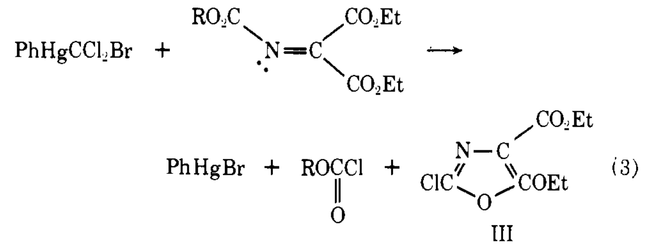
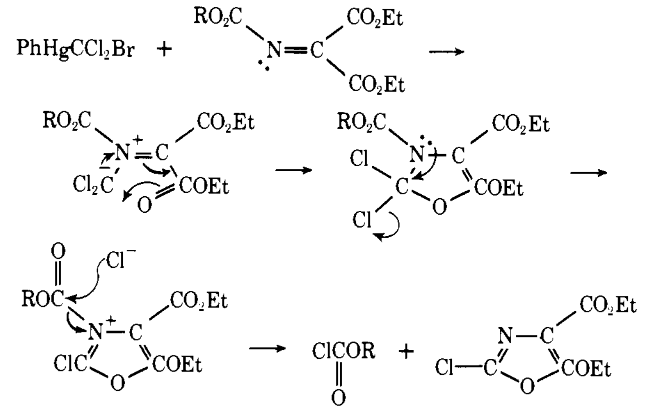
zene at 80° gave the same heterocyclic product (III, a liquid, $n^{25}\mathrm{D}$ 1.4833) in each case (eq 3) in 20–35% yield.



Spectral studies suggested that III was 2-chloro-4-carboethoxy-5-ethoxy-1,3-oxazole, as indicated. Its proton nmr spectrum showed signals due to two non-equivalent OEt groups and its ir spectrum indicated the presence of C=O, C=C, and C=N functions (bands at 1720, 1620, and 1535 cm^{-1}, respectively). A spectroscopic study of this reaction with R = Me after 4 days at room temperature clearly indicated the presence of an intermediate by its ir absorption at 1630 cm^{-1} ($\nu_{\mathrm{C=C}}$). Although the intermediate was not isolated, in view of the isolation of alkyl chloroformate and III as well as the spectral evidence, it is reasonable to explain this reaction also in terms of 1,4(N,O) addition of CCl_2 (Scheme II).

Scheme II



Such 1,4 addition does not appear to occur with $-C{=}CC{=}O$ systems. We had observed simple C=C addition of $PhHgCCl_2Br$ derived CCl_2 with methyl acrylate and mesityl oxide[3] and in the present work examined the reaction of $PhHgCCl_2Br$ with diethyl fumarate. In this case, only diethyl 3,3-dichlorocyclopropane-1,2-dicarboxylate was obtained.[4]

Since the presence of a terminal nitrogen atom seems to facilitate 1,4 addition of CX_2 to α,β-unsaturated systems, it seems reasonable to propose that the initial interaction between the substrate and CX_2 (or possibly with $PhHgCX_2Br$ rather than with free CX_2) occurs at the nitrogen atom and that this is followed by ring closure as indicated in Schemes I and II. This 1,4 addition of CX_2 to $-N{=}NC{=}O$ and $-N{=}CC{=}O$ systems should be capable of further generalization and may find application in the synthesis of heterocyclic systems containing halogen which are difficult to prepare by other routes.

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Dietmar Seyferth,* Houng-min Shih
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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[3] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[4] Formal 1,4 addition of CF_2 to a steroidal α,β-unsaturated ketone was reported by P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966).

Rotational Diffusion Anisotropy in Near Ellipsoidal Molecules

Sir:

While the symmetrical top formulation[1,2] of dipole–dipole spin relaxation has already received attention in carbon-13 studies,[3–7] Woessner's elegant theoretical treatment of an allipsoidal tumbler has not yet been utilized to interpret carbon-13 relaxation data. To be precise, this formulation requires that the D_{2h} symmetry group of an ellipsoid obtain and that the molecule possess three uniquely different carbon atoms with attached protons whose C–H vectors manifest linearly independent sets of directional cosines. These conditions allow diagonalization of the rotational diffusion tensor and provide sufficient data to specify the three diagonal components. Unfortunately, these conditions are so restrictive as to eliminate any extensive application of the theory, and, therefore, we have approximated ellipsoidal symmetry with molecules of slightly lower symmetry. Investigators should be aware that rotational diffusional tensors of asymmetric tops cannot in general be diagonalized and, therefore, the approximation of ellipsoidal symmetry, which is involved here, may at times be severe. In the hydrocarbon molecules considered, the approximation was felt to be reasonable, however, as no larger electric dipoles exist, heavy atoms are not present to shift greatly the center of mass from the effective epicenter of diffusional rotation, and each molecule is near ellipsoidal in shape.

Nuclear Overhauser enhancements (NOE) and relaxation time data were obtained by methods previously reported from this laboratory.[3–7] The T_1 and NOE values obtained for norbornane, cyclopentene, and *trans*-decalin are given in Table I along with the dipolar relaxation time, T_{1D}, which may be calculated from these two values. A sizable spin–rotation constant for the ethylenic carbon in cyclopentene and the relative small size of this molecule are expected to give a significant spin–rotation contribution, and it is felt that this best explains the reduced NOE value recorded for the ethylenic carbon.[8] Collins, Alger, and Grant[8] also observed similar features in the methylethylenes

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[1] D. E. Woessner, *J. Chem. Phys.*, 37, 647 (1962).

[2] D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyers, *ibid.*, **50**, 719 (1969).

[3] K. F. Kuhlman and D. M. Grant, *ibid.*, **55**, 2998 (1971).

[4] J. R. Lyerla, Jr., D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, **75**, 585 (1971).

[5] T. D. Alger, D. M. Grant, and J. R. Lyerla, Jr., *ibid.*, **75**, 2539 (1971).

[6] J. R. Lyerla, Jr., D. M. Grant, and C. H. Wang, *J. Chem. Phys.*, **55**, 4676 (1971).

[7] D. M. Grant, E. P. Black, K. A. Christensen, J. R. Lyerla, Jr., and R. J. Pugmire, 13th ENC, Asilomor, Calif., 1972.

[8] S. W. Collins, T. D. Alger, and D. M. Grant, to be submitted for publication.

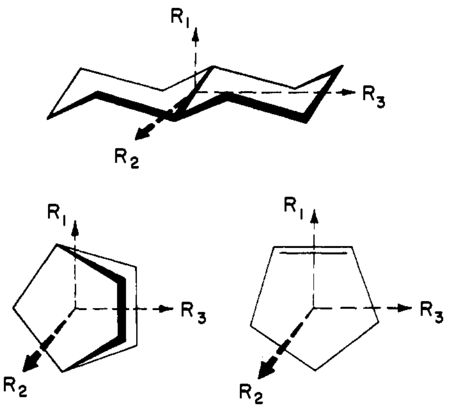

Figure 1. Axes in *trans*-decalin, norbornane, and cyclopentene.

Table I

Compound	Position	T_1	NOE	T_{1D}
Norbornane	1	27.6	3.0	27.6
	2	18.0	3.0	18.0
	7	18.0	3.0	18.0
Cyclopentene	1	29.7	2.0	59.4
	2	32.5	3.0	32.5
	3	33.8	3.0	33.8
trans-Decalin	1	6.8	3.0	6.8
	2	6.3	3.0	6.3
	9	10.0	3.0	10.0

where a significant spin-rotation effect on the nuclear relaxation was found.

The ellipsoidal top equations of Woessner[1] were solved numerically in the manner described[7] for symmetric tops. The directly attached protons were found to dominate the dipole-dipole relaxation rates but long range dipole-dipole interactions between geminal proton-carbon pairs were included in the calculation as they do make a minor contribution to the relaxation rates. These results along with the corresponding values for bicyclooctane and adamantane are presented in Table II for the axes defined in Figure 1. The ellipsoidal axes for the C_{2v} molecules, norbornane and cyclopentene, were selected as the C_2 axis and the two mutually perpendicular axes in the mirror planes. In the C_{2h} *trans*-decalin, the normal to the plane prescribed by alternant carbon atoms, the C_2 axis, and the axis mutually perpendicular to these first two were selected as the ellipsoidal axes for this molecule. It should be noted that two of the principle axes of the moment of inertia tensor deviates very slightly from those chosen here on the basis of shape.

Table II

Compound	R_1	R_2	R_3	I_1	I_2	I_3
	(units are 10^{10} rad/sec)			(units are amu Å^2)		
trans-Decalin	11 ± 3	2.5 ± 1	6 ± 2	645	488	206
Cyclopentene	21 ± 5	17 ± 4	29 ± 7	70	132	178
Adamantane[a]	8 ± 2	8 ± 2	8 ± 2	293	293	293
Bicyclooctane[a]	17 ± 4	9 ± 2	9 ± 2	208	205	205
Norbornane	17 ± 4	10 ± 3	7 ± 2	149	132	178

[a] Taken from ref 7.

It is to be observed in Table II that *trans*-decalin exhibits extensive anisotropy of rotational motion as manifest in the large variation in the components of the rotational diffusion tensor. This molecule does not possess an electric dipole because of its inversion symmetry element, and the rotational diffusion constants are in a range where the reorientation process is sufficiently slow to eliminate significant inertial considerations. Thus, one may attribute the anisotropy primarily to the molecular shape. There is no correlation found between the three rotational constants and the moments of inertia as would be anticipated if an inertial process were dominant. On the other hand, if one estimates crudely the ellipticity about each axis by taking the ratio of the maximum separation of atoms along the two axes perpendicular to the rotation axis under consideration, the following values were obtained: $\epsilon_1 = 1.37$, $\epsilon_2 = 2.53$, $\epsilon_3 = 1.84$. These three numbers correlate in an inverse manner very well with the rotational constants (*i.e.*, the greater the ellipticity the slower the motion). Thus, shape and the associated intermolecular interactions override completely the inertial effects which appear to be important in smaller molecules where reorientation is not dominated solely by diffusional features.

The similarity between norbornane and bicyclooctane[7] account for the two almost identical R_1 values and for the general similarity between R_2 in bicyclooctane and R_2 and R_3 in norbornane. The anisotropy in norbornane is less than that found for *trans*-decalin, but the deviation from isotropic behavior is clearly noted and beyond experimental error. However, the difference between R_2 and R_3 is barely on the edge of the experimental error limits and may be attributed, if real, to subtle differences in the shape factors about these two axes and/or to the slight differences in the moments of inertia about these two axes. It is noted that $I_3 > I_2$ which is compatible with the relative magnitudes of the diffusion constants $R_3 < R_2$.

In cyclopentene the anisotropy only barely exceeds the error limits. As the relaxation data approach isotropic behavior the equations of Woessner become poorly conditioned and even small experimental errors in the T_1 data lead to fairly large error limits in the R's. Even so, R_2 is demonstrably less than R_3 in cyclopentene, a somewhat surprising fact as the R_2 axis has associated with it the greatest cylindrical symmetry. In this instance, however, I_2 is almost twice the value of either of the other two moments of inertia, and the fairly rapid motion may be partially inertially controlled. Cooperative evidence for this position is found in the rather high rotation rates noted for this compound and in the presumable importance of spin-rotation relaxation at the ethylenic carbon. When spin-rotation competes with the dipole mechanism, the diffusion process begins to break down and inertial effects are manifest.[6,9] It is possible, however, that the assumed planar structure and neglect of a slow internal puckering vibration may offer another explanation for the unexpected rotational diffusion constants. Treatment of four important motional degrees of freedom with three relaxation times is, of course, not possible. The higher vibrational frequencies for the other fused ring systems studied in this work is not expected to introduce serious errors in these cases.

(9) C. H. Wang, D. M. Grant, and J. R. Lyerla, Jr., *J. Chem. Phys.*, **55**, 4674 (1971).

Acknowledgment. This study was supported by the National Institutes of Health and Grants No. GM 08521 and RR-574-02.

David M. Grant,* Ronald J. Pugmire
Edward P. Black, Kenner A. Christensen
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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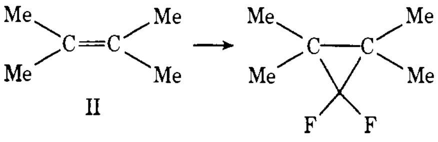
Bromodifluoromethylphosphonium Salts. A Convenient Source of Difluorocarbene[1]

Sir:

In recent years considerable attention has been focused on the generation of difluorocarbene for the synthesis of *gem*-difluorocyclopropanes and other difluoromethylene derivatives. A variety of difluorocarbene precursors have been examined,[2] but these precursors are either inefficient or difficult to obtain in large quantities. For example, difluorodiazirine,[3] Me_3SnCF_3,[4] and $PhHgCF_3$[5] require several steps to prepare and involve expensive and/or toxic materials. The most common precursor, CF_2ClCO_2Na, is hygroscopic and requires large excesses to ensure good yields of products.[6] This communication describes a simple, facile, and convenient one-step method of difluorocarbene generation from readily available commercial reagents.

When bromodifluoromethylphosphonium bromide (I)[7] was treated with sodium methoxide in the presence of tetramethylethylene (II), a 21% yield of the cyclopropane adduct (III) was obtained. Similarly, other olefins gave low yields of cyclopropanes under similar conditions. To the best of our knowledge, this reaction represents the first known example of carbene generation from a phosphonium salt. Presumably, attack by methoxide on the phosphonium salt to displace $[CF_2Br^-]$ or $:CF_2$ had occurred. The low yield of III is presumably due to competition between methoxide and II for the carbene.[8]

$[Ph_3\overset{+}{P}CF_2Br]Br^- + NaOMe +$



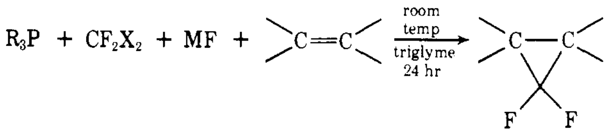
II

III

To circumvent the competition of the nucleophile for the carbene, a base was required which would form a strong bond to phosphorus and generate the carbene but would not compete for the carbene. The strength of the P–F bond[9] (117 kcal/mol) compared to the P–O bond[6] (120 kcal/mol) suggested that fluoride ion[10] would fulfill these requirements. Indeed, substitution of potassium fluoride or cesium fluoride in these reactions provided a smooth high-yield conversion of the phosphonium salt to the cyclopropane adduct.[11]

$$I + CsF + II \longrightarrow III + Ph_3PFBr + CsBr$$

Subsequent investigation of these reactions has shown that prior preparation of I is unnecessary and that the phosphonium salt could be prepared "*in situ*" from the appropriate phosphine and difluorodihalomethanes in the presence of the fluoride salt and olefin. A number of representative olefins were examined to de-



R = Ph or Me₂N; X = Br, Cl; M = K, Cs

termine the utility of this "*in situ*" scheme and are tabulated in Table I. All of the cyclopropane adducts were completely identified by comparison with authentic samples or with reported infrared and/or ^{19}F nmr spectra.

Table I. Formation of 1,1-Difluorocyclopropanes

Olefin	R	M	*n*	% cyclopropane[a]
Tetramethylethylene	Ph	Cs	1	79
Tetramethylethylene	Ph	K	1	74
Tetramethylethylene	Me₂N	Cs	1	65
Trimethylethylene	Ph	Cs	1	75
Isobutylene	Ph	Cs	4	66
trans-2-Butene	Me₂N	Cs	4	12[b]
cis-2-Butene	Ph	Cs	4	6[b]
Cyclohexene	Me₂N	K	5	21[c]

[a] Glpc yield base on phosphine. [b] Cyclopropane adduct is the stereospecific product. [c] Reaction temperature is 85°.

As Table I indicates, all olefins except 1,2-disubstituted olefins gave excellent yields, and stereospecific addition occurred with *cis*- and *trans*-2-butenes. Similar stereospecificity and decreased reactivity of 1,2-substituted olefins were also observed by Mitsch in the reactions of difluorodiazirine. A competition reaction between isobutylene and *cis*-2-butene gave a reactivity ratio of 13.0. For a similar competition experiment with CF_2N_2, Mitsch[12] observed a reactivity ratio of 12.8. Consequently, the discriminating ability of our carbene species appears to be similar to that of Mitsch.

The following procedure is presented to provide operational detail for the generation of difluorocarbene.

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(1) (a) Abstracted in part from Ph.D. Thesis of D. G. N., University of Iowa, 1972. (b) Presented in part at the Seventh International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 1973.

(2) *Cf.* W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 237–271,

(3) R. A. Mitsch, *J. Heterocycl. Chem.*, **1**, 59 (1964).

(4) (a) D. Seyferth, J. Y. -P. Mui, M. E. Gordon, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **87**, 681 (1965); (b) D. Seyferth, H. Dentouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, **32**, 2980 (1967).

(5) D. Seyferth, S. P. Hopper, and K. V. Darragh, *J. Amer. Chem. Soc.*, **91**, 6536 (1969); D. Seyferth and S. P. Hopper, *J. Org. Chem.*, **37**, 4070 (1972).

(6) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, P. W. Landis, and A. D. Cross, *J. Amer. Chem. Soc.*, **85**, 1851 (1963); C. Beard, N. H. Dyson, and J. H. Fried, *Tetrahedron Lett.*, 3281 (1966); C. Beard, I. T. Harrison, L. Kirkham, and J. H. Fried, *ibid.*, 3287 (1966).

(7) Complete characterization and other chemical properties of these phosphonium salts have been made and will be reported in detail in the complete paper.

(8) Unpublished results of H. S. Kesling from this laboratory.

(9) T. L. Cottrel, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

(10) In addition to forming a strong P–F bond, fluoride would also be expected to react reversibly with difluorocarbene.

(11) Other halide ion sources, such as NaCl or NaI, gave only trace amounts of cyclopropane products.

(12) R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 (1965).