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.

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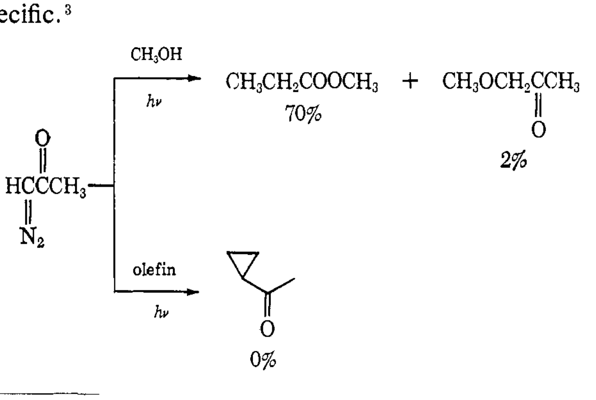
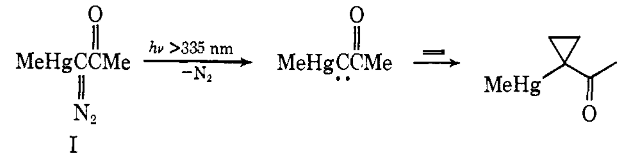
α-Mercuricarbenes. Syntheses of α-Mercuricyclopropanes. Elimination of Wolff Rearrangement in Acylcarbenes

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

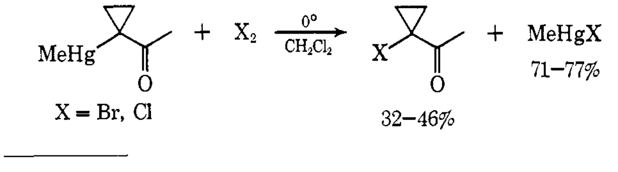
in olefin leads to the formation of 1-methylmercuri-1-acetylcyclopropanes in 70–90% yields *via* an α-mercuricarbene.[5] Typical yield data for several olefins are reported in Table I. In a representative experiment, methylmercuridiazoacetone (5.00 mmol, 1.49 g) was dissolved in refluxing 2-methylpropene (*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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[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.*

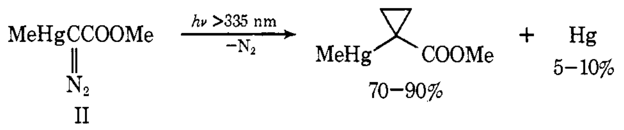
[6] 1-Methylmercuri-1-acetyl-2,2-dimethylcyclopropane: nmr (100 MHz, $CDCl_3$) 0.49 (s, with symmetrically placed Hg^{199}–H^1 doublet, $J = 121$ Hz, 3 H, CH_3Hg), 0.97 1.31 (AX, $J = 4$ Hz, 2 H, ring H), 1.01 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 2.12 (s, with symmetrically placed Hg^{199}–H^1 doublet,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

by various means led either to ring opening or to recovery of starting ketone.

The additions of methylmercuriacetylcarbene to *cis*- and *trans*-2-butene were shown by nmr analyses of the primary reaction products and by glc analyses of the residues after bromination to be completely stereospecific. The lack of radical character in the intermediate was also demonstrated by the absence of any preference for addition to 1,3-butadiene in competition experiments with monoolefins. With the heavy mercury atom in close proximity to the carbene site relaxation to the ground state should be rapid.[8] Thus, a singlet ground state is indicated for $CH_3Hg\underset{\cdot\cdot}{C}{-}COCH_3$.

α-Mercuricarboalkoxycarbenes have also been shown to react with olefins yielding cyclopropanes almost exclusively. The non-mercury-containing carbenes have important competitive pathways of rearrangement[9] and insertion. The photolysis of methyl methylmercuridiazoacetate (II) in olefins produces the corresponding



methyl 1-methylmercuricyclopropanecarboxylates in 70–90% yields.[10,11] The ready cleavage of the carbon–mercury bond by electrophilic reagents affords many possibilities for further syntheses.

The introduction of a mercury atom adjacent to the reactive site in carbenes has produced a chemistry different from that observed for the mercury-free carbenes: the elimination of Wolff rearrangement and insertion reactions in the photolyses of diazo ketones and diazo esters.

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.

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(10) II was prepared from methyl diazoacetate and methylmercuric ethoxide in 80–90% yield as a yellow solid; mp 71–72°. The preparation and characterization are fully detailed in a paper submitted for publication to *J. Org. Chem.*

(11) Also, no Wolff rearrangement product was observed when II was photolyzed in alcohol.

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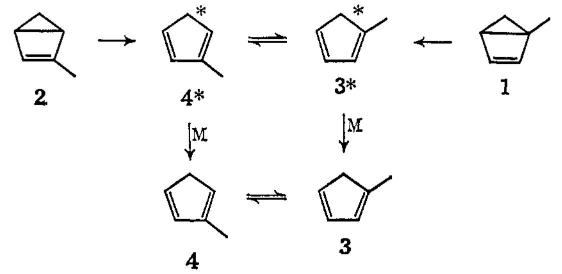
Mechanism of Isomerization of Bicyclo[2.1.0]pent-2-enes

Sir:

The mechanism of isomerization of bicyclo[2.1.0]pent-2-enes to cyclopentadienes is a matter of some controversy.[1-5] We wish to report experimental evidence which makes it clear that cleavage of the central bond in methylbicyclopentenes is the predominant isomerization path and that subsequent hydrogen shifts in the chemically activated product cyclopentadienes can account for rearranged (methyl-shifted) isomers. None of the evidence requires or supports concerted $_{\sigma}2_{s} + {}_{\sigma}2_{a}$ isomerizations.

Recent RRKM calculations of Flowers and Frey[5] show that the chemically activated cyclopentadienes formed by any pathway would be expected to undergo subsequent rearrangement. Thus, observation of rearranged products could not be used to support parallel concerted reactions. On the other hand, parallel concerted isomerizations are also consistent with extensively rearranged products.

Our studies of product ratios in the gas phase show[6] not only that chemical activation is important but also that central bond cleavage to give the non-methyl-shifted isomer is the primary reaction path. See eq 1 and Table I. First, at a given pressure more of the rearranged (methyl-shifted) product appears when nitrogen is used as ambient gas than when the more efficient deactivator pentane is employed.[7] Second, a decrease in rearrangement accompanies increases in pressure when pentane is the bath gas. Thus rearrangement must be occurring competitively with thermal deactivation. Application of the strong collision assumption to the kinetics of eq 1 predicts a pressure dependence of the ratio of products arising from deactivation to those from chemical activation (corrected for back reaction) in general agreement with that observed. Furthermore, the observed ratio in solution is in accord with the same model, assuming a solution collision frequency of 10^{12}. Third, both 1- and 2-methylbicyclopentene show qualitatively similar trends, but in all cases the more reactive 1-methylbicyclopent-2-ene gives



(1)

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(6) Gas-phase experiments were carried out in a 250-ml Pyrex bulb washed with 5% EDTA solution and conditioned with the bicyclopentenes. In all runs, bicyclopentene partial pressure was below 2 Torr. Reactions were studied at *ca.* 30% conversion, and "normal" thermal product isomerization was shown not to contribute significantly. Reactant and product mixtures were analyzed by vpc on a 10 ft × 0.25 in. aluminum column packed with 15% β,β-oxydipropionitrile on Chromosorb P regular. The rate of disappearance of the bicyclopentene was in excellent agreement with previously published results.[4] The difference in product ratios from those reported[4] is understandable in terms of our larger vessel size. Much of the deactivation results from wall collisions, consistent with the weak dependence on N_2 pressure. Runs in a packed vessel showed slight decreases in amount of rearrangement, consistent with this explanation, and simultaneously showed surface catalytic routes to the methyl-shifted isomer to be unimportant.

(7) For a thorough study of bath gas collision deactivation efficiencies, see Y. N. Yin and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 3151 (1970).