CPA, it is of interest to compare the closely related structure of KCPA to that expected for HCPA. The structural differences will be in the configuration at C-4: (1) in KCPA this is planar, whereas in HCPA C-4 would have a tetrahedral configuration, and the six-membered ring would likely have a chair conformation; (2) both KCPA and HCPA have a potential electron-donor oxygen atom on C-4; how closely their positions in space match will depend largely on whether the hydroxyl in HCPA is in the equatorial or axial position; (3) HCPA has the potential of hydrogen-bond formation through its hydroxyl hydrogen. In all other respects the two molecules would be expected to be closely similar in structure.[21]

**Acknowledgments.** We thank Dr. Robert F. Struck for supplying the crystals of 4-ketocyclophosphamide. This work was supported in part by U. S. Public Health Service Research Grant No. 1 R01 NS 09839-02 BBCA from the National Institute of Neurological Diseases and Stroke.

[21] Note Added in Proof. We have recently become aware of a paper on the crystal structure of cyclophosphamide itself: S. Garcia-Blanco and A. Perales, *Acta Crystallogr., Sect. B*, **28**, 2647 (1972). The bond lengths and angles in cyclophosphamide are all very similar to the corresponding ones in KCPA with the exception of the P–N ring bond which is significantly longer in KCPA (1.668 *vs.* 1.625 Å), undoubtedly owing to withdrawal of electrons from this bond by the neighboring carbonyl group in KCPA. The ring angles at N-3 and C-5 are also larger in KCPA, reflecting the difference in configuration at C-4, to which they are bonded.

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# *Communications to the Editor*

## Relaxation of Excited State Carbene to Ground State. An Internal Heavy Atom Effect

*Sir:*

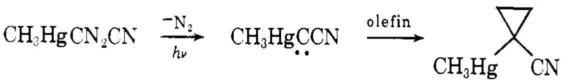
The effect of internal (directly affixed)[1] and external (solvent)[2] heavy atoms on the singlet–triplet interconversions of organic molecules has been the object of much theoretical and spectroscopic work.[3] Experimentally, the effect can be observed as an increase in the rates of both radiative and nonradiative "spin forbidden" electronic transitions as the atomic number of the perturbing atom is increased. The effect has been correlated with theory in terms of spin-orbital coupling.[4,5]

The limitation which this effect places on the kinetic criterion for spin state assignment to carbenes was recognized early.[6] Now the heavy atom effect is employed to accelerate relaxation of carbenes to the ground state to help define that state. The introduction of an α-methylmercuric substituent on the carbene is effective.

The stable esr spectrum observed at −196° from photolyzed diazoacetonitrile has been interpreted as the signal from ground-state triplet cyanomethylene.[7]

Photolysis of diazoacetonitrile in *cis*-2-butene produces 1-cyano-2,3-dimethylcyclopropanes, 94% cis dimethyls, and only 6% trans. The yield of trans product (nonstereospecific addition) is decreased by addition of a radical scavenger such as 1,1-diphenylethylene, or increased by dilution of the reactants with methylene chloride or butane; it is increased to 62% by carrying out a thermal reaction in the gas phase. Thus, photolysis is characterized by decomposition of the diazo compound to the singlet carbene which then reacts stereospecifically with *cis*-2-butene as solvent, somewhat faster than intersystem crossing to the triplet state. Dilution favors the unimolecular intersystem crossing to triplet ground state over the bimolecular trapping.

Photolysis (>335 nm) of α-methylmercuridiazoacetonitrile[8] in olefins results in the formation of 1-methylmercuri-1-cyanocyclopropanes in yields of 65–90%. With *cis*-2-butene as the trapping agent either



$\mathrm{CH_3HgCN_2CN} \xrightarrow[h\nu]{-\mathrm{N_2}} \mathrm{CH_3Hg\ddot{C}CN} \xrightarrow{\text{olefin}}$

direct photolysis or triplet benzophenone sensitized decomposition results in formation of *trans*- and *cis*-dimethylcyclopropanes in a 1.0 ratio (total yield of mercuricyclopropanes is 65–80%). 1,3-Butadiene is much more reactive than 2-butene in trapping the methylmercuricyanomethylene, a 1:1 mixture of olefins yielding only 4% product by reaction with 2-butene. In this latter experiment, the ratio of *trans*- to *cis*-dimethylcyclopropanes is 0.05. These results are rationalized exactly as with cyanomethylene, except that the presence of the α-mercuric group greatly accelerates the intersystem crossing to the triplet ground state.

The ready syntheses of α-mercuridiazo compounds[8] make it possible to apply this method to structures with a variety of other substituents on the diazo compound. For example, an esr signal has not been detected for any of the photodecomposition products of diazoacetic esters. Photo- or thermally initiated additions of the resulting carbalkoxycarbenes are highly stereospecific. On the other hand, triplet benzophenone sensitized decompositions result in nonstereospecific additions.[9] Thus, there is ambiguity regarding the ground state of this carbene. Photodecomposition of α-methylmercuridiazoacetate esters produces the α-methylmercuricarbene which adds stereospecifically to the 2-butenes. Thus, even with an increase of the rate of intersystem crossing the singlet state is the sole reactant. This ob-

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[1] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

[2] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

[3] S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapters 5–8.

[4] M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

[5] G. W. Robinson, *J. Chem. Phys.*, **46**, 572 (1967).

[6] R. C. Woodworth and P. S. Skell, *J. Amer. Chem. Soc.*, **78**, 4496 (1956); **81**, 3383 (1959).

[7] R. J. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **41**, 1156 (1964).

[8] S. J. Valenty and P. S. Skell, submitted for publication to *J. Org. Chem.*

[9] See also T. DoMinh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970), footnote 3.

servation strengthens the assumption that the ground state for a carbalkoxycarbene is a singlet. With analogous lines of evidence ground-state acylcarbenes are also assigned singlet states.

It is proposed that this internal heavy atom effect is a useful kinetic probe for determining the spin multiplicity of the ground states of carbenes. Hitherto, the presence of an esr signal was evidence for a ground-state triplet, but the absence of such a signal could not be accepted as evidence for a ground-state singlet since it had not been possible, in most instances, to demonstrate the presence of a stable carbene.

It now seems a safe conclusion that the failure to observe nonstereospecificity in the addition of $CBr_2$,[10] $CI_2$,[11] and $CHI$[12] to olefins indicates a singlet ground state for these carbenes.

**Acknowledgments.** The financial support of the Air Force Office of Scientific Research (Grant No. 1983) is gratefully acknowledged. S. J. Valenty wishes to thank the National Institutes of Health and the Stauffer Chemical Co. for personal financial support during this work.

(10) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).

(11) J. P. Oliver and U. V. Rao, *J. Org. Chem.*, **31**, 2696 (1966).

(12) N. C. Yang and T. A. Marolewski, *J. Amer. Chem. Soc.*, **90**, 5644 (1968).

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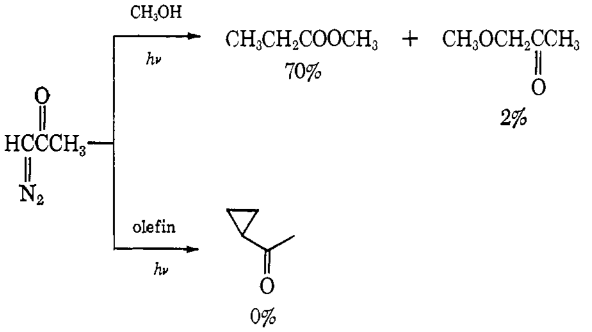
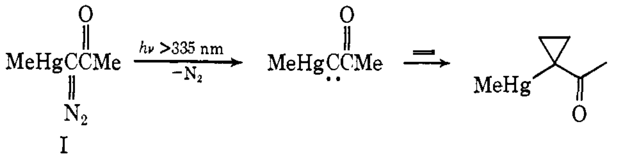
## α-Mercuricarbenes. Syntheses of α-Mercuricyclopropanes. Elimination of Wolff Rearrangement in Acylcarbenes

*Sir:*

Direct photolysis of diazoacetone leads to Wolff rearrangement.[1] Even photolysis of diazoacetone in methanol yields methyl propionate as the main product with only a small amount of methoxyacetone.[2] Similarly, no cyclopropanes have been reported to form when diazoacetone is photolyzed in olefinic solutions.[3,4] On the other hand, copper-bronze catalyzed decompositions in the presence of olefins produce cyclopropanes in good yields; the additions are stereospecific.[3]



In contrast to diazoacetone, we wish to report that the direct photolysis of methylmercuridiazoacetone (I)



I

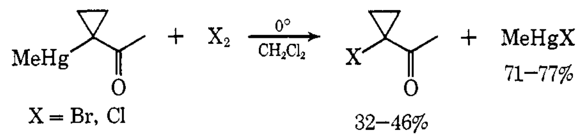
in olefin leads to the formation of 1-methylmercuri-1-acetylcyclopropanes in 70–90% yields *via* an α-mercuricarbene.[5] Typical yield data for several olefins are reported in Table I. In a representative experiment, methylmercuridiazoacetone (5.00 mmol, 1.49 g) was dissolved in refluxing 2-methylpropene (*ca.* 450 ml) and irradiated by a 1000-W A-H6 lamp through a soft-glass filter (>335 nm) until nitrogen gas evolution ceased (98% yield, 30 min). Nuclear magnetic resonance analysis of the photolysis residue remaining after olefin evaporation and elemental mercury filtration (4.3% yield) shows only the discrete proton absorptions assigned to 1-methylmercuri-1-acetyl-2,2-dimethylcyclopropane.[6] Quantitative nmr analysis indicates a 91% yield of the methylmercuricyclopropane was obtained with little, if any, of the Wolff rearrangement product (<4%) being formed. No carbene carbon–hydrogen bond insertion product was detected by inspection of the olefinic proton absorption region of the nmr spectrum. The infrared spectrum of the residue showed that the position of the carbonyl stretch absorption was moved 0.12 μ to longer wavelength (6.03 μ) from that observed in the mercury-free cyclopropane.[7]

**Table I.** Photolysis of Methylmercuridiazoacetone in Olefin

| Olefin | % Yield of mercuricyclopropane[a] | Major[b]/ minor |
|---|---|---|
| 2-Methylpropene | 91 | |
| *trans*-2-Butene | 72 | |
| *cis*-2-Butene | 78 | 8.0 |
| 1-Butene | 76 | 4.0 |
| 1,3-Butadiene | 45 | 5.1 |

[a] Yields of 1-methylmercuri-1-acetylcyclopropanes obtained by quantitative nmr; nitrogen yields = 90+%; mercury yields = 2–6%. [b] Ratio of isomeric cyclopropanes obtained from comparison of the areas of the methylmercury singlets in the nmr.

The carbon–mercury bond can be cleaved by electrophilic reagents. In a useful synthetic reaction, halogenation of the crude photolysis product forms 1-halogeno-1-acetylcyclopropanes in 32–46% yields (based on I). Attempts to brominate methylcyclopropyl ketone



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(1) W. Kirmes, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 119.

(2) With L. S. Wood, Pennsylvania State University.

(3) R. M. Etter, Ph.D. Thesis, Pennsylvania State University, 1959.

(4) M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(5) I was prepared from methylmercuric ethoxide and diazoacetone in 66–79% yield as a pale yellow solid from ether, mp 94.5–96.0° dec. The preparation and characterization are fully detailed in a paper submitted for publication to *J. Org. Chem.*

(6) 1-Methylmercuri-1-acetyl-2,2-dimethylcyclopropane: nmr (100 MHz, $CDCl_3$) 0.49 (s, with symmetrically placed $Hg^{199}$–$H^1$ doublet, $J = 121$ Hz, 3 H, $CH_3Hg$), 0.97 1.31 (AX, $J = 4$ Hz, 2 H, ring H), 1.01 (s, 3 H, $CH_3$), 1.23 (s, 3 H, $CH_3$), 2.12 (s, with symmetrically placed $Hg^{199}$–$H^1$ doublet, $J = 7$ Hz, 3 H, $C(=O)CH_3$).

(7) The mercury-free compound, 1-acetyl-2,2-dimethylcyclopropane, was prepared from the copper salt catalyzed decomposition of diazoacetone in 2-methylpropene.