

Table I

Compound	Solid color	λ_{\max} , $m\mu^a$	μ , BM
$[(C_2H_5)_4N]_2Nb_6Cl_{18}$	Black	~925, 454, 298, 234	0.02 ^b
$[(C_2H_5)_4N]_3Nb_6Cl_{18}$	Dark brown	~970, 435, 289, 218	1.65 ^b
$[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$	Brown	~970, 430, 288	1.46 ^b
$[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$	Dark brown	~970, 434, 291	Paramagnetic
$[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$	Dark brown	~975, 431, 290	Paramagnetic
$Nb_6Cl_{14} \cdot 8H_2O$	Black	914, 401, 278	Diamagnetic

^a Spectra obtained in methanol. All solutions were prepared and maintained at room temperature. ^b Moment obtained from Curie law plot; measured from 77 to 300°K.

collected on a frit, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $[(C_2H_5)_4N]_2Nb_6Cl_{18}$: Nb, 38.28; Cl, 43.83, C, 13.20; H, 2.77. Found: Nb, 38.44; Cl, 43.52; C, 13.73; H, 2.81.

The preparation of the 3+ complex ($x = 3$) was completely analogous except that air oxidation was utilized, rather than oxidation by chlorine. The product was microcrystalline and dark brown but appeared red-brown under the microscope. *Anal.* Calcd for $[(C_2H_5)_4N]_3Nb_6Cl_{18}$: Nb, 35.14; Cl, 40.23; C, 18.17; H, 3.81. Found: Nb, 35.47; Cl, 40.08; C, 18.48; H, 4.14.

Preparation of $[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$. $Nb_6Cl_{14} \cdot 8H_2O$ (1 g) was dissolved in 80 ml of methanol with heating, and then 8 ml of concentrated aqueous hydrochloric acid was added. Tetraphenylarsonium chloride (2.10 g) in 15 ml of methanol was then added, and the solution was heated at the boiling point where, as oxidation proceeded, it slowly changed color from dark green to red-brown. Oxygen was bubbled through the solution for 1 hr prior to cooling and crystallization. The brown crystals (1.4 g) were collected on a frit, washed with methanol, and air dried. *Anal.* Calcd for $[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$: Nb, 28.92; Cl, 29.43; C, 29.91; H, 2.30; O, 1.66. Found: Nb, 28.99; Cl, 29.23; C, 29.22; H, 2.45; O, 1.46 (determined by neutron activation analysis.)

The preparations of $[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$ and $[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$ were analogous to the above except that progressively higher concentrations of hydrogen chloride were maintained in the solution before crystallization of the product. *Anal.* Calcd for $[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$: Nb, 23.95; Cl, 25.90; C, 37.16; H, 2.64; O, 0.69. Found: Nb, 24.11; Cl, 26.34; C, 37.44; H, 2.79; O, 0.91. Calcd for $[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$: Nb, 28.66; Cl, 30.99; C, 29.64; H, 2.18. Found: Nb, 28.53; Cl, 30.50; C, 29.78; H, 2.61.

All of the complexes prepared are slightly soluble in acetone and methanol and less soluble in ethanol. They are insoluble in water and apparently inert to air. A summary of some data obtained on these compounds is presented in Table I.

It is evident that in preparing the complexes in a solvent saturated with hydrogen chloride that a terminal chloride has been coordinated to each niobium atom in the Nb_6Cl_{12} cluster. The structure might be expected to contain a regular octahedron of niobium atoms with bridging chlorides in the normal positions,⁷ and with six other chlorides bonded to the apices of the octahedron. In this arrangement no intercluster bonding is allowed and the isolated ions, $[(Nb_6Cl_{12})Cl_6]^{n-}$, are obtained.

(7) A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

In the preparations of the tetraphenylarsonium complexes a much lower concentration of chloride ion was used, and also air oxidation⁸ was relied on to oxidize the cluster unit. The evidence for hydroxide or water being bonded to the cluster is, in addition to the analytical data, the visible spectra and magnetic moments which indicate a 3+ oxidation state for the cluster. We have been unable to unambiguously assign any bands in the infrared spectra which may arise from coordinated water or hydroxide in these tetraphenylarsonium salts.

It appears that the number of aquo or hydroxyl groups which are coordinated to the $[Nb_6Cl_{12}]^{3+}$ unit is determined by the relative hydrogen chloride concentration in the solution. At the lowest hydrogen chloride concentration, $[(Nb_6Cl_{12})Cl_4(OH)(H_2O)]^{2-}$ was obtained, whereas in ethanol saturated with hydrogen chloride $[(Nb_6Cl_{12})Cl_6]^{3-}$ was obtained.

At this time the spectral data are incomplete, and it has not been established to what extent the ions of the type $Nb_6Cl_{12}Cl_6^{n-}$ may undergo replacement of chloride by solvent molecules. However, the spectra show the interesting trend that the two principal bands in the visible and near-ultraviolet region are shifted to lower energies by about 1500 cm^{-1} on each increase in the oxidation state of the cluster. The intensities of these bands undergo little change. The band in the $950\text{-m}\mu$ region is not shifted so regularly and shows some significant intensity variation. The position of the band in the $400\text{-}450\text{-m}\mu$ region has served as a useful diagnosis of the oxidation state of the cluster.

The magnetic studies have yielded the result that the 2+ and 4+ cluster derivatives are diamagnetic, whereas the 3+ derivatives are paramagnetic. The small moment (0.02 BM) obtained for the 4+ derivative listed in Table I is attributed to about 1% 3+ impurity.

A detailed and systematic study on the preparation, spectra, and magnetic susceptibilities of $[M_6X_{12}]^{n+}$ complexes is currently in progress.

(8) It has been observed that prolonged exposure to air of solutions saturated with hydrogen chloride leads to deposition of mixtures containing the cluster in both the 3+ and 4+ oxidation states.

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Cyclopropyl Semidiones¹

Sir:

The question of delocalization in cyclopropylcarbinyl systems has been investigated by a study of semidiones

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

Table I. Hyperfine Splitting Constants (Gauss) for 1 and 2 in DMSO at 25°

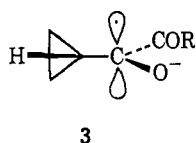
	$a_{\alpha\text{-CH}^{\text{H}}}$	$a_{\text{CH}_3^{\text{H}}}$	$a_{\beta\text{-H}^{\text{H}}}$	$a_{\gamma\text{-H}^{\text{H}}}$
1, R = cyclopropyl	0.57 (2)	...	0.37 (4), 0.20 (4)	
2, R = cyclopropyl	0.57	5.88	0.37 (2), 0.20 (2)	
1, R = cyclobutyl	2.22 (2)		0.45 (4), 0.23 (4)	0.08 (4)
2, R = cyclobutyl	2.11	5.55	0.45 (2), 0.23 (2)	
1, R = cyclopentyl	1.92 (2)		0.44 (4), 0.22 (4)	0.11 (8)
2, R = cyclopentyl	1.92	5.77	0.44 (2), 0.22 (2)	0.11 (4)
1, R = cyclohexyl	1.88 (2)			
2, R = cyclohexyl	1.73	5.73	0.30 (4)	0.08 (4)
1, R = isopropyl	1.92 (2)		0.05 (12)	
1, R = (CH ₃ CH ₂) ₂ CH	1.05 (2)		0.51 (8)	
1, R = (CH ₃ CH ₂ CH ₂) ₂ CH	0.95 (2)			

1 and 2. We have observed unusual stability and a

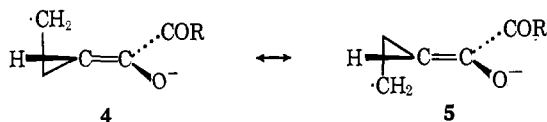


highly preferred conformation when R = cyclopropyl. The semidiones were prepared by the disproportionation of the acyloins in dimethyl sulfoxide containing excess potassium *t*-butoxide at 25°. ²

Semidione **1** with R = cyclopropyl is unusually stable. It is stable for days in dimethyl sulfoxide solution and is formed in a yield of at least 50% from the acyloin. Semidiones of type **1** with R = cyclobutyl, cyclopentyl, cyclohexyl, or isopropyl gave a predominant esr triplet splitting due to the α -methine hydrogen atoms (Table I). This triplet splitting is not obvious from inspection of the spectrum for **1**, R = cyclopropyl. Figure 1 gives the well-resolved spectrum of **2**, R = cyclopropyl, in which the doublet splitting of the α -methine hydrogen is only 0.57 gauss. The small hyperfine splitting constant observed for the α -methine hydrogens of **1** or **2**, R = cyclopropyl, must result from a highly preferred conformation(s) in which the methine hydrogen atom is close to the nodal plane of the π system. ³ The observed hyperfine splitting would be consistent with a single conformer, or a time-averaged pair of enantiomeric conformers in which the methine hydrogen is 8° out of the nodal plane. ⁴ The stability of conformers



such as **3** may be due to nonbonded interactions or to delocalization (structures **4** and **5**). Conformational preferences from nonbonded interactions are important



for the series **1**, R = CH₃, CH₃CH₂, (CH₃)₂CH, (CH₃-CH₂)₂CH, (CH₃CH₂CH₂)₂CH, wherein the value of

(2) E. R. Talaty and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 4867 (1965).

(3) The conformation of cyclopropylcarbiny type radicals is thus similar to the cyclopropylcarbiny type cation (C. V. Pittman and G. A. Olah, *ibid.*, **87**, 5123 (1965)), cyclopropylcarboxaldehyde (L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965)), phenylcyclopropane (G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965)), and vinylcyclopropanes (H. Günther and D. Wendisch, *Angew. Chem. Intern. Ed. Engl.*, **5**, 251 (1966)).

(4) By use of the equation $a^{\text{H}} = 40 \rho_c \cos^2 \theta$, wherein ρ_c is taken as 0.25. ²

a_{α}^{H} decreases from 5.70 for the freely rotating methyl group ($\theta = 45^\circ$) to 4.90, 1.95, 1.05, and 0.95 for the other members of the series. However, the conformational preference of the cyclopropyl group is much more pronounced. Extensive delocalization (structures **4** or **5**) should place a high spin density on the cyclopropyl methylene carbon atoms (ρ_{CH_2}). Values of the hyperfine splitting constant for the methylene hydrogen atoms of the cyclopropane ring are larger than the β -hydrogen atoms of **1**, R = (CH₃CH₂)₂CH (Table I), but the difference is not great, particularly when the hyperfine splitting by the β -hydrogen atom (*anti* C-7)

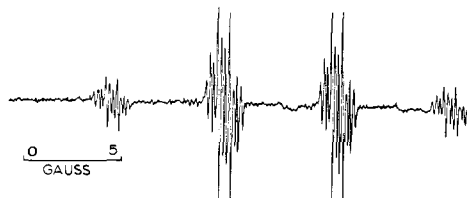


Figure 1. First-derivative esr spectrum of methylcyclopropylsemidione in dimethyl sulfoxide solution at 25° prepared by disproportionation of the acyloin (0.001M) in the presence of potassium *t*-butoxide (0.002M).

of over 6 gauss in bicyclo[2.2.1]heptane-2,3-semidione is considered. ⁵ However, the value of a_{β}^{H} may be a poor measure of ρ_{CH_2} in **1** or **2**, R = cyclopropyl. A spin polarization mechanism would place a negative spin density on the two methylene hydrogens in **4**. Hyperconjugation in **5** would introduce a positive spin density on the adjacent methylene hydrogen atoms. These two effects may nearly cancel. ⁶ The synthesis of **2** with ¹³C substituted at the methylene position is in progress.

Reaction of dicyclopropyl ketone with potassium in purified tetrahydrofuran at 25° produces a paramagnetic substance which shows a triplet splitting of broad lines, $a^{\text{H}} = 3.5$ gauss. This product is believed to be dicyclopropyl ketyl. ⁷ Our results are contradictory with a report of the preparation of dicyclopropyl ketyl. ^{8,9} The spectrum assigned to dicyclopropyl ketyl ⁸ appears

(5) G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965).

(6) In the ethyl radical, spin polarization yields $a_{\text{CH}_2^{\text{H}}} = -22.38$ gauss while hyperconjugation yields $a_{\text{CH}_2^{\text{H}}} = +26.87$ gauss: R. W. Fessenden and R. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(7) The value of a_{α}^{H} in *t*-butyl isopropyl ketyl is reported to be 2.38 gauss: N. Hirota and S. Weissmann, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(8) N. K. Ray, R. K. Gupta, and P. T. Narashimhan, *Mol. Phys.*, **10**, 601 (1966).

(9) See also R. G. Kostyanovskii, S. P. Solodounikov, and O. A. Yuzhakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 735 (1966).

to us to be suspiciously similar to a poorly resolved spectrum of the biphenyl radical anion.¹⁰

(10) The spectrum given in ref 8 involves nine, or possibly 11, lines separated by 2.7 gauss (the spectrum was analyzed in terms of 13 lines). Biphenyl radical anion at high concentration yields a nine-line spectrum, with intensities similar to the central nine lines of the reported spectrum, and with a line separation of 2.7 gauss. It is possible that the central seven lines of this spectrum was previously identified as cyclopropane radical anion: K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963); K. W. Bowers, G. J. Nolti, T. H. Lowry, and F. D. Greene, *Tetrahedron Letters*, 4063 (1966); see also F. Gerson, E. Heilbronner, and J. Heinzer, *ibid.*, 2095 (1966).

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The Vacuum Ultraviolet Photolysis of Benzene¹

Sir:

Two reports of the vapor phase photolysis of benzene at 1849 Å have appeared recently: one by Foote, Mallon, and Pitts,² and one by Shindo and Lipsky.³

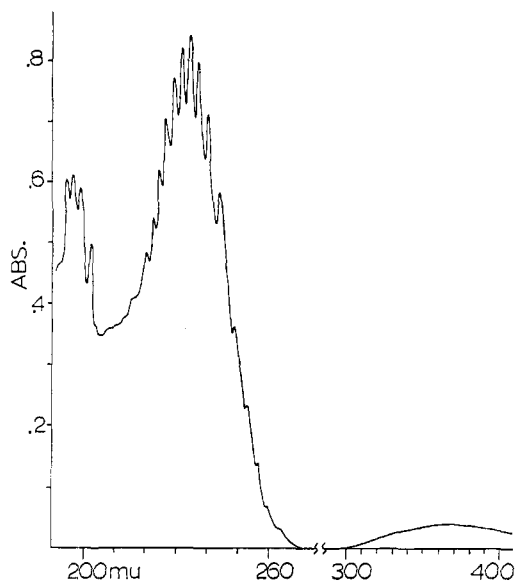


Figure 1. Vapor phase ultraviolet spectrum of fulvene produced by the photolysis of benzene.

Both groups report a single major product in addition to polymeric materials, and both groups suggest that this product is "benzvalene"⁴ (I). In neither case was this product isolated, but the ultraviolet spectra⁵ are nearly identical in the two reports^{2,3} and there is little doubt that both groups have detected the same compound.

As part of a general investigation of vacuum ultraviolet photochemistry, we have examined the products formed from benzene on irradiation with light of 1600–2000 Å. We also find that a single major product is formed when benzene is photolyzed at pressures of 1–

(1) The authors gratefully acknowledge financial support from the National Science Foundation (GP-3496).

(2) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).

(3) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

(4) Tricyclo[2.1.1.0^{5,6}]hex-2-ene.

(5) Lipsky³ states that his published spectrum was obtained by subtracting absorption due to benzene. Pitts² does not report the method by which his spectrum was obtained.

100 mm, and we have succeeded in the isolation of this elusive compound by preparative gas chromatography. The separation was effected by a 0.25-in × 25 ft. Ucon 50-HB-100 column, 25% on 100–120 mesh Chromosorb W, operated at 45°. The effluent stream from the column was split with 10% going to a flame ionization detector, and 90% going to a collector trap. Traps were fitted with vacuum stopcocks and were kept in liquid nitrogen baths at all times during the collection sequence. The trapped material was vacuum-transferred from the traps directly into an absorption cell for determination of the ultraviolet spectrum. For infrared and nuclear magnetic resonance spectra, the sample was transferred onto frozen carbon tetrachloride. The compound is quite stable in the gas phase and in dilute solution (either in benzene or in carbon tetrachloride). Solutions of the compound are bright yellow in color.

The ultraviolet spectrum (vapor phase, Figure 1), although taken under higher resolution than the published spectra, shows the same absorption maxima and relative intensities.⁶ The agreement between our spectrum and that published by Lipsky³ is especially striking in the region 2560 to 2120 Å; both show a 17-member progression of fine structure bands with separations of about 500 cm⁻¹. In addition, the gas chromatographic retention time is nearly the same as that reported by Pitts² on a Ucon-polar column (retention time relative to benzene is 0.90 on a Ucon 50-HB-100 column at 50°). This evidence leads us to believe that the photoproduct formed in our system is the same as that formed by photolysis at 1849 Å.^{2,3}

The compound that we have isolated is *not* "benzvalene" (I) but has been demonstrated conclusively to be fulvene (II).⁷ This product exhibits ultraviolet



and mass spectra and retention times identical with those of authentic fulvene prepared in the conventional way,⁸ and the nuclear magnetic resonance and infrared spectra are the same as those reported⁹ for fulvene.

Considerable attention was given to the possibility that fulvene might result from a rearrangement of "benzvalene" initially formed on photolysis. However, the photoproduct collected at 77°K in a flow system had the characteristic bright yellow color of fulvene, and analysis of samples taken immediately on melting the trapped product showed no evidence of rearrangement on the gas chromatography column. If such a rearrangement occurs it must be an exceedingly facile one.

The formation of fulvene from the irradiation of benzene at its first absorption band in the liquid phase has been reported by Bryce-Smith.¹⁰ In the vapor phase,

(6) Spectra published by Pitts and Lipsky do not extend far enough to show the broad absorption band at about 365 mμ which is present in our spectrum.

(7) Pitts² mentions fulvene as a possible identity for his photoproduct.

(8) J. Thiec and J. Wiemann, *Bull. Soc. Chim. France*, 177 (1956); H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 1409 (1960).

(9) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(10) (a) J. Mc. Blair and D. Bryce-Smith, *Proc. Chem. Soc.*, 287 (1957); (b) H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).