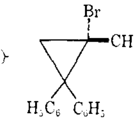
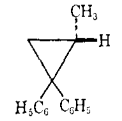
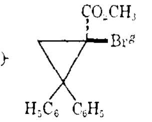
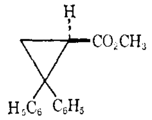
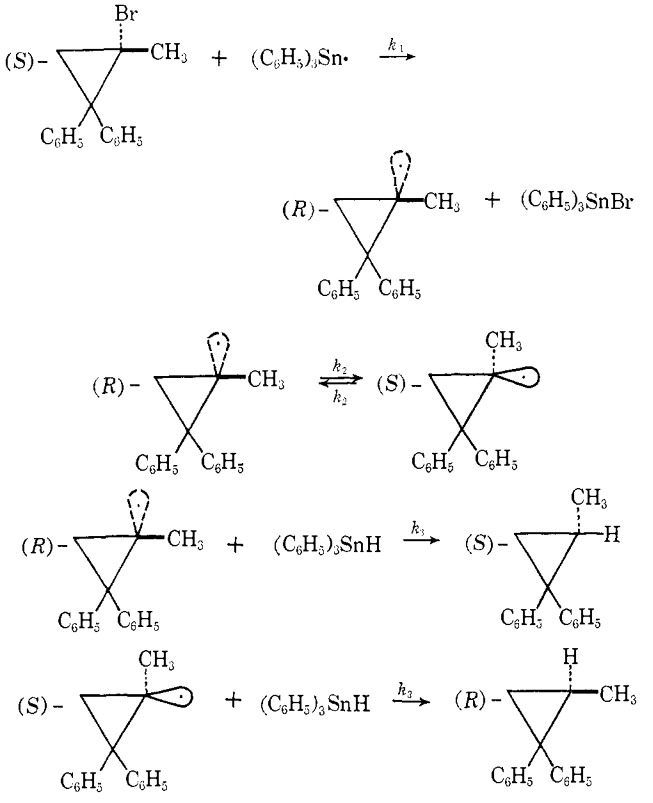
Table I. Reduction[a] of Optically Active Cyclopropyl Bromides

Starting bromide	Temp, °C	Product[b]	Rotation,[c] deg	% enantiomeric excess
(+)-(S)- 	80[e]	(+)-(S)- 	+0.37 ± 0.16	0.29[f]
	63		+1.11 ± 0.11	0.87[f]
	60		+0.82 ± 0.09	0.65[f]
	40		+1.75 ± 0.08	1.38[f]
(−)-(R)- 	65	(−)-(R)- 	−4.44 ± 0.08	2.28[h]

[a] In neat triphenyltin hydride with AIBN as initiator unless noted. [b] Chromatographically pure; analyses of all samples give satisfactory C, H values and show less than 0.02% Br. Absolute configurations are those of H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Am. Chem. Soc.*, **83**, 2517 (1961); H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962). [c] Determined in $CHCl_3$. [d] $[\alpha]^{26}D$ +108 ± 1° (*c* 0.80, $CHCl_3$) (H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86**, 3283 (1964). [e] Without initiator. [f] Based on a specific rotation of the enantiomerically pure hydrocarbon of +127° (H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964). [g] Prepared from acid with $[\alpha]^{24.5}D$ −117 ± 4° (*c* 0.73, $CHCl_3$) (Walborsky, *et al.*, footnote *d*). [h] Based on a comparison of the saponified product $[\alpha]^{23.9}D$ −4.87 ± 0.24° with enantiomerically pure acid $[\alpha]^{24}D$ −230° (Walborsky, *et al.*, footnote *b*).

(Table I). Surprisingly, the net result of these reductions is inversion! This is in direct contrast to the results of Jacobus and Pensak,[1] who reduced (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane with sodium dihydronaphthilide in dimethoxyethane and obtained 29% optically pure (−)-(*R*)-1-methyl-2,2-diphenylcyclopropane with net retention of configuration.

One possible mechanistic interpretation of the present results is that the free radical undergoes a backside reduction by triphenyltin hydride. Assuming the following kinetic scheme and a value of $3.1 \times 10^6\ M^{-1}\ sec^{-1}$ for k_3,[3] we calculate a value at 40° of $3.3 \times 10^8\ sec^{-1}$ for k_2, the inversion frequency of the cyclopropyl radical, in good agreement with the estimate of 10^8–$10^{10}\ sec^{-1}$ of Fessenden and Schuler.[4] However, if the assignments of Ando, *et al.*,[1] are correct, this mechanistic interpretation is improbable as it is unlikely that the attack of the tin hydride is on the front side of an α-fluorocyclopropyl radical and on the backside of an α-methylcyclopropyl radical.



A more plausible mechanism is that the radical undergoes rapid inversion[5] but that the front side is blocked by the triphenyltin bromide and reduction thus gives net inversion.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Eli Lilly and Company for partial support of this research.

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(3) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1055 (1968); **90**, 7047 (1968).

(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(5) Our results are consistent with those of Ando, *et al.*,[1] if the α-fluorocyclopropyl radical is configurationally stable.

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The Reactions of Carboalkoxycarbenes with Allyl Sulfides

Sir:

Diazo compounds have been known to produce singlet carbenes in direct reactions,[1] triplets in photosensitized decompositions,[2] and carbenoids in copper-catalyzed thermal reactions.[3]

In previous papers[4,5] we reported that photolysis

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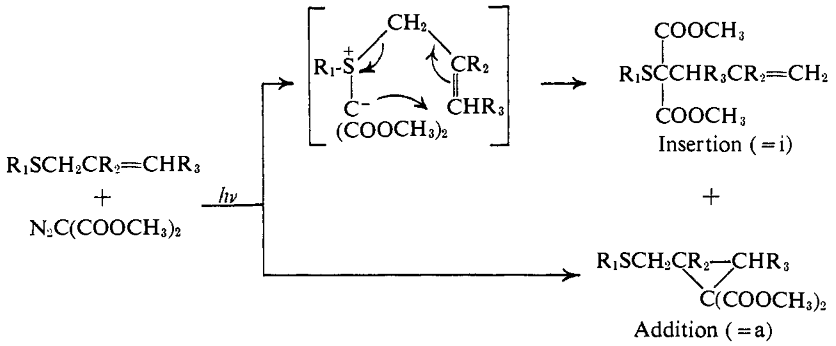
(1) P. P. Gasper and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964.

(2) (a) K. R. Kopecky, G. S. Hammond, and Leermarkers, *J. Am. Chem. Soc.*, **84**, 1015 (1962); (b) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Letters*, 1391 (1967).

(3) (a) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961); (b) W. Kirmse and D. Grassmann, *Chem. Ber.*, **99**, 1746 (1966); (c) P. Yates and R. J. Crawford, *J. Am. Chem. Soc.*, **88**, 1562 (1966); (d) W. von E. Doering and W. R. Rogh, *Angew. Chem.*, **75**, 27 (1963); (e) H. Musso and U. Biethan, *Chem. Ber.*, 100, 119 (1967).

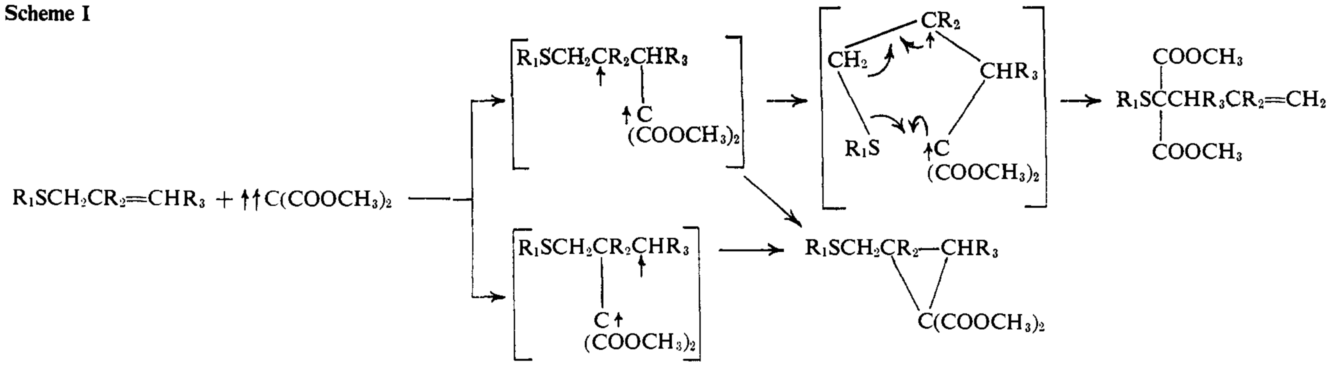
(4) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Letters*, 1979 (1969).

(5) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Am. Chem. Soc.*, **91**, 2786 (1969).



I, $R_1 = n\text{-}C_4H_9$; $R_2 = R_3 = H$
II, $R_1 = t\text{-}C_4H_9$; $R_2 = R_3 = H$
III, $R_1 = n\text{-}C_4H_9$; $R_2 = CH_3$; $R_3 = H$
IV, $R_1 = C_6H_5$; $R_2 = R_3 = H$
V, $R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$

Scheme I



and copper sulfate catalyzed thermal decomposition of dimethyl diazomalonate in dialkyl sulfides give stable alkylsulfonium bis(carbomethoxy)methylides, and we suggested the reaction involves electrophilic singlet carbenes or carbenoids which attack the sulfur atom. On the other hand, from our preliminary results, the benzophenone-photosensitized decomposition of diazo compounds in sulfides did not form the sulfonium ylide, which indicates that triplet carbenes cannot be intermediates in the formation of sulfonium ylides.

We have extended our studies on the reaction of diazo compounds with allyl sulfides. The reactions of carbenes with allyl sulfides have been studied by several workers,[6,7] but there seems to be no report on photochemically induced reactions, especially photosensitized reactions.

Irradiation of a solution of dimethyl diazomalonate in allyl sulfide was carried out in a Pyrex vessel with a high-pressure mercury lamp.[8] In all cases, the expected sulfonium ylides were not isolated. The reaction of *n*-butyl allyl sulfide (I) with bis(carbomethoxy)carbene produced by direct photolysis of dimethyl diazomalonate afforded the principal product (Ii) in 57% and the minor product (Ia) in 11% yield. Ii was found to be an insertion product of bis(carbomethoxy)carbene into the allyl–sulfur bond and Ia to be an addition product of bis(carbomethoxy)carbene into the carbon–carbon double bond. The structures of these products were determined by elemental analysis and nmr and ir spectra. The reaction of dimethyl diazomalonate with γ-methylallyl phenyl sulfide which contained 2% (by vpc) isomeric sulfide[9] gave a 47% yield of Vi and 10% addition product (Va) of bis(carbomethoxy)carbene to olefin.[10] Vi was identified by: nmr, 1.24 (CH_3, doublet), 2.95 (–CH–, quartet), 3.62 ($COOCH_3$, singlet), 5.02 ($C{=}CH_2$, multiplet), 6.01 ($-CH{=}C$, multiplet), and 7.39 ppm (C_6H_5, multiplet), intensity ratio 3:1:6:2:1:5; ir, absorption maxima at 1740 (C=O), 1645 (C=C), and 920 cm^{-1} ($C{=}CH_2$). Va showed nmr signals at 0.98 (CH_3, doublet), 1.78 (cyclopropyl-CHCH-multiplet), 2.91 (CH_2S–, doublet), 3.69 ($COOCH_3$, singlet), and 7.26 ppm (C_6H_5, multiplet); intensity ratio 3:2:2:6:5; ir absorption maximum at 1740 cm^{-1} (C=O) and no double bond band.

An attractive mechanism for the formation of insertion product may involve sulfonium ylide formation followed by intramolecular allylic rearrangement, as suggested by other workers,[6,7] but no direct insertion, since the insertion product from γ-methylallyl sulfide was only α-methylallyl thiomalonate, with no γ-methylallyl thiomalonate.

In the presence of benzophenone, reaction with *n*-butyl allyl sulfide gave the addition product in 55% yield and the insertion product in 28% yield. Table I gives the yield of insertion and addition products in the reaction of bis(carbomethoxy)carbene with various allyl sulfides under direct and sensitized photolysis.

It is interesting to note that the relative yield of insertion to addition products varies with the mode of decomposition of the diazomalonate.

In direct photolysis, the insertion reaction appeared to be about four–five times faster than the addition. This fact may support the mechanism for the formation of insertion product involving ylide intermediate, since ylide formation of bis(carbomethoxy)carbene with dimethyl sulfide has been found to be about four times faster than addition to the olefinic bond of cyclohexene.[5]

In the sensitized reaction, on the other hand, the addi-

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[6] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964).

[7] W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 1004 (1968).

[8] Rikosha high-pressure mercury lamp, 3600 Å.

[9] α-Methylallyl phenyl sulfide.

[10] Insertion products such as $C_6H_5SC(COOCH_3)_2CH_2{=}CHCH_3$ were not obtained.

tion products were more favored than the insertion products. This might appear to indicate that triplet carbene reacts with the double bond in preference to the sulfur atom. However, since the triplet bis(carbomethoxy)carbene formed by the benzophenone-photosensitized reaction does not interact with the sulfur atom, the insertion product may probably be considered to be formed through other pathways than those involving ylide intermediates.

Table I. Yield of Products from Dimethyl Diazomalonate

Sulfide	Product	Yield, % Direct	Sens.	Thermal[a]
Allyl *n*-butyl	Ii	57	28	93
	Ia	11	55	0
Allyl *t*-butyl	IIi	34	Trace	13
	IIa	14	50	0
β-Methylallyl *n*-butyl	IIIi	54	*b*	100
	IIIa	12	*b*	0
Allyl phenyl	IVi	32	0.34[c]	90
	IVa	7		0
γ-Methylallyl phenyl	Vi	47	0.13[c]	92
	Va	10		0

[a] Copper sulfate catalyzed thermal reaction at 90°. [b] The products could not be separated from benzophenone in the gas chromatograph. [c] The yields of insertion and addition products were very low, and only the molar ratio of the products, i/a, was determined from their peak area in gas chromatography.

A possible pathway is proposed involving addition of the triplet carbene to the unsaturated carbon. The biradical thus formed undergoes homolytic transfer of the thiyl group through the cyclic transition state as well as cyclopropane ring formation.

In the addition of triplet carbene to olefin involving two bond-forming processes, spin inversion is required in the intermediate step. During the step, internal rotations which gives the conformation leading to the cyclic structure illustrated in Scheme I may occur. This situation is reminiscent of nonstereospecific addition of a triplet to olefins.[1]

Copper salt or copper metal powder catalyzed thermal decompositions of diazo compounds in allyl sulfides yield insertion products in high yield. No addition product was obtained (Table I).[11] This high selectivity can be explained in terms of a copper complex of carbene. This is to be expected since the possible back-donation from the copper to the vacant p_z orbital of the carbenic carbon may contribute to stabilize the complex.[12]

It is hoped that the control over product formation demonstrated in the preceding examples will be useful in synthesis and be capable of extension to the reactions of carbenes with molecules containing hetero atoms.

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(11) Copper-catalyzed thermal reaction of dimethyl diazomalonate in an equimolar solution of cyclohexene and dimethyl sulfide gave only dimethylsulfonium bis(carbomethoxy)methylide; no adduct to cyclohexene was observed.

(12) H. Nozaki, H. Takya, S. Moriuti, and R. Noyori, *Tetrahedron*, 24, 3655 (1968).

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Stereochemistry of the Low-Spin Iron Porphyrin, Bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) Chloride[1]

Sir:

Recent structure determinations for high-spin iron porphyrins demonstrate that the iron atom lies 0.40–0.50 Å out-of-plane from the four porphine-nitrogen atoms, that it forms rather long bonds, 2.06–2.07 Å, with these atoms, and that it generally forms one short bond with a single axial ligand to complete square-pyramidal five-coordination.[2,3] The coordination group within the high-spin heme of ferrimyoglobin has the iron atom displaced ~0.30 Å out-of-plane toward the tightly bound axial ligand (imidazole nitrogen), has five Fe–N bonds all estimated as ~1.9 Å in length, and has as a sixth ligand a weakly coordinated water molecule that is partially stabilized in this position by hydrogen bonding.[4–7] (This water molecule is lacking in the heme of deoxymyoglobin.[7]) From application of the protein structure analyst's version of Fourier difference synthesis[5–7] in its lowest order of approximation[2a] to the structural study of various myoglobin derivatives, the Cambridge workers seem to infer that the out-of-plane displacement of the iron atom and Fe–N bond parameters which characterize the heme in ferrimyoglobin are essentially maintained in the several myoglobin derivatives, changes in oxidation state, coordination number, and spin state of the iron atom notwithstanding.[5–7] The chemical implausibility of this sweeping inference and the quantitatively severe limitations on the approximate procedures from which it derives are treated in detail elsewhere.[2a] We report herein the results of an X-ray analysis of crystalline structure for bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) chloride (written as $Im_2FeTPP^+Cl^-$), the first low-spin iron porphyrin to be thus analyzed.

$Im_2FeTPP^+Cl^-$, prepared by the procedure of Epstein, *et al.*,[8] was obtained as monoclinic crystals of the 1:1 solvate by recrystallization from methanol. Preliminary X-ray study by photographic techniques established a four-molecule unit corresponding to calculated and measured densities of 1.365 and 1.36 g cm^{-3}, respectively, and $P2_1/n$ as the uniquely probable space group. Intensity measurements from the largest crystal, 0.10 × 0.13 × 0.23 mm, obtainable from controlled recrystallizations utilized nickel-filtered Cu Kα radiation on an automated Picker four-circle diffractometer at an ambient laboratory temperature of 19 ± 1°; of the

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(1) This investigation was supported in part by Grant 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, by National Science Foundation Grant GP-6710X, and by the Advanced Research Projects Agency.

(2) (a) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, pp 573–594; (b) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); (c) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965).

(3) D. F. Koenig, *Acta Cryst.*, **18**, 663 (1965).

(4) J. C. Kendrew, R. E. Dickerson, B. E. Strandberg, R. G. Hart, D. R. Davies, D. C. Phillips, and V. C. Shore, *Nature*, **185**, 422 (1960).

(5) L. Stryer, J. C. Kendrew, and H. C. Watson, *J. Mol. Biol.*, **8**, 96 (1964).

(6) H. C. Watson in "Hemes and Hemoproteins," B. Chance, R. W. Estabrook, and T. Yonetani, Ed., Academic Press, New York, N. Y., 1966, pp 63–66.

(7) C. L. Nobbs, H. C. Watson, and J. C. Kendrew, *Nature*, **209**, 339 (1966).

(8) L. M. Epstein, D. K. Straub, and C. Marcondi, *Inorg. Chem.*, **6**, 1721 (1967).