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).

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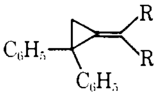
Photofragmentation of Arylmethylenecyclopropanes to Alkylidenecarbenes

Sir:

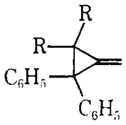
Photolysis of small-ring compounds bearing aryl substituents is known to initiate expulsion of fragments having chemical properties that are characteristic of carbenes.[1] In fact, irradiation of phenylcyclopropane[1a] and of stilbene oxide[1b] produces fragments whose properties are essentially identical 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.

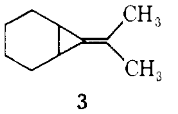
(8) Heptane was used in this run in order to facilitate isolation of the acetylenes uncontaminated with solvent.

(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

0.5% solution in cyclohexene, is irradiated[3] for 8 hr at −40°, 7-isopropylidenebicyclo[4.1.0]heptane (**3**) is obtained in *ca.* 3% yield (isolated). The alkene **3**, purified by preparative glpc, is identical[12] with an authentic sample prepared by an alternate route.[2b] Furthermore, irradiation[3] of a 0.5% solution of **1c** in cyclohexane at 30–40° for 9 hr affords the anticipated carbon–hydrogen insertion product, 1-cyclohexyl-2-methylpropene (**4**),[13] albeit in less than 1% yield. Thus, both of the characteristic reactions that might be anticipated for isopropylidenecarbene, *viz.*, addition to carbon–carbon double bonds and insertion into carbon–hydrogen bonds, are exhibited by the species resulting from photolysis of **1c**.[14]



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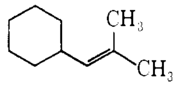

4

It is noteworthy that observation of the insertion reaction with alkanes differentiates our photochemically generated species from that studied by Newman, *et al.*[2] Generation of isopropylidenecarbene in cyclohexane by their procedure gives no insertion product.[15] Consequently, the possibility arises that the chemistry previously[2] ascribed to isopropylidenecarbene, and the provocative mechanisms associated therewith, should actually be attributed to some other intermediate, *e.g.*, a carbenoid.

Additional aspects of the chemistry of the intermediate formed by irradiation of arylmethylenecyclopropanes, such as the sensitivity of the addition reaction to steric and electronic effects in substrate alkenes and the possibility that intramolecular processes may account for the inefficiency of the intermolecular insertion reaction, are the subjects of current investigations.

(*Tetrahedron Lett.*, 845 (1970)) for a discussion of thermal isomerizations of this type.

[12] Identity was established by comparison of ir and nmr spectra and by equivalence of retention times on three different glpc columns.

[13] An authentic sample of **4** was obtained as the major isomer from the dehydration of 1-cyclohexyl-2-methyl-2-propanol: nmr (CCl_4) δ 4.9 (doublet of multiplets, $J = 9.0$ and $J \sim 1.3$ Hz, 1 H), 1.64 (d, $J \sim 1.2$ Hz, CH_3), 1.57 (d, $J \sim 1.3$ Hz, CH_3), 2.5–0.7 (broad m, total area of 17); ir 1670, 830 cm^{-1}; *m/e* 138.1410 (calcd for $C_{10}H_{18}$, 138.1408). The adduct **4** isolated from the photolysis had a retention time identical with that of the authentic material on three different glpc columns [4 m 30% TCEP on 60–80 Chromosorb P(AW); 2 m 30% SE-30 on 60–80 Chromosorb P; 5 m FFAP on 60–80 Chromosorb P(AW)] and gave an ir spectrum (CCl_4) which, although very weak owing to the low yield of the insertion reaction, had all of the major peaks of authentic 4, and no spurious absorptions.

[14] Initial observations are that photolysis of **1c** in either *cis*- or *trans*-4-methyl-2-pentene affords a mixture of both the cis and the trans adducts. Control experiments have shown, however, that the methylenecyclopropanes undergo a facile photochemical geometrical isomerization which accounts for at least part, if not all, of the nonstereospecificity.

[15] We estimate that had **4** been formed, a yield of as little as 0.1% could have been detected by our glpc method of analysis.

[16] The support of this research by the Robert A. Welch Foundation is gratefully acknowledged. The mass spectrometer was purchased with funds provided by the National Science Foundation (Grant No. GP-8509).

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Photofluorination with Fluoroxytrifluoromethane, a General Method for the Synthesis of Organic Fluorine Compounds. Direct Fluorination of Bioactive Molecules

Sir:

We wish to report the discovery of the first general method for substitutive fluorination of organic compounds.

The known methods for substitutive fluorination (RH → RF) are either nonselective and degradative (*e.g.*, the methods involving elementary fluorine or high-valency oxidative metallic fluorides, as CoF_3, etc.) or are applicable (*e.g.*, perchloryl fluoride) only with especially activated substrates. A further deterrent is the extremely dangerous nature of most of the above reagents.[1]

We found that light-induced—thus presumably radical type—liquid-phase interaction of fluoroxytrifluoromethane, CF_3OF,[2] with organic compounds represents an exceedingly useful new approach for the substitution of hydrogen atoms by fluorine in a variety of organic compounds. Irradiation with very high luminous flux density is of key importance for the success of this method.[3]

$$RH + CF_3OF \xrightarrow[\text{liquid phase}]{h\nu} RF$$

A solution of benzene (25 mmol) in 80 ml of trichlorofluoromethane was irradiated[3] at −78° (acetone–Dry Ice bath) under stirring while CF_3OF gas[4] (20 mmol) was passed in within 1 hr.[5] After 30 min of further irradiation the solvent was distilled off and the residue analyzed by quantitative gas–liquid chromatography,[6] indicating 65% yield of fluorobenzene, with 10% trifluoromethoxybenzene ($C_6H_5OCF_3$) as by-product.[7] A similar experiment, without irradiation, gave a complex mixture of products with only 17% yield of fluorobenzene; addition of CF_3OF in the dark followed by uv irradiation also gave a low yield. These results may be explained as follows: the rate of the nonradical (electrophilic) interaction of benzene and CF_3OF—giving an untractable mixture of products—is unaltered by the uv irradiation, whereas the radical reaction—leading to fluorobenzene—is accelerated. The decisive influence of the conditions is reflected by the result recorded in the pioneering work of Allison and Cady,[8] according to which the *gas-phase* reaction between CF_3OF and benzene gave—even under uv

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[1] W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 52–70 and 132–149.

[2] K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, 70, 3986 (1948); G. H. Cady, *Inorg. Syn.*, **8**, 165 (1966). CF_3OF is commercially available from PCR Inc., Gainesville, Fla. 32601.

[3] A 1000-W Hanovia mercury–xenon lamp (Catalog No. 9778-1) fitted into a quartz projector (Type LH 151-N of Schoeffel Instrument Co., Westwood, N. J.) was employed throughout this work. The luminous flux density provided by this source—parallel beam of ~5 cm diameter—is ~100–200 times higher than what is generally employed in photochemical experiments.

[4] From PCR Inc., ref 2.

[5] A special KEL-F reactor designed and built with the cooperation of Mr. R. Geiger, equipped with transparent KEL-F window [J. Kollonitsch, G. A. Doldouras, and V. F. Verdi, *J. Chem. Soc. B*, 1093 (1967)], was employed.

[6] 20% QF-1 on 80–100 Gas-Chrom Z.

[7] The identity of products was ascertained by glc–mass spectrometry (LKB 9000). Mass spectra were compared in every case with those of the authentic fluorine compounds.

[8] J. A. C. Allison and G. H. Cady, *J. Amer. Chem. Soc.*, **81**, 1089 (1959).