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.

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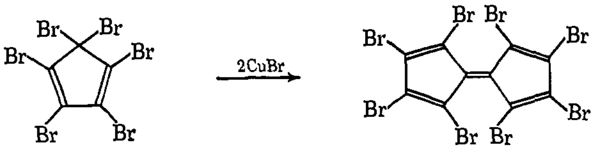
Octabromofulvalene[1]

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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[3] P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).

[4] V. Mark, *Tetrahedron Letters*, 333 (1961).

[5] A. E. Ginsberg, R. Pautz, and F. Korte, *ibid.*, 779 (1962).

[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.

[7] F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930). The hexabromocyclopentadiene used in the present study was prepared from hexachlorocyclopentadiene and boron tribromide by a new method which will be fully described in a forthcoming paper.

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[9] C. F. Law, Thesis, University of Wisconsin, 1966.

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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.

[2] H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966), and references therein.

[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).