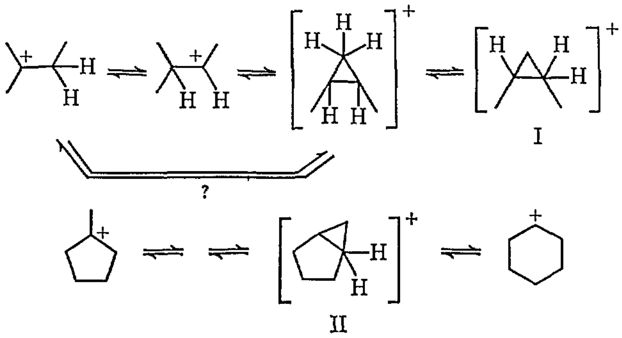
Processes involving protonated cyclopropane intermediates should have lower activation energies. In the *sec*-butyl cation,[12] a process with an E_a of 7.5 kcal/mol is accounted for on the basis of a transition from a secondary ion to a protonated cyclopropane. In the tertiary ion *t*-amyl such a process might require an additional 12 or 13 kcal/mol, *i.e.*, an E_a of approximately 20 kcal/mol, a value close to that observed. The mechanism might be represented as in Scheme I.

Scheme I



The rearrangement finds analogy in the mechanism proposed by Baird and Aboderin[13] for the reaction of cyclopropane in deuterio acid. Edge-protonated species might be intermediates rather than transition states as proposed here, but we have no direct evidence on this point. We also cannot rule out direct formation of protonated cyclopropanes from tertiary ions by simultaneous hydride shift and closure. A complicating factor in the case of the methylcyclopentyl cation is the likelihood that the two angular protons in II are sterically nonequivalent, in contrast to the situation in I, and therefore hydrogen exchange might not occur. A further shift around the three-membered ring or pseudorotation might get around this difficulty.

Another possibility we considered was that protonated cyclopropanes might open reversibly to cyclohexyl or *sec*-pentyl cations, making the hydrogens in question equivalent. The probability matrices[6] were not sufficiently different to distinguish these possibilities by line-shape analysis; however carbon labeling could. Interchange of methyl hydrogen and ring hydrogen might occur in the protonated cyclopropane, but only reversible isomerization to cyclohexyl cation can readily explain exchange of methyl *carbon* with ring carbon. To determine the relative rates of methyl hydrogen and carbon exchange with ring hydrogen and carbon, 1-methylcyclopentyl chloride was synthesized starting with equal amounts of $^{13}CH_3I$ (60% ^{13}C) and CD_3I (~95% D) *via* Grignard on cyclopentanone and converted to cations at low temperature. At about −25°, the ^{13}C methyl side bands rapidly decreased and the methyl peak grew, indicating that ^{13}C was *indeed* moving into the ring. Deuterium in the methyl group was simultaneously replaced by hydrogen from the ring. The rates at −33°, methyl carbon mixing with ring carbon, $5 \pm 2 \times 10^{-4}$ sec^{-1}, and methyl hydrogen mixing with ring hydrogens, $3 \pm 2 \times 10^{-4}$ sec^{-1}, were very close. We conclude that the protonated cyclopropane continues on to the cyclohexyl ion most of the time.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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[12] M. Saunders, E. Hagen, and J. Rosenfeld, *J. Am. Chem. Soc.*, **90**, 6882 (1968).

[13] R. Baird and A. Aboderin, *ibid.*, **86**, 252 (1964).

[14] Fellow of the Alfred P. Sloan Foundation.

[15] National Institutes of Health predoctoral fellow.

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Received August 11, 1969

Metal Ions and Hydrogen Peroxide.[1,2] Evidence for a Catalase-Like Activity of the *cis*-Diaquo Isomer of the Cu^{2+}–2,2′-Bipyridyl 1:2 Complex

Sir:

In a recent study[3] the catalytic activity of the Cu^{2+}–2,2′-bipyridyl system on the decomposition of H_2O_2 was investigated. The results obtained from the kinetic investigation of Cu^{2+}–2,2′-bipyridyl 1:1 mixtures can be summarized in eq 1, where v_0 is the initial rate of the decreasing concentration of H_2O_2

$$v_0 = -\frac{d[H_2O_2]}{dt} = k\frac{[Cu(bipy)][H_2O_2]^2}{[H^+]} \qquad (1)$$

Increasing amounts of 2,2′-bipyridyl at constant concentrations of Cu^{2+} and H_2O_2 inhibit the catalytic activity; however, at higher pH values (>7), v_0 is still noticeable (Figure 3 in ref 3). Calculations on the basis of the concentration of the Cu^{2+}–2,2′-bipyridyl 1:1 complex, where the formation of $[Cu(bipy)OH]^+$ [4] or $[(Cu(bipy)OH)_2]^{2+}$ [5] was taken into account, lead to no satisfactory agreement between $v_{0,\mathrm{exptl}}$ and $v_{0,\mathrm{calcd}}$ at high pH with large excesses of 2,2′-bipyridyl. It was concluded that this is due to the formation of Cu^{2+}–peroxo-2,2′-bipyridyl complexes.[3] (The stability constants of such complexes are not known; hence, no calculations could be done.)[3] This conclusion was based on the observation that Cu^{2+} in aqueous solution usually has a square-planar (or strongly distorted octahedral) coordination sphere[6] and that Cu^{2+} complexes formed with cyclic tetradentate ligands are catalytically inactive.[7] Therefore, the Cu^{2+}–2,2′-bipyridyl 1:2 complex was also considered as inactive.[3]

In a recent esr and nmr study by Noack and Gordon[8] of the Cu^{2+}–2,2′-bipyridyl system, it was shown that the Cu^{2+}–2,2′-bipyridyl 1:2 complex exists as two isomers, one where the two hydrated coordination positions are *trans* and another where they are *cis*. In addition, strong evidence was given that the equilibrium between these two isomers in aqueous solution and at room tem-

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[1] Part XXII of the series. This work was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

[2] Part XXI: H. Erlenmeyer, C. Flierl, and H. Sigel, *J. Amer. Chem. Soc.*, **91**, 1065 (1969).

[3] H. Sigel, C. Flierl, and R. Griesser, *ibid.*, **91**, 1061 (1969).

[4] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback, and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).

[5] D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 1271 (1966).

[6] D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc., A*, 1755 (1967).

[7] H. Sigel, *Angew. Chem.*, **81**, 161 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 167 (1969).

[8] M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968); *cf.* also I. M. Procter and F. S. Stephens, *J. Chem. Soc., A*, 1248 (1969); C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

Table I. Comparison of the Logarithms of the Initial Velocities of the Decreasing Concentration of H_2O_2 Experimentally Found (Log $v_{0,\text{exptl}}$)[3] with Calculated Ones (Log $v_{0,\text{calcd}}$)

pH	$[\text{bipy}]_{\text{tot}}{}^a$	$[\text{Cu(bipy)}]^b$	$[\text{Cu(bipy)}_2]^b$	$[\text{Cu(bipy)}_3]^b$	$[(\text{Cu(bipy)OH})_2]^b$	$v_{0/1}{}^c$	$v_{0/2}{}^c$	Log $v_{0,\text{calcd}}{}^c$	Log $v_{0,\text{exptl}}$
6.0	4.00×10^{-4}	3.61×10^{-4}	1.80×10^{-5}	7.14×10^{-9}	1.14×10^{-6}	1.41×10^{-5}	2.37×10^{-6}	−4.78	−4.80
7.0	6.00×10^{-4}	1.60×10^{-4}	1.93×10^{-4}	1.84×10^{-6}	2.24×10^{-5}	6.25×10^{-5}	2.53×10^{-5}	−4.06	−4.10
7.0	8.00×10^{-4}	4.25×10^{-5}	3.34×10^{-4}	2.08×10^{-5}	1.57×10^{-6}	1.66×10^{-5}	4.37×10^{-5}	−4.22	−4.43
8.0	1.00×10^{-3}	7.37×10^{-6}	2.92×10^{-4}	9.16×10^{-5}	4.73×10^{-6}	2.87×10^{-5}	3.82×10^{-5}	−4.18	−4.23
8.0	1.28×10^{-3}	2.28×10^{-6}	2.23×10^{-4}	1.74×10^{-4}	4.53×10^{-7}	8.90×10^{-6}	2.93×10^{-5}	−4.42	−4.33
9.0	2.00×10^{-3}	4.07×10^{-7}	1.19×10^{-4}	2.77×10^{-4}	1.44×10^{-6}	1.59×10^{-5}	1.57×10^{-5}	−4.50	−4.35
9.5	4.00×10^{-3}	5.43×10^{-8}	4.90×10^{-5}	3.50×10^{-4}	2.57×10^{-7}	6.70×10^{-6}	6.42×10^{-6}	−4.88	−4.31

[a] In all cases $[\text{Cu}^{2+}]_{\text{tot}} = 4 \times 10^{-4}\ M$, $[H_2O_2]_{\text{tot}} = 8 \times 10^{-3}\ M$; v_0 is given in mole l.$^{-1}$ sec^{-1}; *cf.* Figure 3 and Table I in ref 3 (in ref 3 v_0 is given in mole l.$^{-1}$ min^{-1}). [b] Calculated with a computer (IBM 1620) with the aid of the constants given by Irving and Mellor[10,13] and taking hydrolysis into account according to Perrin and Sharma:[5] $([\text{Cu(bipy)OH})_2][\text{H}^+]^2)/[\text{Cu(bipy)}]^2 = 10^{-11.06}$. [c] Calculated according to eq 5.

perature favors the *cis* form.[9] For the *trans* isomer, it can be expected,[3] based on experience with Cu^{2+} complexes of cyclic tetradentate ligands,[7] that it is catalytically inactive. However, this is not true for the *cis* isomer, the structure of which rather suggests that it may be a catalytically active species. The observed[3] catalytic activity of the Cu^{2+}–2,2′-bipyridyl system under conditions where the known catalytically active species, $[\text{Cu(bipy)}]^{2+}$, occurs only in very low concentrations might, therefore, be due to the *cis* diaquo isomer of the Cu^{2+}–2,2′-bipyridyl 1:2 complex. This possibility was tested using the experimental data of the recent work.[3]

For those conditions where the Cu^{2+}–2,2′-bipyridyl 1:1 complex is not the only catalytically active species, one can write

$$v_{0,\text{exptl}} = -\frac{d[H_2O_2]}{dt} = k\frac{[\text{Cu(bipy)}][H_2O_2]^2}{[\text{H}^+]} + k'[H_2O_2]^y X \quad (2)$$

Since the initial concentration of H_2O_2 was constant in the experiments, eq 2 can be simplified to

$$v_{0,\text{exptl}} = k_1\frac{[\text{Cu(bipy)}]}{[\text{H}^+]} + k_2X \quad (3)$$

Equation 3 can be transformed to

$$v_{0,\text{exptl}}\frac{[\text{H}^+]}{[\text{Cu(bipy)}]} = k_1 + k_2X\frac{[\text{H}^+]}{[\text{Cu(bipy)}]} \quad (4)$$

A plot of $v_{0(\text{exptl})}[\text{H}^+]/[\text{Cu(bipy)}]$ against $X[\text{H}^+]/[\text{Cu(bipy)}]$ should give a straight line (*cf.* also ref 14) if eq 4 is valid. This was tested with $X = [\text{Cu(bipy)}][\text{Cu(bipy)}_2]$, $[\text{Cu(bipy)}_2]^2$, $[\text{Cu(bipy)}_2]/[\text{H}^+]$, and $[\text{Cu(bipy)}_2]$;[15,16] only in the last case is a straight line observed. This straight line was drawn according to a simple regression (least-squares) method; from the intercept and slope, respectively, k_1 and k_2 were obtained. For eq 3, eq 5 can now be written.[17]

$$v_{0,\text{exptl}} = 3.91 \times 10^{-8}\frac{[\text{Cu(bipy)}]}{[\text{H}^+]} + 0.131[\text{Cu(bipy)}_2] = v_{0/1} + v_{0/2} \quad (5)$$

Using eq 5 and the concentrations of the different complex species present in the several experiments,[3] log v_0 values were calculated and are given in Table I. The agreement between calculated and observed values for log v_0 is very reasonable.[18] Hence, these results strongly suggest that the *cis*-diaquo isomer of the Cu^{2+}–2,2′-bipyridyl 1:2 complex[19] is the species responsible for the catalytic activity of the Cu^{2+}–2,2′-bipyridyl–H_2O_2 system, under conditions where the concentration of the Cu^{2+}–2,2′-bipyridyl 1:1 complex is small.[20] For the complex in which the catalytic decomposition of H_2O_2 occurs, a structure derived from the *cis*-diaquo isomer can be proposed, analogous to the one suggested earlier for the Cu^{2+}–2,2′-bipyridyl 1:1 complex (*cf.* eq 7 in ref 3).

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(9) This is in agreement with the stability constants;[10] the differences, $\log K^{\text{Cu}}_{\text{CuL}} - \log K^{\text{CuL}}_{\text{CuL}_2} = 2.60$ and $\log K^{\text{CuL}}_{\text{CuL}_2} - \log K^{\text{CuL}_2}_{\text{CuL}_3} = 2.10$, are about the same. This is quite different with ethylenediamine as ligand: $\log K^{\text{Cu}}_{\text{CuL}} - \log K^{\text{CuL}}_{\text{CuL}_2} = 10.72 - 9.31 = 1.41$, and $\log K^{\text{CuL}}_{\text{CuL}_2} - \log K^{\text{CuL}_2}_{\text{CuL}_3} = 9.31 - (-1.0) = 10.3$[11], where a *trans*-diaquo Cu^{2+}–ethylenediamine 1:2 complex is formed;[8,12] hence, the third ethylenediamine can bind only monodentatally or bidentatally after rearrangement of the complex.

(10) Log $K^{\text{Cu}}_{\text{Cu(bipy)}} = 8.10$, $\log K^{\text{Cu(bipy)}}_{\text{Cu(bipy)}_2} = 5.50$, $\log K^{\text{Cu(bipy)}_2}_{\text{Cu(bipy)}_3} = 3.40$,[13] $\text{p}K^{\text{H}}_{\text{Hbipy}} = 4.59$.[5]

(11) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

(12) W. B. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, **45**, 4003 (1966); *cf.* also R. Uggla, *Suomen Kemistilehti, B*, **41**, 345 (1968).

(13) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(14) J. Schubert, V. S. Sharma, E. R. White, and L. S. Bergelson, *J. Amer. Chem. Soc.*, **90**, 4476 (1968).

(15) In these cases $[(\text{Cu(bipy)OH})_2]^{2+}$ was taken into account.[5] With $[\text{Cu(bipy)OH}]^+$ [4] no reasonable results were obtained, except again for $X = [\text{Cu(bipy)}_2]$; however, the deviations from the straight line were much smaller using $[(\text{Cu(bipy)OH})_2]^{2+}$ in the calculations instead of $[\text{Cu(bipy)OH}]^+$ (*cf.* ref 5). Equation 4 was also tested with $X = [\text{Cu(bipy)OH}]/[\text{H}^+]$, $[\text{Cu(bipy)OH}]$, $[(\text{Cu(bipy)OH})_2]/[\text{H}^+]$, $[(\text{Cu(bipy)OH})_2]$, $\sqrt{[(\text{Cu(bipy)OH}_2]}$, and $\sqrt{[(\text{Cu(bipy)OH}_2]/[\text{H}^+]}$; in all these cases no straight lines resulted.

(16) To be able also to test $X = [\text{Cu(bipy)OOH}]$ (taking into account $[(\text{Cu(bipy)OH})_2]^{2+}$)[5] for $\log K^{\text{Cu(bipy)}}_{\text{Cu(bipy)OOH}}$ of the ternary peroxo complex, the values 5.0, 6.0, 7.0, 8.0, and 9.0 were assumed. In all these cases, straight lines (*cf.* also ref 14) parallel to the y axis resulted, so k_1 and k_2 could not be calculated. No straight lines were observed using $X = [\text{Cu(bipy)OOH}]/[\text{H}^+]$. A comparison of log $v_{0,\text{exptl}}$ with calculated values using $v_0 = k^*[\text{Cu(bipy)OOH}][H_2O_2]$ (*cf.* eq 1 and ref 3) and values of $\log K^{\text{Cu(bipy)}}_{\text{Cu(bipy)OOH}}$ between 4.0 (with lower values the concentration of $[\text{Cu(bipy)OOH}]^+$ was always negligible) and 9.5 also gave poor agreement between log $v_{0,\text{exptl}}$ and log $v_{0,\text{calcd}}$. In addition, the standard deviations showed no minimum for the whole mentioned range of the values used for $\log K^{\text{Cu(bipy)}}_{\text{Cu(bipy)OOH}}$, but increased constantly. To assume that $\log K^{\text{Cu(bipy)}}_{\text{Cu(bipy)OOH}}$ is greater than 9.5 is not reasonable, since in this case the concentration of $[\text{Cu(bipy)OOH}]^+$ would be very high in Cu^{2+}–bipy 1:1 solutions even at low pH values (*e.g.*, more than 75% of the total Cu^{2+} present at pH 5). Absorption measurements at 360 nm[7] show this is not so: H. Brintzinger and H. Erlenmeyer, *Helv. Chim. Acta*, **48**, 826 (1965). The acidity constant of H_2O_2 which was used in these calculations is $\text{p}K^{\text{H}}_{H_2O_2} = 11.81$: V. A. Kargin, *Z. Anorg. Allg. Chem.*, 183, 77 (1929).

(17) From $k_1 = 3.91 \times 10^{-8}$, the velocity constant, k, can be calculated: $k_1/[H_2O_2]^2 = 3.91 \times 10^{-8}/(8 \times 10^{-3})^2 = 6.11 \times 10^{-4}$ mole^{-1} l. sec^{-1}. This value agrees reasonably with 6.87×10^{-4} mole^{-1} l. sec^{-1} ($= 4.12 \times 10^{-2}$ mole^{-1} l. min^{-1}) which was found in the Cu^{2+}–2,2′-bipyridyl 1:1 systems.[3]

(18) The only exception is the last value, where the excess of 2,2′-bipyridyl is very high and the concentrations of $[\text{Cu(bipy)}]^{2+}$ and $[\text{Cu(bipy)}_2]^{2+}$, therefore, very small (for these reasons this point was omitted for the calculation of the best straight line); in this case Cu^{2+}–peroxobipyridyl complexes probably become important.

(19) For the redox potential of the Cu^{2+}–2,2′-bipyridyl 1:2 complex, *cf.* B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).

(20) This could also be true for the peroxidase-like activity (reactions between H_2O_2 and NH_2OH or NH_2NH_2)[2] of the Cu^{2+}–2,2′-bipyridyl system, but not enough experimental data[2] were available for a definite conclusion.

Interesting features of this result are that *cis*-diaquo Cu^{2+}–bidentate ligand 1:2 complexes so far have not been considered as catalytically active species, and that the geometry of the coordination sphere of Cu^{2+} can have unexpected qualities which strongly depend on the kind of ligand bound.

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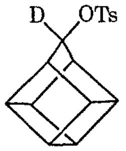
Received September 9, 1969

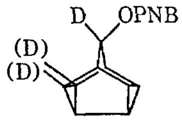
Degenerate Rearrangements of the 9-Barbaralyl Cation[1]

Sir:

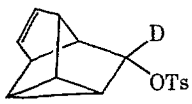
Potentially degenerate $C_9H_9^+$ systems already studied have given a spectrum of results.[1–5] The solvolysis of 9-homocubyl tosylate (I) is accompanied by extensive deuterium label scrambling.[2] Similar experiments conducted with the 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system II resulted only in threefold trishomocyclopropenyl-type degeneracy,[3] while solvolysis of 5-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enyl-5-D-tosylate (III) was not accompanied by label scrambling at all.[4] Finally the "antibicycloaromatic"[5] bicyclo[3.2.2]nonatrienyl cation (IV), a potentially degenerate species (IV ⇄ V ⇄ etc.), does not retain structural identity, but rearranges to give barbaralyl[6] products VI (9-tricyclo[3.3.1.0^{2,8}]-nona-3,6-diene derivatives).[5]



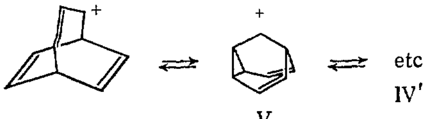
I



II

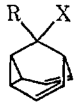


III



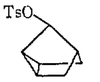
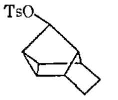
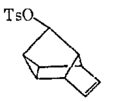
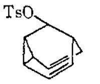
IV V

Barbaralyl tosylate[7] (VI, R = H, X = OTs) has been described as "a yellow oil" which was "recovered with unchanged IR spectrum" after standing in acetic acid for 72 hr at room temperature.[7] In contrast, we found 9-barbaralyl tosylate, prepared by the powdered KOH procedure,[8] to be a white crystalline solid, mp 83° dec, whose rate of acetolysis is rapid, corresponding to a half-life of 5 min at 16.5° (Table I).



VI

Table I. Acetolysis Data for Polycyclic Cyclopropylcarbinyl Systems

Compound	$k_{16.5°}$, sec^{-1}	k_{rel}	ν_{CO}, cm^{-1}	Rel acceleration based on ν_{CO}[9]
	1.08×10^{-6} [a]	$10^{-3.3}$	1762[a]	$10^{2.5}$
	5.02×10^{-6} [a]	$10^{-2.5}$	1765[c]	$10^{3.6}$
	1.37×10^{-7} [a]	$10^{-4.2}$	1755[a]	$10^{0.6}$
	2.28×10^{-3}	1	1716[b]	1

[a] Reference 4. [b] We thank Thomas M. Gorrie for an accurate determination of ν_{CO} for barbaralone. [c] Value kindly supplied by Professor R. S. Bly.

It is difficult to assess accurately the degree to which barbaralyl tosylate is anchimerically assisted. Its acetolysis rate is considerably faster than other polycyclic cyclopropylcarbinyl analogs, but the lower carbonyl frequency of the corresponding ketone suggests that angle strain at the reaction site is more favorable in the barbaralyl system. On the ketone carbonyl frequency basis, however, a much faster rate than actually observed would be expected.[9] The unfavorable inductive effect of the double bonds may be responsible for this difference. It is difficult to decide at this time whether "antibicycloaromaticity"[5] or another adverse electronic situation in the cation is involved.

Solvolysis of 9-D-barbaralyl tosylate (VI, R = D; X = OTs) gives predominantly barbaralyl products, accompanied, however, by extensive deuterium scrambling.[10] The alcohol isolated after solvolysis in aqueous acetone (VI, X = OH) exhibited deuterium distributed *almost exclusively* between C_3, C_7, and C_9 (Table II). In acetic acid, a solvent of lower nucleophilicity, deuterium was again concentrated at C_3, C_7, and C_9, but significant amounts of deuterium also appeared in the remaining positions, due to longer effective ion lifetime.

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(1) Paper III in a series on degenerate and potentially degenerate cations. This work was presented in preliminary form at the IUPAC Symposium on Valence Isomerization, Sept 1968, at Karlsruhe, Germany, Abstracts, p 17.

(2) Paper I: P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. Di Pasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); *cf.* J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967); and W. Dauben, private communication.

(3) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968).

(4) Paper II: P. von R. Schleyer and R. E. Leone, *ibid.*, **90**, 4164 (1968); *cf.* G. W. Klumpp, *Rec. Trav. Chim.*, **87**, 1053 (1968).

(5) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967); M. J. Goldstein and B. J. Odell, *ibid.*, **89**, 6356 (1967).

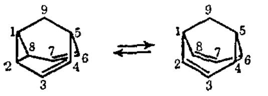
(6) Trivial name derived from that of its progenitor barbaralone.[7]

(7) W. von E. Doering, B. M. Ferrier, E. D. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967).

(8) K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

(9) C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86** 1854, 1856 (1964).

(10) Positions 1 and 5 and positions 2, 4, 6, and 8 are rendered equivalent by a process well established for these systems:[7,11] the Cope rearrangement of the homotropilidene moiety within the molecule.



The scrambling we have found is in addition to this process.

(11) For a review of this subject, see G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).