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[21] Alfred P. Sloan Foundation Research Fellow.
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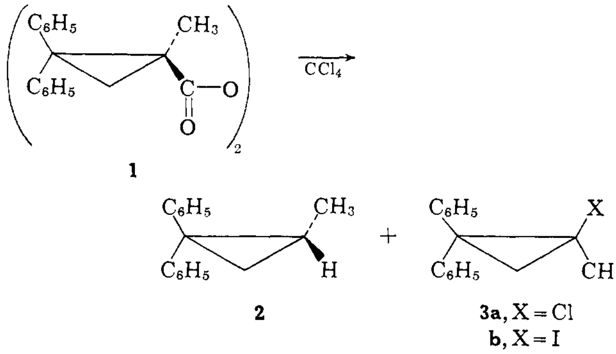
## Cyclopropanes. XXII. Cage Disproportionation of Optically Active 1-Methyl-2,2-diphenylcyclopropyl Radical[1]

*Sir:*

In our previous studies[2] on the decomposition of the diacyl peroxide (**1**) of (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, we found that, in hydrogen atom donating solvents, the 1-methyl-2,2-diphenylcyclopropane (**2**) formed was racemic. This was interpreted to mean that the 1-methyl-2,2-diphenylcyclopropyl radical was incapable of maintaining its configuration, a conclusion which had also been reached for radicals generated at a trigonally hybridized carbon[3] as well as for those produced at a tetrahedrally hybridized carbon.[4] Although the latter radicals have been shown to be planar, the vinyl and cyclopropyl radicals are believed to be bent and to possess inversion frequencies of $10^8$–$10^{10}$ sec$^{-1}$.[5] In order for the vinyl or cyclopropyl radical to be able to maintain its configuration to any appreciable extent, it must react with another substrate at a rate equal to or greater than this inversion frequency. The most likely place to find such a rapid reaction would be within a solvent cage. At this time, we wish to report on the stereochemistry of what we believe to be a reaction occurring in a solvent cage.



**3a**, X = Cl
**b**, X = I

The diacyl peroxide **1** of (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid when decomposed in hydrogen atom donating solvents (*i.e.*, toluene, ether, THF, etc.) leads to the formation, *inter alia*, of 1-methyl-2,2-diphenylcyclopropane (**2**) which is racemic. When the decomposition is carried out in pure (vpc) carbon tetrachloride one obtains, besides the expected essentially racemic 1-chloro-1-methyl-2,2-diphenylcyclopropane (**3a**), a 2% yield of **2**. We feel that **2** results from a disproportionation of the 1-methyl-2,2-diphenylcyclopropyl radical within the solvent cage.

Our evidence for the above supposition is based not only on the formation of **2** in a completely halogenated solvent such as carbon tetrachloride but also on the fact that **2** is also formed in a 3% yield when a good radical trap such as iodine[6] is added. Under these conditions no **3a** is formed, only **3b**. Another criterion for cage product is that the amount of product formed is independent of concentration of the initial substrate. As can be seen from Table I the yield of **2** was the same whether one started with a 0.02 *M* solution of **1** or a 0.01 *M* solution. Finally, the best evidence is the stereochemical result. Decomposition of (−)-(*S*)-**1**-yielded (−)-(*R*)-**2** with an optical purity of 37% and with over-all retention of configuration.[7] Starting with the enantiomer, (+)-(*R*)-**1**, the hydrocarbon (+)-(*S*)-**1** was obtained with an optical purity of 31%.

**Table I.** Decomposition of (+)-, (−)-, and (±)-Diacyl Peroxides of 1-Methyl-2,2-diphenylcyclopropanecarboxylic Acid in $CCl_4$ at 67°

| Run | **1** [α]$^{25}$ Hg, deg | Concn, *M* | % yield (**2**) | **2** [α]$^{25}$ Hg, deg |
|---|---|---|---|---|
| 1 | (±) | 0.02 | 2.13 ± 0.07 | ... |
| 2 | (±) | 0.01 | 2.12 ± 0.02 | ... |
| 3 | −30.0[a] | 0.015 | ... | −40.0[c] |
| 4 | +40.0[b] | 0.016 | ... | +46.2[d] |

[a] Optical purity of **1** 72%. [b] Optical purity of **1** 98%. [c] Optical purity of **2** 37.4%. [d] Optical purity of **2** 31.4%.

To our knowledge the only other example of retention of configuration in a cage reaction is the example provided by Bartlett,[8] who demonstrated that the photolyses of *meso*- and (±)-azobis(3-methyl-2-phenyl-2-butane) in frozen solvents (−196°) yield pure *meso*- and (±)-2,3,4,5-tetramethyl-3,4-diphenylhexane, respectively. At temperatures greater than 0° the stereospecificity is lost. This contrasts the stereochemical behavior of a tetrahedrally hybridized radical[9] with the bent cyclopropyl radical which was able to maintain its configuration to a large extent in a cage reaction at 67°.

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[1] This investigation was supported by Public Service Research Grant No. CA 04065-09 from the National Cancer Institute, and in part by the National Science Foundation.
[2] H. M. Walborsky, C. Chen, and J. L. Webb, *Tetrahedron Letters*, 3551 (1964).
[3] J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966); L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966).
[4] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.
[5] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
[6] G. S. Hammond, *J. Am. Chem. Soc.*, **72**, 3737 (1950).
[7] H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).
[8] P. D. Bartlett, *Chem. Eng. News*, **42**, 106 (Feb 2, 1966).
[9] E. I. Heibe and R. M. Dessau, *J. Am. Chem. Soc.*, **89**, 2238 (1967), have reported trapping an asymmetric radical before it completely racemized. The reaction involved was an intramolecular cyclization reaction. The optical purities of the diastereomeric products were not given.

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## Structure and Infrared Spectrum of the Solvated Proton in Dimethyl Sulfoxide

*Sir:*

In the course of other work we have recently found that the equilibrium constant for reaction 1[1] in di-

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[1] I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962).

$$H_3O^+(solv) \rightleftharpoons H^+(solv) + H_2O(solv) \qquad (1)$$

methyl sulfoxide (DMSO) is almost unaffected by replacing all the exchangeable hydrogens with deuterium. $K_H/K_D$ is 1.2. Since this requires an unusually low zero point energy for $H^+$(solv) we examined the infrared spectra of methanesulfonic acid solutions in DMSO. These solutions show no conventional OH bands. Spectra of the deuterated solutions are analogous, but less intense. Typical spectra are shown in Figure 1. The sharp bands in the region of 1200 $cm^{-1}$ seem to be those of the methanesulfonate anion.[2] Further evidence for the more or less complete ionization of the methanesulfonic acid is the disappearance of the very strong bands around 1150 and 1330 $cm^{-1}$. The only spectrum to be associated with the hydroxylic protons is a *very* broad, very intense band extending from somewhere in the neighborhood of 2000 $cm^{-1}$ to below the cut-off point of the Irtran windows at 800 $cm^{-1}$. Similar spectra have been reported by Hadži[3a,b] and by Whateley.[3c]

The proton is probably bound to an oxygen of one DMSO molecule and strongly hydrogen bonded to another.[3] This, alone, however, would not seem to explain the lack of a band structure in the OH spectrum.[4] An attractive supplement is the postulate that the proton jumps between two DMSO molecules with a frequency not much less than $10^{14}$ $sec^{-1}$.[5] It also helps to explain the position of the absorption. When the hydrogen moves from one to the other of its two potential energy minima the O–H valence vibration and the OH···O hydrogen-bond vibration, $\nu_{OH}$ and $\nu_{OH\cdots O}$,[4] are interchanged, and this process seems to be fast enough to partially merge these bands. In nmr terminology, the system is somewhere near the "coalescence point" of the two bands.[6] Broadness may also result from the variety of solvent environments in which the $H(DMSO)_2^+$ ion may find itself and from the variety of interactions between the cation and the methanesulfonic ion. These factors, however, would also act on the spectrum of the methanesulfonate ion, and the latter is reasonably normal. The spectrum of $H^+$ in DMSO and the foregoing explanation of it are fully consistent with the low zero-point energy.

The spectra obtained from ordinary and deuterated solutions suggest that the isotope effect on the rate of this process may be small. This could be explained as

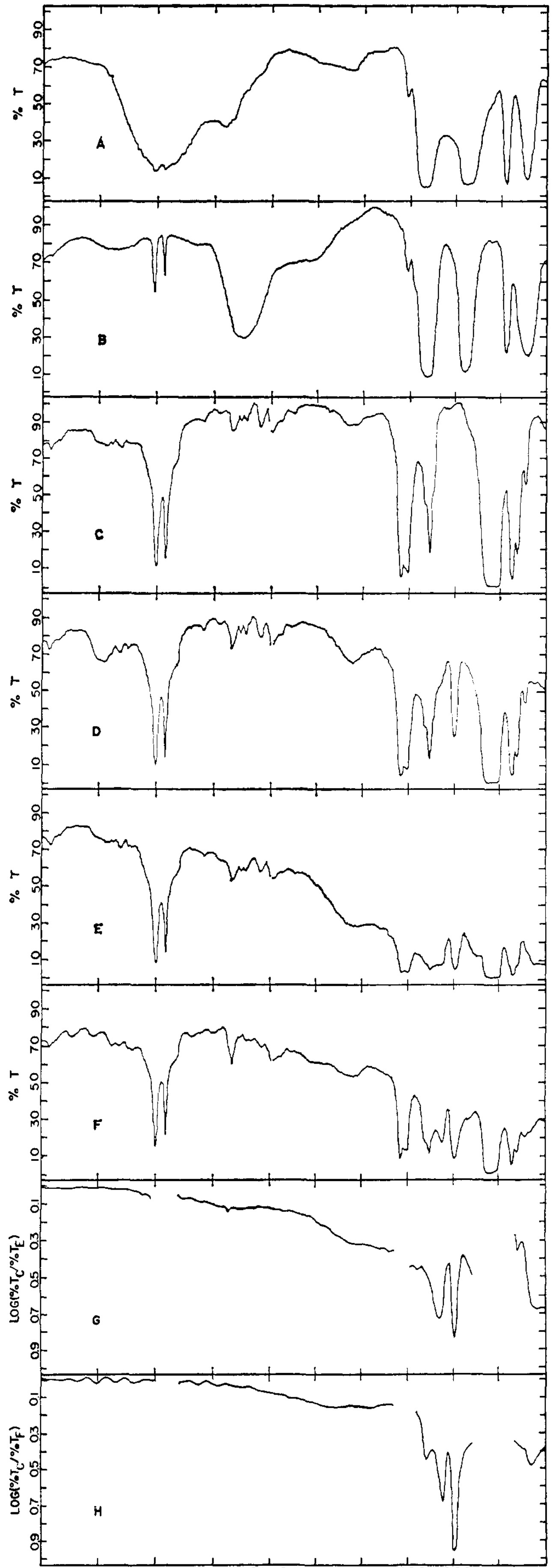

Figure 1. Infrared spectra: A is neat methanesulfonic acid in a capillary film; B is the same, deuterated on oxygen; C is DMSO in a 30-μm cell; D is 1% methanesulfonic acid in DMSO, 30-μm cell; E is 10% methanesulfonic acid in DMSO, 30-μm cell; F is 10% O-deuteriomethanesulfonic acid in DMSO, 19-μm cell; G is the difference between spectra E and C, corrected to a 19-μm path length; H is the difference between spectra F and C. All spectra were taken on a Perkin-Elmer 521 spectrophotometer using Irtran cell windows. The blank spaces in the difference spectra are regions in which the absorption of energy by the solvent makes it impossible to evaluate the solute spectrum.

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(2) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(3) (a) D. Hadži, *ibid.*, 5128 (1962); (b) D. Hadži and N. Kobilarov, *ibid.*, *Sect. A*, 439 (1966); (c) T. L. Whateley, *Nature*, **212**, 279 (1966).

(4) N. Sheppard, "Hydrogen Bonding," D. Hadži, Ed., Pergamon Press, New York, N. Y., 1959, p 85.

(5) M. M. Kreevoy and C. A. Mead, *J. Am. Chem. Soc.*, **84**, 4596 (1962).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

it is so fast as to be very close to the "high temperature limit," approximately $\sqrt{2}$.[7]

These ideas are similar to those used by Ackermann[8] to interpret the spectra of concentrated aqueous acid and base. However, the spectra are much less ambiguous, because DMSO, unlike water, does not seriously interfere with the observation of the spectrum due to the solvated proton. DMSO solutions also do not have the possibility of correlated proton motion, which may be important in the spectra of aqueous acids.

(7) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960.

(8) T. Ackermann, *Z. Physik. Chem.* (Frankfurt), **27**, 253 (1961).

(9) National Science Foundation Postdoctoral Fellow, University of Minnesota, 1966–1967.

(10) The support of the National Science Foundation through Grant GP-5088 is gratefully acknowledged.

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## New Gaseous Molecules of the Pnictides

*Sir:*

It is well known from spectroscopic and vaporization studies that the homonuclear gaseous molecules of the group Va elements (N, P, As, Sb, Bi) are diatomic and tetratomic species.[1] The dissociation energies of these molecules have been reasonably well established, and on the basis of these values one can speculate with confidence that a very large number of heteronuclear molecules formed from intercombinations of the atoms of these elements should be stable species. Until now, only a few of these possible molecules, principally the diatomic species and the tetratomic species of As–P, have been observed and studied.[2] We wish to report here experimental confirmation of the existence of additional diatomic and tetratomic molecules of these atoms.

We have investigated the gaseous molecules formed on vaporization of liquid solutions of Bi–Sb, Bi–As, and Bi–Sb–As and mixtures of the solid elements of Sb–As by mass spectrometry in the temperature range 300–750°. The samples were contained in a graphite Knudsen cell in a Bendix Time-of-Flight mass spectrometer. At the highest temperatures, the pressures of the major species were of the order of $10^{-5}$ atm. In general, the samples studied were not congruently vaporizing phases, so that the composition of the vapor changed slightly during an experiment. For this and other reasons, the molecules were not formed under complete equilibrium conditions.

Ions were formed by impact with 20-v electrons. Appearance potential measurements were carried out to differentiate parent and fragment ion species. Positive identification of the Sb-containing ion species was facilitated by comparing the observed relative peak intensities with those computed from the normal abundance of $Sb^{121}$ and $Sb^{123}$. In all cases, however, there was no ambiguity in the assignment of the spectra because of the absence of overlapping peaks. In each of the four systems studied, all ion species were observed in *all* possible combinations of one, two, three, and four atoms, giving a total of 14 species for each of the binary systems and 34 species for the ternary system.

No ions corresponding to species containing more than four atoms were observed. Thus, the tetratomic ion species are parent ions, and consequently we may conclude that the following neutral molecules are stable species: $Bi_3Sb$, $Bi_3As$, $Bi_2Sb_2$, $Bi_2As_2$, $Bi_2SbAs$, $BiSb_2As$, $BiSbAs_2$, $BiSb_3$, $BiAs_3$, $Sb_3As$, $Sb_2As_2$, $SbAs_3$. In addition to these, the well-known homonuclear molecules $Bi_4$, $Sb_4$, and $As_4$ were observed. The appearance potentials of these molecules were comparable to the first ionization potentials of the free atoms and within their precision (±0.3 ev) varied in a reasonably systematic manner depending on the number and kind of each constituent between the limits of the atomic potentials.

The diatomic ion species were found to consist of both parent and fragment ions. The appearance potentials of the diatomic species, like those of the tetratomic ions, also had values nearly identical with the ionization potentials of the isolated atoms with similar systematic trends. Their ionization efficiency curves showed slight breaks several volts above the appearance potentials, suggesting both fragmentation contributions to the ion current and enhancement due to excitation processes. In general, the tetratomic species were in larger concentrations in the vapor, so that their electron-impact fragmentation undoubtedly contributed to the ion current enhancement at increased electron energies. On the basis of their appearance potentials, we can conclude that the following neutral diatomic molecules, in addition to the known homonuclear molecules, are stable species: BiSb, BiAs, SbAs. The first of these has been observed before in spectroscopic studies.[3]

The triatomic ions composed of all combinations of Bi, Sb, and As had appearance potentials several volts above those of the atomic, diatomic, and tetratomic ions. This is reasonable evidence that they were entirely fragments of the tetratomic molecules which were in larger concentrations. Evidence for this and other conclusions cited above are illustrated by the data given in Table I for the Bi–Sb system. The data

**Table I.** Relative Intensities and Appearance Potentials of Ions Observed in the Vapor from a Liquid Solution of 58 Mole % Bi and 42 Mole % Sb at 625°

| Ion | Intensity | Appearance potential, ev |
|---|---|---|
| $Sb_4^+$ | 100 | 8.3 |
| $Sb^+$ | 45 | 9.3[a] (IP = 8.6) |
| $Sb_2^+$ | 43 | 8.7 |
| $Sb_3^+$ | 25 | 10.4[a] |
| $BiSb_3^+$ | 24 | 7.8 |
| $Bi^+$ | 17 | 7.3[b] (IP = 7.3) |
| $BiSb^+$ | 6.7 | 8.0 |
| $Bi_2^+$ | 4.2 | 7.5 |
| $Bi_2Sb_2^+$ | 3.6 | 7.7 |
| $BiSb_2^+$ | 2.5 | 10.5[a] |
| $Bi_2Sb^+$ | 0.4 | 10.6[a] |
| $Bi_3Sb^+$ | 0.3 | 7.2 |
| $Bi_4^+$ | 0.02 | 7.6 |
| $Bi_3^+$ | ~0.01 | Insufficient intensity |

[a] Fragment ions. [b] Standard for calibrating voltage scale.

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(1) F. J. Kohl, O. M. Uy, and K. D. Carlson, *J. Chem. Phys.*, in press.

(2) H. B. Gutbier, *Z. Naturforsch.*, **16a**, 268 (1961); K. D. Carlson, F. J. Kohl, and O. M. Uy, "Inorganic Applications of Mass Spectrometry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

(3) G. Herzberg, "Spectra of Diatomic Molecules," D. C. Van Nostrand Co., Princeton, N. J., 1950, p 566.