

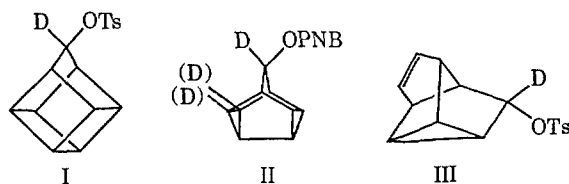
Interesting features of this result are that *cis*-diaquo Cu^{2+} -bidentate ligand 1:2 complexes so far have not been considered as catalytically active species, and that the geometry of the coordination sphere of Cu^{2+} can have unexpected qualities which strongly depend on the kind of ligand bound.

Rolf Griesser, Bernhard Priejs, Helmut Sigel
 Institute of Inorganic Chemistry, University of Basel,
 Basel, Switzerland
 Received September 9, 1965

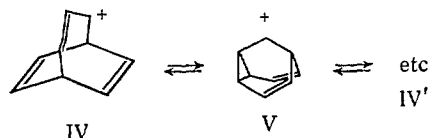
Degenerate Rearrangements of the 9-Barbaralyl Cation¹

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 \rightleftharpoons V \rightleftharpoons etc.), does not retain structural identity, but rearranges



to give barbaralyl⁶ products VI (9-tricyclo[3.3.1.0^{2,8}]nona-3,6-diene derivatives).⁵

Barbaralyl tosylate⁷ (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

(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. Daubea, 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).

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).

Table I. Acetolysis Data for Polycyclic Cyclopropylcarbinyl Systems

Compound	$k_{16.5^\circ}$, 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 ^a	$10^{3.6}$
	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.

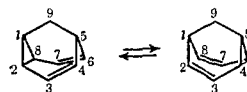
It is difficult to assess accurately the degree to which barbaralyl tosylate is anchimerically assisted. Its acetolysis rate is considerably faster than other polycyclic cyclopropylcarbinyl analogs, but the lower carbonyl frequency of the corresponding ketone suggests that angle strain at the reaction 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 C₃, C₇, and C₉ (Table II). In acetic acid, a solvent of lower nucleophilicity, deuterium was again concentrated at C₃, C₇, and C₉, but significant amounts of deuterium also appeared in the remaining positions, due to longer effective ion lifetime.

(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.



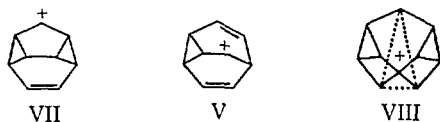
The scrambling we have found is in addition to this process.

(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).

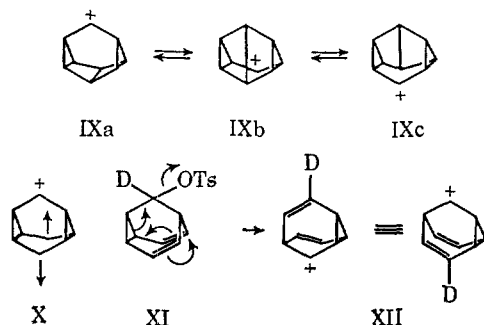
Table II. Deuterium Scrambling in Barbaralyl Solvolysis Products

Compound	Solvolysis conditions	% Deuterium in various positions ($\pm 3\%$)			
		C _{1,5}	C _{2,4,6,8}	C _{3,7}	C ₉
VI, X = OH	80% acetone, 18°, 1 hr	5.2	1.7	39.9	53.2
VI, X = OAc	HOAc, 25°, 30 min	7.4	18.2	46.1	28.3
Statistical distribution		22.2	44.4	22.2	11.1

These results exclude the most obvious mechanistic possibilities: cyclopropylcarbinyl \rightarrow homoallylic rearrangement to the bicyclo[3.2.2]nonatrienyl cation (IV) and allylcarbinyl \rightarrow cyclopropylcarbinyl rearrangement to the interesting bishomotropylium system (VII). Such rearrangements would give rise to quite different deuterium distributions than were observed experimentally.



The observation that high percentages of deuterium, relative to a statistical distribution, appear at C₃, C₇, and C₉, and low percentages over the remainder of the molecule suggests that the carbonium ion either has threefold symmetry (as in VIII) or undergoes an operation which leads to such threefold symmetry (such as the rapid equilibration IXa \rightleftharpoons IXb \rightleftharpoons IXc). Since distances between C₃, C₇, and C₉ probably are much too large to permit effective bonding, a better representation of VIII may be X, in which symmetrization by cyclopropylcarbinyl resonance is obvious. Alternatively, the observed deuterium distribution can be rationalized by a "synchronous" formulation (XI \rightarrow XII), but it is not clear why this should be favored.



Besides this "threefold symmetrization" mechanism, there must be a second, less rapid, process, e.g., through IV or VII, which distributes deuterium more widely. Perhaps rearrangement through IV is disfavored because of "antibicycloaromaticity,"⁵ while VII may not be a very favorable intermediate due to the enforced nonplanarity of the bishomotropylium system. Further work is planned to clarify these matters.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the

Petroleum Research Fund, administered by the American Chemical Society.

(12) National Institutes of Health Postdoctoral Fellows: (a) 1969–1970; (b) 1968–1969.

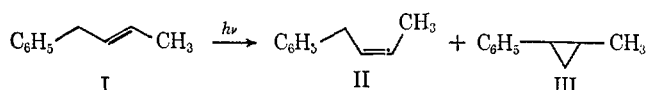
(13) NATO Postdoctoral Fellow, 1967–1968.

J. C. Barborak,^{12a} J. Daub¹³
D. M. Follweiler,^{12b} P. von R. Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received October 17, 1969

Molecular Rearrangement in the Gas Phase Photolysis of 1-Phenyl-2-butene

Sir:

We wish to report the photochemical rearrangement of a nonconjugated 1,4-diene to a cyclopropane derivative obtained for the first time in the gas phase by direct irradiation.¹ The effects of exciting wavelength and of foreign gas indicate that the cyclization proceeds *via* the formation of a vibrationally excited intermediate.



Irradiation of the *trans*-1-phenyl-2-butene (I) at four different wavelengths (λ 266, 261, 252, 247 nm) with a 1000-W mercury-xenon lamp and at a pressure of 0.8 Torr leads to the formation of two products:² the *cis* isomer, II, already reported in the liquid phase photolysis³ and a new photoproduct III eluting shortly after II on the MBMA⁴ column of a capillary gas chromatograph. *t*-Butylbenzene was added to the photolysate mixture as an internal standard. Subsequent addition of bromine demonstrated that III reacted much more slowly than I and II as shown by successive injections in the capillary gas chromatograph. The new photoproduct, III, did not react at all with ozone while I and II completely disappeared to form the corresponding ozonides which did not elute from the column. During these chemical tests, the concentration of the *t*-butylbenzene in the mixture did not change, ruling out the possibility of an attack on the aromatic ring. The evidence then indicates that III lacks an aliphatic double bond. In earlier similar solution studies, it was shown that cyclopropane derivatives may be formed from irradiation of a nonconjugated 1,4-diene.^{1,5}

trans-1-Phenyl-2-methylcyclopropane was prepared by treatment of *trans*- β -methylstyrene with methylene iodide and a zinc-copper couple according to the Simmons-Smith procedure⁶ and was identified by its nmr spectrum. Comparison of its retention time with the photoproduct III and direct comparison by glpc enhancement of a mixture of III and of *trans*-1-phenyl-2-

(1) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(2) A third unidentified product with a lower boiling point is formed in only trace amount.

(3) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968).

(4) *m*-Bis(*m*-phenoxy)benzene + Apiezon L.

(5) G. W. Griffin, J. Covell, R. C. Peterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(6) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).