 3.64 (d, 0.99 H), 5.34 (m, 0.98 H), 4.57 (m, 1.06 H), 5.66 (s, broad, 2.7 H), and 5.83 (s, broad, 2.2 H). The proton assignments made are shown in the structure, where the hydrogens in the butadiene moiety are not resolved. The addition of 30 mg of  $\text{Eu}(\text{fod})_3$  to the 45-mg sample of VI-OAc shifts some of the peaks in the olefinic region

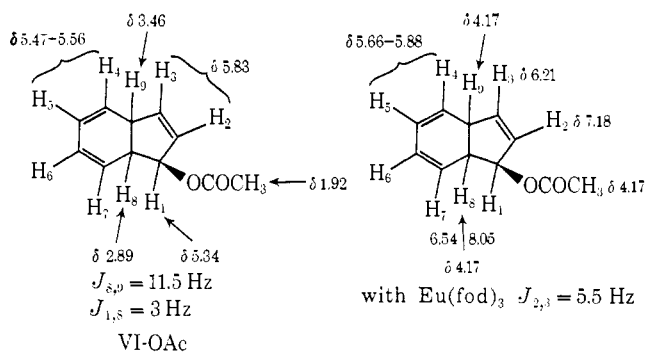
(8) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 618 (1961).

(9) From models one estimates the angle  $\text{C}_8\text{--C}_1\text{--C}_9$  at 154° in IV-OTs compared to 126° for the analogous angle in 7-norbornenyl-OTs.

(6) (a) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6356, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(7) (a) T. A. Antkowiak and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5361 (1972); (b) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter *ibid.*, **94**, 5366 (1972).

(10) The *exo* assignment for the *cis*-fused system is based on the nmr coupling constant  $J_{1,8}$  of 3 Hz. The *exo*- and *endo*-dihydroindenyl alcohols have  $J_{1,8}$  values equal to 4 and 7 Hz, respectively: D. Cook, A. Diaz, J. P. Dirham, D. L. Harris, M. Sakai, S. Winstein, J. Barborak, and P. v. R. Schleyer, *Tetrahedron Lett.*, **18**, 1405 (1971).



downfield. The relative shifts are H<sub>1</sub> (10), H<sub>2</sub> (5.0), H<sub>3</sub> (1.4), H<sub>7</sub> (4.0), and H<sub>4</sub>-H<sub>6</sub> (<0.5).

The spectra for VI-OAc-*d* produced in the acetolysis of  $\alpha$ -D-I-OTs is identical with the undeuterated material except that the signal at  $\delta$  5.83 integrates for one hydrogen. In the presence of  $\text{Eu}(\text{fod})_3$  the peak at  $\delta$  7.18 disappears, the  $\delta$  6.12 doublet collapses to a singlet, and the rest of the spectrum is unchanged.

Therefore, effectively all the deuterium appears at one position, the C<sub>2</sub> position of VI-OAc.<sup>11</sup> This result eliminates the possibility of rearrangement occurring *via* a simple shift of the C<sub>1</sub>-C<sub>2</sub> bond to the C<sub>3</sub> cationic center of I as observed in the reaction of 9-phenylbicyclo[4.2.1]nona-2,4,7-trien-9-ol with  $\text{SOCl}_2$  in pyridine<sup>12</sup> and is more in line with reaction of this carbinol with toluenesulfonic acid in  $\text{HCCl}_3$  to produce 2-phenylindene.<sup>12</sup> The acetolysis of IV-OTs in NaOAc buffered acetic acid produces IV-OAc, which was recovered in 97% yield, and no other products were observed. Thus, the solvolysis of IV-OTs must proceed *via* a bishomocyclopropenyl cation intermediate. On the other hand the acetolysis of V-OTs produces a four to one mixture of the epimeric *exo*-V-OAc and a rearranged olefin.

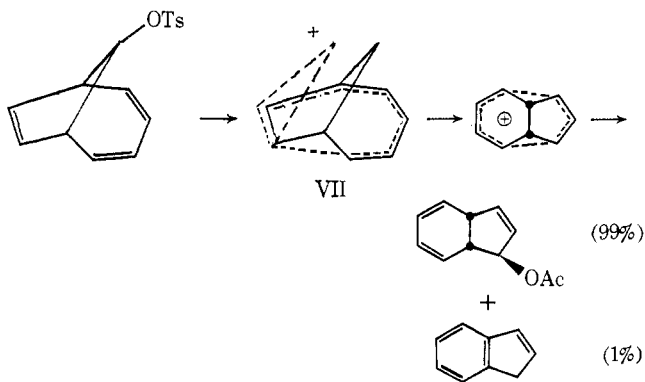
The enhanced reactivity of I-OTs in spite of the rate retarding inductive effect of the butadiene moiety is ascribed to a stabilizing interaction by this group with the incipient bishomocyclopropenyl cation (involving carbons 7, 8, and 9) in the rate-determining step to produce a bicycloaromatic cation (VII). The bicycloaromatic character of this cation contributes *ca.* 7.2 kcal of additional stabilization to the transition state from I-OTs (calculated from the relative *k*'s for I-OTs and IV-OTs), while the stabilization attributed to homo-

(11) While in press, a report appeared showing that the product from 9-D-I-OTs in DMSO at 74° is indene with the deuterium located specifically in the 2 position: D. C. Sanders and H. Shechter, *J. Amer. Chem. Soc.*, **95**, 6858 (1973).

(12) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, **35**, 3383 (1967).

aromaticity is a small portion of the total resonance stabilization.<sup>13</sup> In contrast, for the 7-norbornadienyl cation, 75% of the stability is due to homoaromaticity and only 25% to bicycloaromaticity.<sup>4</sup>

Since the photoelectron spectroscopy data reported by Heilbronner, *et al.*, suggest no interaction between the monoene and the diene in the bicyclo[4.2.1]nonatriene,<sup>14</sup> the interaction upon ionization of I-OTs must occur with a considerable amount of motion of the atoms involved and little or no vertical stabilization. Thus the ionization of I-OTs is consistent with the formation of a bicycloaromatic cation generated by extensive laticyclic interaction between the bishomocyclopropenyl cation and the butadiene moiety (VII).<sup>15,16</sup> However the stabilization of the initial cation is not large and it efficiently rearranges in a specific and symmetrical way to the more stable bishomotropylium ion which gives chemical capture products primarily.



(13) Analysis of the homoaromaticity and bicycloaromaticity contributions to the stability of this system will be presented in a fuller paper with the necessary definitions of the *k*'s selected for the various ROTs esters.

(14) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(15) Interaction of the olefinic groups with the developing cationic center in solvolysis is consistent with the photoelectron spectra data on the 9-methylenebicyclo[4.2.1]nonatriene<sup>16</sup> which shows a stabilizing interaction between the isolated double bonds when the polarization of the *exo* methylene makes C-9 a positive center (see footnote 8 of ref 16).

(16) M. Reetz, R. W. Hoffmann, W. Schafer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **12**, 81 (1973).

(17) Deceased Nov 23, 1969.

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## Book Reviews\*

**Advances in Catalysis. Volume 23.** Edited by D. D. ELEY, H. PINES, and P. B. WEISZ. Academic Press, New York, N. Y. 1973. ix + 352 pp. \$19.00.

This volume has contributions on both heterogeneous and homogeneous catalysis. J. R. Anderson writes about skeletal re-

arrangements of hydrocarbons catalyzed by metals, and J. H. Sinvelt discusses metal-catalyzed hydrogenolysis of hydrocarbons. Chemisorption of benzene, hydrogen-deuterium exchange, and hydrogenation of benzene are the subject of a contribution by R. B. Moyes and P. B. Wells. The photocatalytic effect, discussed by Th. Wolkenstein, is less well known; it is defined as the change in catalytic activity of the surface of a semiconductor under illumination and has been applied particularly to hydrogen-deuterium ex-

\* Unsigned book reviews are by the Book Review Editor.