OCH_3, 6.29, 6.34; β-CH_3, 7.82 (2), 7.92, 8.16; $-CH_2-$, 7.0–7.5 multiplet; ($-CH_2$)CH_3, 8.84, 8.93). The spectral changes in the foregoing conversion correspond very closely with those observed by earlier workers[9,10] who employed oxyporphyrins prepared by direct oxidation of porphyrins. These compounds, like those prepared by our rational syntheses, must have the general structure exemplified in II and its mesomeric dipolar forms.

(19) Parke, Davis Studentship.

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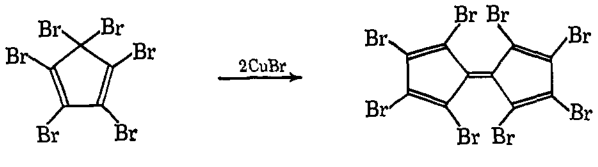
Received July 29, 1966

Octabromofulvalene[1]

Sir:

Other than fused-ring species, only three fulvalenes have been described as pure substances.[2-6] This communication reports the synthesis and characterization of the fourth such compound, octabromofulvalene (I), by the reductive coupling of hexabromocyclopentadiene[7] with copper(I) bromide.



I

In a typical experiment 10.90 g (0.020 moles) of hexabromocyclopentadiene in 27 ml of 90% 1,2-dimethoxyethane–10% water was chilled to −80°, and 5.75 g (0.040 mole) of copper(I) bromide was added. The reaction mixture was allowed to warm to 0° with stirring. Reaction took place as the water melted and within 3 min at 0° the copper(I) bromide was consumed. The reaction mixture was immediately filtered through sintered glass to separate the crude violet solid product. This solid was dissolved in chloroform–hexane and chromatographed on silicic acid yielding 0.50 g (6.6%) of pure I as dark blue crystals, mp 170° dec. *Anal.* Calcd for $C_{10}Br_8$: C, 15.93; Br, 84.1; H, nil. Found: C, 15.95; Br, 82.9; H, nil.

Octabromofulvalene is strikingly similar in its spectral properties to the known compound octachlorofulvalene.[4,5] The electronic absorption bands for the two compounds are listed in Table I. The three bands observed for the octachloro compound also appear in the spectrum of I, all with about the same intensity but shifted to lower energy. The highest energy infrared absorption, presumably a C=C stretching mode, appears at unusually low frequency in octachlorofulvalene as a sharp doublet (1525 and 1540 cm^{-1}). A similar doublet appears in the spectrum of of I at 1490 and 1505 cm^{-1}.

Table I. Electronic Spectra of Octahalofulvanes

$C_{10}Cl_8$[5]		$C_{10}Br_8$ (I)	
λ_{max}, cm^{-1} (A)	log ϵ	λ_{max}, cm^{-1} (A)	log ϵ
48,100 (2080)	4.45	45,300 (2210)	4.32
25,600 (3900)	4.61	24,200 (4140)	4.67
16,400 (6100)	2.40	15,700 (6375)	2.37

A two-dimensional X-ray diffraction study of octachlorofulvalene has shown that two five-membered rings are twisted out of plane, forming a dihedral angle of 41° at the central C–C bond.[8] The nonplanarity is presumed to result from steric interactions of the chlorine atoms at the 1, 4, 5, and 8 positions. Because the corresponding interactions should be even greater in octabromofulvalene, the structural and electronic properties of this compound will be of especial interest. Chemically, I is more reactive than octachlorofulvalene, and it is doubtless for this reason that methods of synthesis which are successful for the chloro analog[4,5,9] do not yield I. Detailed studies of the chemistry of both I and octachlorofulvalene are in progress.

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(1) This work was supported by a grant from the National Science Foundation.

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(6) The parent compound, fulvalene, has been prepared by several methods but is unstable and has never been obtained pure. See K. V. Scherer, Jr., *J. Am. Chem. Soc.*, **85**, 1550 (1963), and references therein.

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The Stereochemistry of the Thermal Decomposition of Vinylic Copper(I) and Silver(I) Organometallic Compounds[1]

Sir:

The thermal decomposition of organometallic compounds of copper(I) and silver(I) is important in the oxidative coupling of aryl Grignard reagents by copper(I) and silver(I) halides,[2] and is probably involved in the Ullman and related reactions.[3,4] These thermal decomposition reactions have been variously suggested to proceed by a bimolecular or concerted mechanism, in which dimer formation occurs within an aggregate of the organometallic compound,[3a,4] or by a radical mechanism, in which dimers arise from free radicals generated by homolytic cleavage of the carbon–metal bonds.[2,5]

We have explored the question of the intermediacy of free radicals in the thermal decomposition of vinylic copper(I) and silver(I) organometallic compounds by

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(1) Supported in part by the National Science Foundation under Grant GP-2018.

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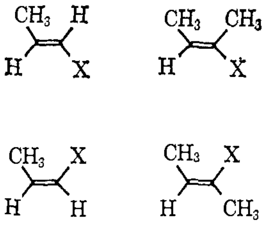
(3) (a) A. H. Lewin and T. Cohen, *Tetrahedron Letters*, 4531 (1965); (b) H. C. Brown and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1002 (1961).

(4) E. A. Bickley and J. H. Gardner, *J. Org. Chem.*, **5**, 126 (1940).

(5) F. Glockling and D. Kingston, *J. Chem. Soc.*, 3001 (1959); C. E. H. Bawn and F. J. Whitby, *ibid.*, 3923 (1960).

examining the stereochemistry of the diene products obtained on decomposition of 1-propenyl- and 2-butenylcopper(I) and -silver(I) compounds of known stereochemistry.[6] In each of the decompositions studied, the result obtained was that, within our limits of detection, the decomposition of the organometallic compound to the corresponding diene took place with complete *retention* of configuration around the carbon–carbon double bond.



X=Cu(I), Ag(I), Cu(I)–P(butyl)$_3$, Ag(I)–P(butyl)$_3$

In a typical experiment, *cis*-1-propenyl(tri-*n*-butylphosphine)silver(I) (I) was prepared at −78° in ether solution by treating 1 equiv of tetrakis[iodo(tri-*n*-butylphosphine)silver(I)][10] with 1 equiv of 1-propenyllithium[11] (97% *cis*, as determined by vpc analysis of the propenyl bromides obtained after reaction with 1,2-dibromoethane). After precipitation of lithium halides from the cold reaction mixture with dioxane, addition of iodine to the solution of the organosilver reagent at −28° gave 1-iodopropene having 96% *cis* stereochemistry in 84% yield,[12] indicating that formation of the carbon–silver bond occurred with retention of stereochemistry. Thermal decomposition of either the halogen-free or halogen-containing solutions of I at ambient temperature over 4 hr gave silver(0) (95%), *cis,cis*-2,4-hexadiene (95%), and *cis,trans*-2,4-hexadiene (4.8%), corresponding to 97% *cis*-propenyl groups and 100% stereospecificity in the decomposition, based on 1-propenyllithium.[13]

By an analogous procedure, *trans*-1-propenyllithium (97% *trans*) could be converted quantitatively to a mixture of *trans,trans*- and *cis,trans*-2,4-hexadienes containing 97% *trans*-propenyl groups. Although these organometallic reagents have not yet been characterized as solids, analysis of the products from the thermal decomposition of the halogen-free solutions has established their empirical composition as $[C_3H_6]_{1.0}[Ag]_{0.95\pm0.1}[P(C_4H_9)_3]_{1.1\pm0.1}$, with less than 0.5% lithium ion remaining in solution.

Tri-*n*-butylphosphine complexes of *cis*- and *trans*-2-butenylsilver(I) and -copper(I) were prepared and characterized using similar procedures. Solutions of copper(I) and silver(I) compounds which contained no tri-*n*-butylphosphine could be prepared in ether at −28° by heterogeneous reaction between the corresponding vinylic lithium reagents and copper(I) or silver(I) iodide. Decomposition of these reagents was complete after 1 hr at ambient temperature. In each case, dimeric products were produced in 70–90% yields, with greater than 99% retention of configuration.

These stereochemical results strongly suggest that free propenyl radicals are not intermediates in these reactions. Making the reasonable assumption that the rate of inversion of configuration of 1-propenyl radical is approximately the same as that established by epr spectroscopy for vinyl radical ($k_{\text{inversion}} = 10^8\text{–}10^{10}$ sec^{-1}),[14] the rate of conversion of an intermediate propenyl radical into dimer must be at least 10^2 faster than the rate of its inversion of configuration in order to be consistent with the observed stereochemical results. Under the reaction conditions used, the undecomposed organometallic compound is the most concentrated solution component potentially capable of reaction with propenyl radicals to form dimers. Therefore

$$k_{\text{coupling}}[\mathrm{R}\cdot][\mathrm{RM}] \geq 10^2 k_{\text{inversion}}[\mathrm{R}\cdot]$$

In these reactions, $[\mathrm{RM}] \leq 0.1\ M$; hence, k_{coupling} must be greater than $10^{11}\ M^{-1}\ \text{sec}^{-1}$ to compete with inversion. The possibility that a reaction is taking place in solution whose rate constant is of this magnitude can clearly be excluded by consideration of the maximum rates attained by other fast reactions.[15]

These results do not rigorously exclude the occurrence of solvent-caged radicals as intermediates; however, we feel that a cage mechanism is improbable because the yield of dimeric products observed in the decomposition of I would require that the efficiency of cage combination approach 100%. An alternative path for the decomposition, in which vinylic radicals are formed but remain π bonded to the metal atoms of an aggregate, cannot be excluded.

Although the rate of inversion of 2-butenyl radical is probably slower than that of vinyl radical,[14] recent studies have indicated that this inversion is also rapid onthe time scale of most reactions.[16] The retention of stereochemistry observed in decomposition of the 2-butenyl organometallic compounds lends qualitative support to the proposal that long-lived free radicals are not intermediates in the decomposition of vinylic copper(I) and silver(I) compounds. However, in the absence of a reliable quantitative value for the rate of inversion of configuration of 2-butenyl radical, it is not possible to define a lower limit for the lifetime of any radical intermediates in the decomposition of these compounds.

These proposals cannot be extended without modification to include the thermal decomposition of *ali-*

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(6) No direct experimental evidence on the extent of aggregation of these compounds is presently available. However, the related compounds phenylethynyl(trimethylphosphine)copper(I),[7] phenylethynyl-(trimethylphosphine)silver(I),[8] and tetrakis[iodo(tri-*n*-butylphosphine)-copper(I)][9] are aggregated both in solution and as crystalline solids.

(7) P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, 16, A-71 (1963).

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(10) F. G. Mann, A. F. Wells, and D. Purdie, *ibid.*, 1828 (1937).

(11) D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, 86, 883 (1964).

(12) We are indebted to Dr. R. C. Neuman, Jr., for an authentic sample of 1-iodopropene: R. C. Neuman, Jr., *J. Org. Chem.*, 31, 1852 (1966).

(13) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, 86, 622 (1964).

(14) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(15) For example, the absolute rate constant for combination of methyl radicals is approximately $10^{10}\ M^{-1}\ \text{sec}^{-1}$: A. F. Trotman-Dickenson, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **55**, 36 (1958).

(16) J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966); L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 2089 (1966). In related experiments, we have observed that tri-*n*-butyltin hydride reduction[17] at ambient temperatures of either *cis*- or *trans*-2-bromo-2-butene yields the same mixture of 65% *trans*- and 35% *cis*-2-butene.

(17) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).

phatic copper(I) compounds, since these reactions give fundamentally different types of products. For example, thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) at room temperature in ether gives butane (50%) and 1-butene (50%), but no detectable octane. Details of these reactions will be discussed in later papers.

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Received July 14, 1966

Nortricyclene Precursors in Bamford–Stevens Reactions[1]

Sir:

Diazohydrocarbons can be generated and decomposed in hot alkoxide solutions of aldehyde and ketone tosylhydrazones.[2,3] Studies of product ratios revealed a strong solvent dependence and led to the generalization that cationic paths prevail in "protic" media whereas carbenoid intermediates are involved under "aprotic" conditions.[4,5] Subsequent investigations uncovered additional complexities and have made it clear that carbenes and energetic cations can behave similarly with respect to carbon skeleton rearrangements, hydride shifts, and the formation of insertion products, and therefore product ratios are not reliable criteria for the existence of carbenoid or cationic precursors.[3,6–9] We wish to report direct experimental evidence that distinguishes insertion and cationic mechanisms in a bicyclo[2.2.1]heptane system and imposes restrictions on the nature of the cations.

Thermal decomposition of norbornan-2-one tosylhydrazone with an excess of alkali in diglyme and in ethylene glycol gives a hydrocarbon mixture that consists almost entirely of nortricyclene (*ca.* 99%[4d] and 93%, respectively). The experiments described below establish that (i) the three-membered ring arises completely by an intramolecular insertion path in the diglyme system, (ii) in ethylene glycol a cationic path competes in which an external proton is incorporated on carbon,[10] (iii) protonation of 2-carbenanorbornane[11] to the corresponding carbonium ion is not the only cationic path (and may even be a minor one), and (iv) an ionic progenitor of nortricyclene exists which is not the norbornyl cation encountered in solvolytic studies.

Norbornan-2-one (**1a**, mp 90–92°), 6-*exo*-deuterionorbornan-2-one (**2a**, mp 91–92°; 10.3% d_0, 89.7% d_1, 0% d_2), and 6-*endo*-deuterionorbornan-2-one (**3a**, mp 90–92°; 13.4% d_0, 86.6% d_1, 0% d_2)[12,13] were converted to their corresponding tosylhydrazones.[14] Each derivative was thermally decomposed in "aprotic" medium (diglyme containing an excess of dissolved sodium methoxide) and in "protic" medium (ethylene glycol containing an excess of dissolved sodium). The nortricyclene was isolated and assayed for deuterium mass spectroscopically. Results are summarized in Table I.

Table I. Decomposition of Norbornan-2-one Tosylhydrazones

		Non-deuterated (**1b**)	6-*exo*-Deuterio (**2b**)	6-*endo*-Deuterio (**3b**)
Concn (*M*) of substrate	Aprotic	0.26	0.26	0.26
	Protic	0.18	0.21	0.21
Concn (*M*) of alkali	Aprotic	2.11	2.36	2.36
	Protic	0.65	0.72	0.72
% nortricyclene in hydrocarbon	Aprotic	>99	>99	>99
	Protic	93.2	92.9	92.3
% loss of original deuterium[a]	Aprotic	...	0	0
	Protic	...	19	52

[a] Independent combustion analyses indicated that the mass spectroscopic assays are accurate to *ca.* ±1.5%.

In the "aprotic" runs the nortricyclene had the same deuterium content as did its corresponding deuterated precursor. Therefore the new ring arose from the diazohydrocarbon entirely by an insertion path (path A) involving intramolecular transfer of hydrogen (in the case of **4**) or deuterium (in the case of **6**).[15] This is the behavior expected for a carbenoid intermediate or its equivalent.

In the "protic" runs each labeled substrate lost an appreciable fraction of its deuterium. Consequently a substantial proportion of the nortricyclene is produced from an intermediate that acquired an external proton. Importantly, the different deuterium loss from each substrate (*cf.* 19 and 52%)[16] reveals the existence of an intermediate whose behavior is that expected for neither a bridged norbornyl cation nor a pair of equilibrated classical norbornyl cations, because these species do not preserve the original stereochemical distinction at C-6 and require that the fraction of isotope loss be identical from each substrate.[17] These

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for financial support.

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(4) (a) J. W. Powell and M. C. Whiting, *Tetrahedron*, **1**, 305 (1959); (b) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (c) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **82**, 634 (1960); (d) L. Friedman and H. Schechter, *ibid.*, **83**, 3159 (1961).

(5) For relevant observations and comments on the "protic" and "aprotic" character of solvents see ref 3, 4b, and 8.

(6) (a) J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965); (b) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *ibid.*, **31**, 1543, (1966).

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(15) In nortricyclene the cyclopropyl C–H stretching vibration appears as a doublet at *ca.* 3070 cm^{-1} in CS_2, whereas the deuterated nortricyclene showed a single band at this position with reduced intensity.

(16) The different outcome from each labeled compound also establishes that the deuterium is not lost from nortricyclene after its formation. Loss of deuterium by homoenolization is not expected under the experimental conditions.[12,13]

(17) A classical norbornyl cation that is neutralized by proton loss before it can undergo Wagner–Meerwein or other rearrangements could preserve the *exo–endo* distinction at C-6. Such behavior, though conceivable, is presently contrary to known experience with the norbornyl cation: J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.