τ 4.01 (m, 2, inner vinyl $H_{6,7}$), 4.60 (m, 2, outer vinyl $H_{5,8}$), 8.10–8.85 (m centered at 8.46, 2, allylic $H_{4,9}$), 8.85–9.50 (m centered at 9.10, 3, nonallylic tertiary $H_{1,2}$ and anti methylene H at C_{10}), 9.86 (m, 1, syn methylene H at C_{10}).

The assignment of the stereochemistry of the products is based on the greater chemical-shift differences in the nmr between "inner" ($H_{6,7}$) and "outer" ($H_{5,8}$) vinyl protons expected in the trans compound IV.[5] The high-field protons of the vinyl multiplet adjacent to the cyclopropane ring are also further shielded by the ring current in the trans isomer IV.

It should be noted that in the reaction of II with carbon tetrachloride the *only* products obtained resulted from adjacent biscycloproponation with the cis isomer predominating. The fact that the cis isomer predominates in this reaction is contrary to the results expected. By using steric considerations we are lead to the prediction that the second cyclopropyl ring would be more stable and more easily formed if it were oriented trans to the cyclopropyl ring already present in the molecule. However, in the reaction of II with carbon tetrachloride there is a preference for the cyclopropyl rings to be oriented cis to each other by a factor of 2:1 based on the yields of the two products. In view of this, and in view of the predominating stereochemistry of the products obtained from the reaction of alkali metal cyclooctatetraenides with gem dihalides,[3] it is likely that the cyclooctatetraenyl dianion and the monohomocyclooctatetraenyl dianion react with carbon tetrachloride *via* the same mechanism, and that this mechanism does involve the generation of a divalent carbon species which then combines with bicyclo[6.1.0]-nonatriene (I). However, still unexplained in both dianion reactions is what determines the stereochemistry of the products.

Reactions of the dianion II with other organic compounds are now under investigation.

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(5) This assignment is based on analogous adjacent bishomocyclooctatetraene compounds which will be discussed in a future paper.

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Electron Paramagnetic Resonance of CD_2 and CHD. Isotope Effects, Motion, and Geometry of Methylene

Sir:

We have observed that the epr spectra of CD_2 and CHD in a solid matrix differ significantly from the spectrum of CH_2. We assign the changes to differences in zero-point motion. Comparing CH_2 and CD_2 allows the first experimentally based determination of a zero-field parameter for rigid (or gas phase) methylene. Also, the apparent asymmetry of CHD is greater than that of either CH_2 or CD_2. This variation is consistent with methylene and its deuterated derivatives being substantially bent (HCH angle 136°) and rotating about the long axis. The electronic spectra of all three species have been previously observed in the gas phase by Herzberg.[1] These spectra were compatible with a "linear or nearly linear" geometry for the ground state.

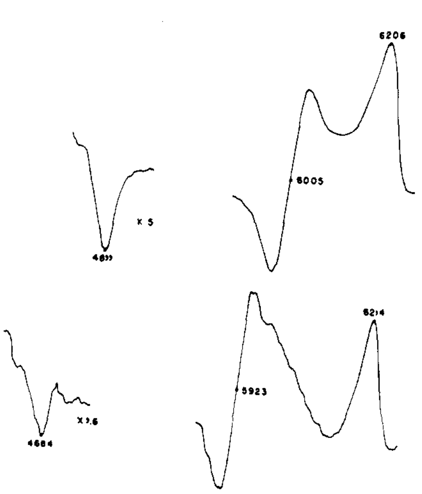

Figure 1. Spectra of CD_2 (top) and CHD (bottom) with $h\nu/g\beta$ = 3279.2 and 3277.4 G, respectively.

The precursors, mono- or dideuteriodiazirene, were condensed with xenon at 77°K and irradiated at 4°K. After irradiation ceased spectra remained unchanged for hours with the sample at 4°K, as expected for ground-state triplets (Figure 1).[2] The zero-field parameters which characterize the spectra[4,5] are D_{HD} = 0.7443, E_{HD} = 0.00640 cm^{-1} for the major triplet of CHD[2] and D_{DD} = 0.7563, E_{DD} = 0.00443 cm^{-1} for CD_2. The values which have been previously observed for CH_2 are D_{HH} = 0.6881, E_{HH} = 0.00346 cm^{-1}.[3,6] The presence of three and only three distinct spectra for the three isomeric precursors shows that the triplet contains two hydrogens.

To extrapolate from the above observations to a rigid methylene we note that $D \propto \langle(3z^2 - r^2)/r^5\rangle$, while $E \propto \langle(y^2 - x^2)/r^5\rangle$, where r and its coordinates refer to the distance between the two unpaired electrons.[7] Both parameters are largest for a triplet fixed in space, decrease with increasing motion, and vanish for a randomly tumbling molecule.[8] The 10% decrease in D_{HH} compared to D_{DD} indicates that CH_2 has a significantly larger wobble of the long (z) axis than CD_2. We assume that this motion takes place in a potential

(1) (a) G. Herzberg, *Proc. Roy. Soc., Ser. A*, 262, 291 (1961); (b) "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967, p 491.

(2) A second triplet species, which can dominate some CH_2 spectra and which we have assigned to a second crystalline form of the matrix,[3] is less in evidence in CHD and barely detectable in CD_2. This second triplet of CHD is visible on the high-field side of the 5923-G line.

(3) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, 7, 409 (1970).

(4) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 41, 1764 (1964).

(5) P. Kottis and R. Lefebvre, *ibid.*, 41, 379 (1964).

(6) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *ibid.*, 53, 1280 (1970). We are grateful to Dr. Bernheim for making available a preprint of this first publication of an epr of CH_2. We disagree with the geometrical conclusion given.

(7) M. Goutermann and W. Moffitt, *ibid.*, 30, 1107 (1959).

(8) See, for example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapters 3 and 8.

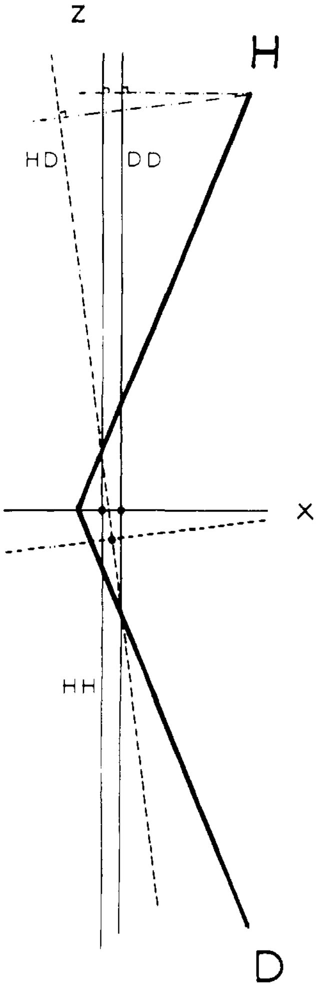

Figure 2. Rotational axes for the three species. The y axes are perpendicular to the plane at the center of gravity, which is indicated by a dot at the x, z intersection for each species. The x axis is the same for CH_2 and CD_2. The x and the z axes for CHD are tilted by 7° from those of the other species. The distance swept out on rotation about z is indicated by the perpendiculars from H to the z axes.

well $V = V_z(1 - \cos 2\alpha)$, with α the angular deviation of the z axis from its equilibrium position. Then[9]

$$D_{\text{obsd}} = D_n\left\langle\frac{3\cos^2\alpha - 1}{2}\right\rangle \tag{1a}$$

$$\approx D_n[1 - (3/4)(\hbar^2/IV_z)^{1/2}] \tag{1b}$$

I is the moment of inertia for rotation of the z axis about the x or y axes, which, for the moment, we consider the same. D_n corresponds to a methylene with "infinitely heavy hydrogens" ($I = \infty$) so that no motion occurs. Equation 1b is valid if we can approximate the potential well as that of a harmonic oscillator. With I available from the electronic spectra,[1] D_{HH} and D_{DD} yield $V_z = 122$ cm^{-1} and $D_n = 0.93$ cm^{-1}. This D_n agrees well with Higuchi's calculation of 0.905 cm^{-1} for the spin-spin contribution to D.[10] One should add the computed spin-orbit contribution ~0.05 cm^{-1} [11] to give a total of 0.95 cm^{-1}.

From (1a) we then have that the deviation from the equilibrium position $\langle\alpha^2\rangle^{1/2} = 24°$ for CH_2 and 20° for CD_2. Since kT at 4°K is much less than the difference between energy levels in the well (87 cm^{-1} for CH_2 and 62 cm^{-1} for CD_2), this is zero-point motion.

The angle about the divalent carbon is related to E which measures the difference in the magnetic properties along the x and y axes (Figure 2; y is perpendicular to the paper). E will vanish for a linear molecule. The relationship between angle and zero-field parameters is[3,10]

$$E_n/D_n = \frac{\cos^2\theta}{2 - 3\cos^2\theta} \tag{2}$$

Here E_n and D_n are the parameters if the molecule is not moving and 2θ is the angle at the carbon. Using the observed parameters in (2) we might conclude that 2θ is 172° for CH_2, 168° for CD_2, and 165° for CHD. Such a variation of angle is unusual on isotopic substitution.[12] In any case, the largest E and smallest angle arise with CHD, a trend which does not fit a smooth change of angle with increasing isotopic mass.

A resolution of the paradox lies in the consideration of rotation about the z axis. In the analysis of the spectrum of CH_2 we argued that such rotations are almost free.[3] Only the lowest rotational state of this one-dimensional rotator is populated at 4°K. In zero order this state is cylindrically symmetric, a form which will have $E = 0$.[13] A small twofold barrier to rotation, V_2, provides a first-order mixing of this ground state with the second rotational state of the free rotator. This perturbed ground state will then exhibit an epr spectrum with

$$E = E_n(V_2/W_2) \tag{3}$$

W_2 is the energy of the second rotational level. For CH_2 we concluded that $V_{2HH} = 14.5$ cm^{-1} and $W_{2HH} = 260$ cm^{-1}, so that $2\theta = 136°$.[3] The observed E is but a small fraction of the E_n characteristic of a rigid methylene.

In using (3) for the deuterated species, W_2 will change with the mass of the hydrogen isotopes. For $2\theta = 136°$, $W_{2DD} = 152$ cm^{-1} and $W_{2HD} = 205$ cm^{-1}. The barriers V_2 will also change. CD_2 is expected to have a smaller barrier than CH_2 as the former's z axis, passing through the center of gravity, is closer to the heavier deuteriums than is the z axis in CH_2 to its protons (Figure 2). The barrier will be dependent on the distance swept out by the hydrogens on rotation about the z axis. Assuming a parabolic expansion about the equilibrium position, $V_{2DD} = 0.75V_{2HH} = 10.9$ cm^{-1}. For CHD the rotational z axis is tilted by 7° from the perpendicular to the angle bisector (Figure 2). The hydrogen is further out during rotation, giving rise to a larger barrier than for CH_2. Again assuming that the barrier is proportional to the square of the displacement, $V_{2HD} = 24.6$ cm^{-1}. With (3) we expect that $E_{DD}:E_{HD}:E_{HH}$ should go as

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(9) H. Meyer, M. C. M. O'Brien, and J. H. Van Vleck, *Proc. Roy. Soc., Ser. A*, **243**, 414 (1958).

(10) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963). Equation 2 summarizes the calculations reported here. See also H. Sternlicht, *ibid.*, **38**, 2316 (1963).

(11) S. H. Glarum, *J. Chem. Phys.*, **39**, 3141 (1963). This value is interpolated from the data given. S. J. Fogel and H. F. Hameka, *ibid.*, **42**, 132 (1965), have also computed this contribution for a linear methylene.

(12) Reference 1b, p 181; K. Dressler and D. A. Ramsay, *Phil. Trans. Roy. Soc. London, Ser. A*, **251**, 553 (1959), found that NH_2 and ND_2 have the same angle within 7'.[8]

(13) This zero-order view justifies the assumption in eq 1a and 1b that the x and y axes are equivalent.

1.00:1.67:0.79 compared to the observed 1.00:1.46: 0.77.[14]

The above argument allows us to explain the large E_{HD} as due to the larger barrier seen on rotation. The isotopic data thus provide strong support for almost free rotation about the *z* axis. With a 40–48° arc for the zero-point wobble of the *z* axis, we feel that methylene is sufficiently free in the matrix to assume its preferred geometry. Together with our previous observations that substituted methylenes keep the same angle at the divalent carbon under a variety of conditions,[15] we conclude that free methylene has a preferred angle of 136°.[16] A number of theoretical calculations are in agreement with this value.[17,18a] Additional evidence that a rare-gas matrix does not distort a guest molecule is found in the electronic spectrum of NH_2 in argon at 4°K.[18b] The NH_2 is a largely free rotator and the rotational structure parallels that observed in the gas phase.[12]

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(14) The observed E_{HH} shuould be multiplied by D_{DD}/D_{HH} to compensate for the increased motion of CH_2. The term in the ratio would then be 0.84.

(15) (a) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, 61, 1663 (1964); (b) L. Barash, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **89**, 3931 (1967).

(16) The uncertainty is given as ±8° in ref 3, assuming a variation in V_2 of a factor of 4. This range may be viewed as a standard deviation, with an angle of >150° unlikely. An angle of <128° is most improbable for free CH_2, following Herzberg.[1]

(17) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969), give an extensive review of the theoretical literature. See also C. F. Bender and H. F. Schaefer III, *ibid.*, **92**, 4984 (1970); W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, in press.

(18) (a) The value is also supported by the lack of hyperfine broadening on going from CHD to CD_2 (Figure 1). If anything, the latter has broader lines. A linear methylene should have a substantial hyperfine broadening (P. H. Kasai, L. Skattebol, and E. B. Whipple, *ibid.*, **90**, 4509 (1968)), while at 135–140° the contribution from the two unpaired electrons should cancel: E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964). (b) G. W. Robinson and M. McCarty, Jr., *ibid.*, **30**, 999 (1959).

(19) Bell Telephone Laboratories, Inc.

(20) Rutgers University.

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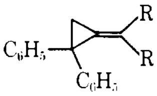
Photofragmentation of Arylmethylenecyclopropanes to Alkylidenecarbenes

Sir:

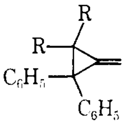
Photolysis of small-ring compounds bearing aryl substituents is known to initiate expulsion of fragments having chemical properties that are characteristic of carbenes.[1] In fact, irradiation of phenylcyclopropane[1a] and of stilbene oxide[1b] produces fragments whose properties are essentially identical with the methylene and the phenylcarbene, respectively, which result from photolysis of the corresponding diazo compounds. In view of the current interest in the chemistry of methylenecarbenes [$:C{=}CR_2$],[2] we wish to report the preliminary results of studies that suggest that carbenes of this type can be generated by photolysis of arylmethylenecyclopropanes.

Irradiation[3] of a 0.5% solution in pentane of 2,2-diphenyl-1-methylenecyclopropane[4] (**1a**) at −40° results in the formation of 1,1-diphenylethylene and acetylene,[5] as well as in a photochemical methylenecyclopropane rearrangement;[7] complete disappearance of starting material requires *ca.* 10 hr. Repetition of the photolysis using **1b** in heptane[8] gave acetylene having the composition, 54% d_2, 3% d_1, and 43% d_0. Significantly, the observed ratio of d_2:d_1 acetylenes corresponds within experimental error to the deuterium distribution of the starting material. This observation requires that the mechanism by which acetylene is formed from **1** accommodate the lack of incorporation of solvent hydrogen into the acetylene as well as the strictly pairwise distribution of deuterium (or hydrogen) in the isolated acetylene.

A mechanistic hypothesis consistent with these requirements is that photolysis of **1** results in extrusion of the elusive methylenecarbene, [$:C{=}CH_2$], which subsequently rearranges to acetylene faster than it can be trapped[9] by solvent. The fact that such a significant amount of acetylene-d_0 is observed suggests that the photoinitiated degenerate interconversion of **1b** and **2a** is fast relative to the process that results in expulsion of the two-carbon fragment.



1a, R = H
b, R = D
c, R = CH_3



2a, R = D
b, R = CH_3

More conclusive evidence that a methylenecarbene can be produced from arylmethylenecyclopropanes is available from the results of photolysis of 2,2-diphenyl-1-isopropylidenecyclopropane (**1c**).[10] When **1c**, as a

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(1) (a) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Amer. Chem. Soc.*, **87**, 2763 (1965); (b) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (*London*), 1562 (1966); (c) H. Dietrich and G. W. Griffin, *Tetrahedron Lett.*, 153 (1968); (d) M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Waller, *J. Amer. Chem. Soc.*, **88**, 3167 (1966).

(2) (a) M. S. Newman and T. B. Patrick, *ibid.*, **92**, 4312 (1970); (b) M. S. Newman and T. B. Patrick, *ibid.*, **91**, 6461 (1969).

(3) A 450-W Hanovia medium-pressure mercury lamp was employed.

(4) J. C. Gilbert and J. R. Butler, *J. Amer. Chem. Soc.*, **92**, 2168 (1970).

(5) (a) The 1,1-diphenylethylene was isolated by preparative glpc and exhibited ir and nmr spectra identical with those of an authentic sample.[6] The acetylene was identified by the mass spectrum of a sample obtained by bubbling argon through the pentane solution during the course of the photolysis and passing the emerging gases through a trap held at −80°. (b) The photofragmentation of **1a** to produce an ethylene and acetylene is directly analogous to that of methylenecyclopropane itself to yield ethylene and acetylene as reported by R. K. Brinton, *J. Phys. Chem.*, **72**, 321 (1968).

(6) C. F. H. Allen and S. Converse, "Organic Syntheses," Collect. Vol. I, 2nd ed, H. Gilman, Ed., Wiley, New York, N. Y., 1932, p 226.

(7) J. C. Gilbert and J. R. Butler, in preparation.

(8) Heptane was used in this run in order to facilitate isolation of the acetylenes uncontaminated with solvent.

(9) Trapping would presumably be by a carbon–hydrogen insertion reaction. Although a completely exhaustive search has as yet not been made, no C-7 alkenes have been detected by glpc analysis of the solvent recovered from the photolysis of **1a** in pentane.

(10) Newman and Patrick[2a] report a synthesis of this substance. Unfortunately, the material that they have isolated is probably a mixture of **1c** and 1,1,2-trimethyl-3-phenylindene, the latter being formed by thermal isomerization of **1c** under the glpc conditions used in their purification procedure.[11] In our hands, **1c** is obtained in 14–16% yield by the procedure described[2a] except that purification is accomplished by column chromatography over alumina. The nmr spectrum (60 MHz, CCl_4) of **1c** exhibits two multiplets at δ 1.75 and 1.93 (2 H and 6 H, respectively), and a broad singlet at δ 7.11 (10 H).

(11) See M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler