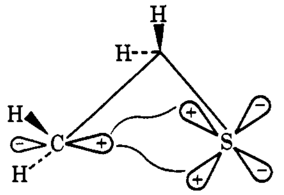
trimethylene species has a planar structure and lies $\sim$64 kcal above the ground state.[3,7] The energy barrier for rotation of the terminal methylenes has been estimated as $\sim$12 kcal.

Our extensive kinetic data on both the addition reactions of sulfur atoms to olefins and the thermolysis of episulfides suggest a similar excited π-thiacyclopropane structure intermediate. This state should then lie not more than 40.2 kcal above the ground state and, in order to maintain the geometrical configuration of the starting material in the product, the terminal methylene should be nonplanar, distorted out of the plane of the two carbon and sulfur atoms, one hydrogen being above and the other below the plane. This is not an unreasonable conformation for this species. In the episulfide molecule the presence of the nonbonding 3p orbital (and the possible participation of d orbitals) may be expected to alter the bonding situation considerably. (π-Cyclopropane belongs to the C_{2v} symmetry while π-thiacyclopropane to the C_s symmetry group.) If the two nonbonding p orbitals of the sulfur become degenerate one may envisage a σ–π hybrid bond between the terminal methylene carbon and the sulfur which would be fully capable of accounting for all of our kinetic and stereochemical observations. We also believe that in the addition of $S(^3P)$ atoms to olefins the π-thiacyclopropane is in a triplet state which, in contrast to trimethylene, still possesses a relatively high energy barrier to rotation of the terminal methylene.



Finally a brief comment on the apparent long lifetime of the π-thiacyclopropane intermediate would be appropriate. Benson[8] estimated the activation energy of the ring-closure reaction of the trimethylene intermediate in the thermolysis of cyclopropane as 8.2 kcal. This value is now meaningless since it is based on a double doublet trimethylene, while the actual intermediate is more likely a singlet excited trimethylene.[3,7] The only estimate of E_a (ring closure) presently available is that of Hoffmann's computed value[3] of 1 kcal. In the excited thiacyclopropane the σ–π hybrid bond may be considerably stronger than the π bond in trimethylene, and consequently E_a (ring closure) could be higher as well. It should also be noted that the temperature of the thiacyclopropane reaction was about 200° lower than that of the cyclopropane thermolysis studies.

Acknowledgments. We thank the National Research Council of Canada and Imperial Oil Enterprises Ltd. for financial support and Mr. A. Jodhan for helpful experimental assistance.

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Electron Spin Resonance Evidence for Bromide Ion Exchange with the Tetrabromomanganese(II) Complex in Acetonitrile

Sir:

Recently, the electron paramagnetic resonance spectrum of the tetrahedral $[MnBr_4]^{2-}$ complex in acetonitrile was reported.[1] The widths of the ^{55}Mn nuclear hyperfine components were found to be unusually broad, and it was noted that the line broadening became more pronounced with increasing bromide concentration. It was suggested that the bromide-dependent line broadening might be due to ligand exchange. In this communication, we set forth evidence to confirm this interpretation.

The resonance widths of the esr spectrum of the $[MnBr_4]^{2-}$ complex were studied as a function of both temperature and excess bromide concentration. All solutions were prepared by dissolving tetra-*n*-butylammonium bromide and $MnBr_2$ in acetonitrile. Bromide concentrations in excess of the stoichiometric 4:1 ratio were taken to be the excess concentration. Intensity measurements indicated that in solutions containing the stoichiometric concentration of bromide, the Mn(II) had been converted almost completely to the complex.[1] Resonance widths were extracted by comparing experimental and computer-synthesized spectra.

The possibility of resonance broadening due to superexchange *via* the diamagnetic solvent molecules and halide ions was eliminated by studying the resonance widths as a function of Mn(II) concentration. The resonance widths were found to change insignificantly over the Mn(II) concentration range of 0.005–0.05 *m*, provided the excess bromide concentration was constant. The effect of the tetraalkylammonium counterion was also considered, and, although it influences the over-all resonance width, it does not contribute to the observed bromide-dependent width. Details of the counterion effect will be treated in a subsequent paper.

Garrett and Morgan[2] have established that electron spin relaxation of the unpaired electrons in solvated Mn(II) complexes arises principally from modulation of the dynamical axial zero-field splitting resulting from transient distortions of the complex by solvent fluctuations in the immediate surroundings of the paramagnetic ion. If this mechanism were the only one operative here, the resonance widths would vary linearly with the correlation time characteristic of the solvent fluctuations and would not be strongly dependent upon the bromide concentration. It has been suggested[2,3] that this correlation time is proportional to $\eta M/\rho T$, where η is the viscosity of the solution, M is the molecular weight of the solvent, and ρ is the density of the solvent at temperature T. In Figure 1, we have plotted the variation of the esr resonance widths *vs.* $\eta M/\rho T$ for three solutions, each containing a different excess bromide concentration (0, 0.084, 0.304 *m*). It is interesting that, whereas the resonance widths for each of these solutions do vary linearly with $\eta M/\rho T$ as the solvent structural correlation

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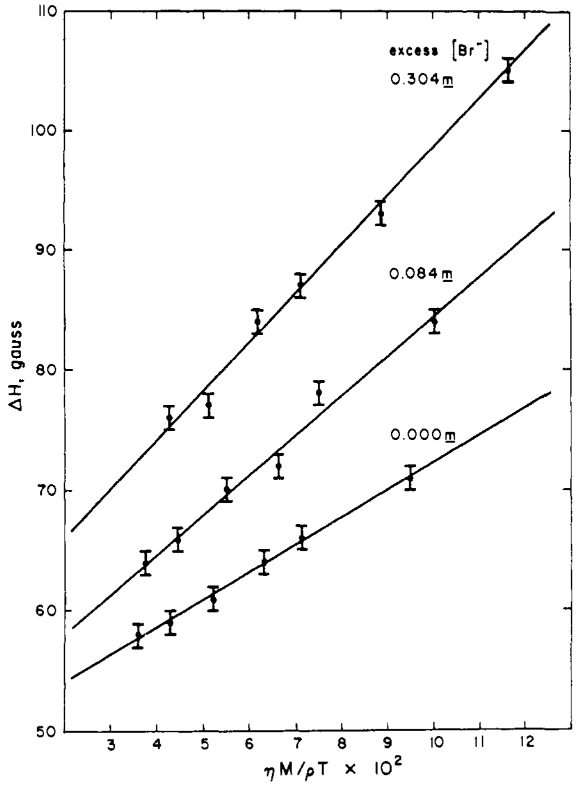

Figure 1. Variation of the observed resonance widths, ΔH (gauss), with $\eta M/\rho T$, for three $[\text{MnBr}_4]^{2-}$ solutions, each containing a different excess bromide concentration: (a) zero excess bromide; (b) 0.084 *m* excess bromide; (c) 0.304 *m* excess bromide. Estimated errors in resonance widths, ±1 G; temperature, ±2°. All solutions contained 0.05 *m* manganese in acetonitrile.

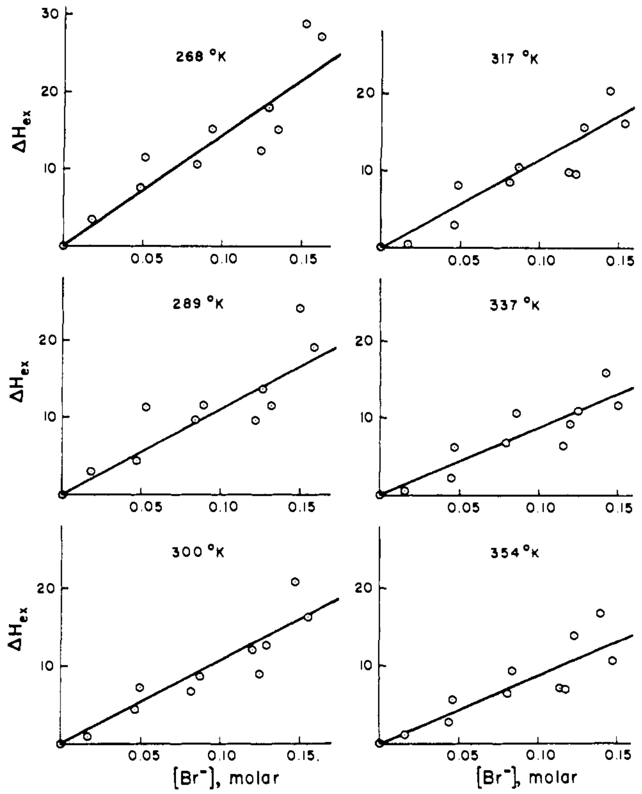

Figure 2. Ligand exchange widths, $\Delta H_{\text{exchange}}$ (gauss), *vs.* the excess bromide concentration at several temperatures. All solutions contained 0.05 *m* manganese in acetonitrile.

time is varied with temperature, the data points corresponding to different excess bromide concentrations do not fall on the same line. This clearly indicates the onset of a new relaxation mechanism which is dependent upon the excess bromide concentration.

In Figure 2, the excess widths attributable to the new bromide-dependent relaxation mechanism are plotted *vs.* the excess bromide concentration at several temperatures. These widths have been corrected for small variations in the solvent viscosity resulting from the addition of the excess bromide. The corrections amounted, at most, to several gauss and hence do not affect the final data significantly. The excess bromide concentrations have also been compensated for the incomplete dissociation of tetra-*n*-butylammonium bromide in acetonitrile. The known dissociation constant of 0.5 reported[4] at 25° was used for all temperatures since temperature data concerning the dissociation of this salt were unavailable.

The most plausible interpretation of the significant bromide-dependent resonance widths is bromide ligand exchange. Presumably, the electronic distortion during the ligand exchange process is strong, so that the lifetimes of the spin states, and hence both the longitudinal and transverse relaxation times, are limited to the chemical lifetime of the complex. The linear variation of the bromide-dependent widths with excess bromide concentration depicted in Figure 2 suggests that the ligand exchange is bimolecular, involving one bromide and one $[\text{MnBr}_4]^{2-}$. Analysis of the data according to the following well-known expression[5,6]

$$(1/T_2)_{\text{exchange}} = k[\text{Br}^-] = \sqrt{3}\beta\pi(g/h)\Delta H_{\text{exchange}}$$

yielded the following bimolecular rate constants (l. mole^{-1} sec^{-1}) for the ligand-exchange process: k = 2.2 × 10^9 (268°K); 1.7 × 10^9 (289°K); 1.7 × 10^9 (300°K); 1.8 × 10^9 (317°K); 1.3 × 10^9 (337°K); 1.3 × 10^9 (354°K).

The rate constants deduced suggest that the kinetics of the ligand exchange is possibly diffusion controlled. Analysis of the kinetic data by classical transition-state theory therefore has questionable validity. When the standard Arrhenius plot is made, one obtains an apparent enthalpy of activation of −1 kcal/mole, and an apparent entropy of activation of −22 eu. The small and negative apparent energy of activation is probably not too meaningful. The large and negative apparent entropy of activation, however, is consistent with an association mechanism for the ligand-exchange process.

Previous studies[2,7] on the electron spin relaxation in Mn(II) complexes in solution have dealt exclusively with octahedral complexes, and, with a few exceptions at high temperatures, these octahedral complexes have been shown to be kinetically stable on the esr time

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scale of observation, even though they are generally considered to be labile. Tetrahedral complexes are known to undergo ligand replacement in the first coordination sphere more readily than octahedral complexes, presumably because of the ease with which the classical five-coordinate intermediate is formed. The lability of the tetrahedral $[MnBr_4]^{2-}$ complex toward ligand replacement demonstrated in this work is thus consistent with these trends.

(8) (a) NASA Predoctoral Fellow, 1966–1967; (b) Alfred P. Sloan Research Fellow.

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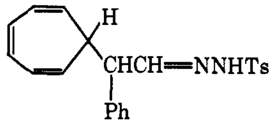
Isolation of a Potential Intermediate Leading to 9-Phenylbicyclo[4.2.1]nona-2,4,7-triene in the Thermal Decomposition of α-Phenyl-α-tropylacetoaldehyde Tosylhydrazone[1]

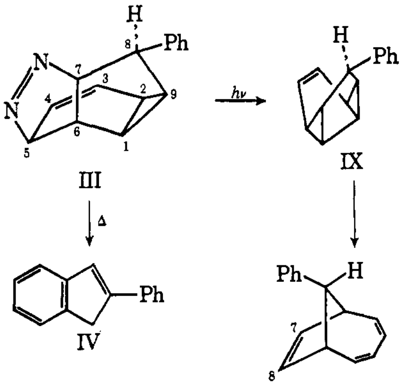
Sir:

In connection with recent progress in the chemistry of C_9H_{10} hydrocarbons,[2,3] the unexpected formation of bicyclo[4.2.1]nona-2,4,7-triene in the thermal decomposition of tropylacetoaldehyde tosylhydrazone[4] directed us to carry out more detailed studies in this field. We chose the thermal decomposition of α-phenyl-α-tropylacetoaldehyde tosylhydrazone (I), from which we could isolate an interesting rearranged product (II) and a potential intermediate (III) leading to bicyclo[4.2.1]nona-2,4,7-triene and indene derivatives.

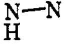
Heating of the sodium salt of I in dioxane at 80–83° afforded two products, II, mp 134° (25%), and III, mp 94° (7%), both having formula[5] $C_{15}H_{14}N_2$ (*m/e* 222), and 2-phenylindene (IV; 2%) in addition to the reported products[4] 9-phenylbicyclo[4.2.1]nona-2,4,7-triene[6] (V; 30%) and 9-phenyltricyclo[3.3.1.0^{4,6}]nona-2,7-diene (VI; 3%).[7] Product II was confirmed to be 1-phenyl-6-(3-pyrazolyl)-1,3,5-hexatriene from the following chemical and spectral evidence: ir (KBr) 3175, 2883 (hydrogen bonding and NH band of pyrazole), 987 (*trans* CH=CH), 746 cm^{-1} (*cis* CH=CH); uv (MeOH) 340 mμ (ε 46,710); nmr (60 Mc) ($CDCl_3$) τ 2.4–3.9 (very complex), including an AB pattern at τ 2.46 and 3.59 (J = 2.0 Hz) ascribed to pyrazole ring protons. The decisive evidence for the presence of the pyrazole ring was oxidation of II with potassium permanganate, from which pyrazole-3-carboxylic acid[8] and benzoic acid were obtained. Catalytic reduction of II resulted in the absorption of 3 mol of hydrogen, giving a hexahydro compound (VII), bp 175–178° (3 mm).[9] When II was heated in benzene containing iodine, an isomer (VIII), mp 202°, was obtained, and its uv spectrum (325, 344, and 360 mμ in MeOH) is very similar to that of all-*trans*-1,6-diphenyl-1,3,5-hexatriene.[10] These facts could establish the structure of II, except for the geometry of the triene system, which contains at least one *cis* ene.



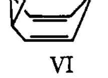
I



III IX IV V



II



VI

The structure of III could be deduced on the basis of the following spectral data and chemical evidence: ir (KBr) 1642, 725 (*cis* CH=CH), and 1534 cm^{-1} (N=N);[11] uv (MeOH) 260 sh (ε 1080), 269 sh (660), and 340 mμ (240) (N=N). The mass spectrum of III is very similar to that of V except for the molecular ion (*m/e* 222). Nmr spectra (100 Mc, $CDCl_3$) and decoupling experiments permitted the following assignment of the signals of III (chemical shifts in τ values in parentheses) and provided the following coupling constants: H-1 (triplet of doublet, 7.90), H-2 (octet, 8.42), H-3 (split quartet, 3.84), H-4 (quartet, 4.01), H-5 (split doublet, 4.97), H-6 (octet, 7.37), H-7 (triplet, 4.29), H-8 (split doublet, 7.48), and H-9 (split quartet, 8.13); $J_{1,2}$ = 7.5, $J_{1,6}$ = 7.0, $J_{1,9}$ = 7.0, $J_{2,3}$ = 4.5, $J_{2,9}$ = 8.0, $J_{3,4}$ = 10.5, $J_{3,5}$ = 2.0, $J_{4,5}$ = 2.8, $J_{5,6}$ = 8.0, $J_{6,7}$ = $J_{7,8}$ = 8.7, and $J_{8,9}$ = 2.0 Hz. These nmr data are consistent with the formulation of structure III and are also similar to those of the pyrazoline obtained from the tosylhydrazone of bicyclo[6.1.0]nona-2,4,6-triene-9-al.[12] In addition, the fact that irradiation of

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(5) Satisfactory elemental analyses were obtained for all new compounds.

(6) The melting point reported in ref 4 should be revised to 39–41°.

(7) Although inspection of the nmr spectrum (τ 2.90 (m, 5 H), 4.34 (m, 2 H), 6.00 (m, 4 H), 7.58 (m, 3 H)) proved the structure of VI, the similar retention times on vpc of VI and V made it impossible to separate a pure sample.

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(9) The nmr spectrum (60 Mc, CCl_4) of VII shows signals at τ 2.63 and 4.07 (doublet, J = 2.0 Hz, 2 H, pyrazole ring), 2.88 (5 H, phenyl ring), 7.42 (broad quartet, 4 H, α protons of the aromatic rings), and 8.61 (multiplet, 8 H, methylene protons).

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