

The driving force for this reversibility seems to be the release of steric compression about the carbinol carbon, since we have also found that α -methylallyldi-*t*-butylcarbinoxymagnesium bromide (VI) reverses⁶ much

Table I. Reaction^{a,b} of Crotylmagnesium Bromide with *t*-Butyl Isopropyl Ketone in THF

Time	<i>t</i> -Butyl isopropyl ketone, ^c %	Carbinol products, %		
		α -Methylallyl	<i>trans</i> -Crotyl	<i>cis</i> -Crotyl
5 min	6.4	78.6	3.3	6.7
6 hr	8.0	51.6	11.1	22.3
24 hr	7.8	19.6	19.0	40.7
48 hr	7.8	8.5	23.7	56.2
72 hr	8.7	2.5	23.4	56.1
96 hr	9.6	1.8	24.0	59.7
192 hr	10.3	.8	22.7	61.7

^a It should be noted that the values listed in both Tables I and II are actual *yields* of products since internal standards were employed in the vpc analysis. Accordingly, it becomes apparent that the material balance in every case was quite high. ^b The initial concentration of the ketone was 0.3 *M* and Grignard reagent was present in 10% excess. ^c Several explanations occur to us for this unexpected formation of ketone in the presence of presumed excess Grignard reagent. Dr. E. C. Ashby (private communication) has kindly suggested that the purity of the magnesium may play an important role here. Further work will be necessary to assess the importance of such variables.

more rapidly than I and that α -methylallyldiisopropylcarbinoxymagnesium bromide (VIII) remains unchanged under identical reaction conditions. When these reactions are carried out in diethyl ether, the rates of reversal are much slower than in THF. This difference can probably be attributed to the greater basicity of THF.⁹

The conversion of I to its crotyl isomers (V), presumably *via* a cyclic transition state (II), was further substantiated by treating an isomeric mixture of butenyl-*t*-butylisopropylcarbinols (of which 87.0% was the α -methylallyl isomer, 4.5% *trans*-crotyl isomer, and 8.5% *cis*-crotyl isomer), with 1 equiv of methylmagnesium bromide, in THF (Table II). These results clearly show a smooth increase in the yields of the *cis*- and *trans*-crotyl isomers and *t*-butyl isopropyl ketone accompanying the decrease of the α -methylallyl isomer. Again, the rate of disappearance of the α -methylallyl isomer was found to be faster in THF than diethyl ether.

It is interesting to note that treatment of this isomeric mixture of alcohols with 3 equiv of methylmagnesium bromide in THF or diethyl ether produced less than a

(6) Earlier work^{7,8} has shown that crotyl products form exclusively from the reaction of crotylmagnesium bromide with di-*t*-butyl ketone when the reaction is carried out at room temperature overnight. However, we now find that VI can be detected at *short* reaction times (*e.g.*, 5 min) in both diethyl ether and THF but reverses completely to crotyl products (VII) within 6 hr. This is a clear-cut example of a rate *vs.* an equilibrium process.

(7) K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, **72**, 218 (1950).

(8) R. A. Benkeser, *et al.*, *ibid.*, **91**, 132 (1969).

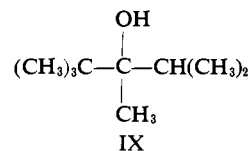
(9) Since THF is a stronger Lewis base than diethyl ether, it could be expected to complex more strongly with the magnesium atom of I, thereby causing the magnesium-oxygen bond to be more ionic in THF.

Table II. Reaction^{a,b} of Methylmagnesium Bromide with an Isomeric Mixture of Butenyl-*t*-butylisopropylcarbinols in THF

Time	<i>t</i> -Butyl isopropyl ketone, ^c %	Carbinol products, %		
		α -Methylallyl	<i>trans</i> -Crotyl	<i>cis</i> -Crotyl
5 min	3.1	81.0	4.9	7.7
6 hr	10.1	63.0	10.0	18.5
24 hr	10.8	33.7	20.0	41.7
48 hr	12.4	13.5	23.3	49.9
72 hr	10.8	6.7	26.2	57.9
96 hr	13.1	3.0	25.5	57.3

^a See footnote a in Table I. ^b The initial concentration of the carbinols was 0.3 *M* and the ratio of Grignard reagent to carbinols was 1:1. ^c As is indicated in Table I (footnote c), the origin of this ketone is presently under investigation.

5% yield of *t*-butylisopropylmethylcarbinol (IX).



Greater than 95% of the α -methylallyl isomer that disappeared was converted to the *cis*- and *trans*-crotyl isomers, even in the presence of this large excess of methylmagnesium bromide. This suggests that the collapse of the ketone-Grignard complex (III) to form crotyl products (eq 2) may possibly occur at a much faster rate than dissociation (eq 3).

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Net Inversion in the Reduction of Optically Active Cyclopropyl Bromides by Triphenyltin Hydride

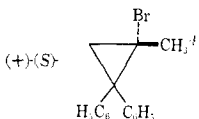
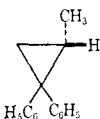
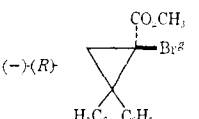
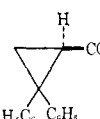
Sir:

There has been much interest recently¹ in the generation and trapping of cyclopropyl radicals before configurational equilibration can occur. Evidence has been presented² that the reduction of alkyl halides by triphenyltin hydride proceeds through a free-radical intermediate. We have carried out the reductions of two optically active cyclopropyl bromides in a large excess of neat triphenyltin hydride and report evidence that confirms the trapping of cyclopropyl radicals before complete configurational equilibration has occurred

(1) H. M. Walborsky, C. Chen, and J. L. Webb, *Tetrahedron Letters*, 3551 (1964); T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967); J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969); M. J. S. Dewar and J. M. Harris, *J. Am. Chem. Soc.*, **91**, 3652 (1969).

(2) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964).

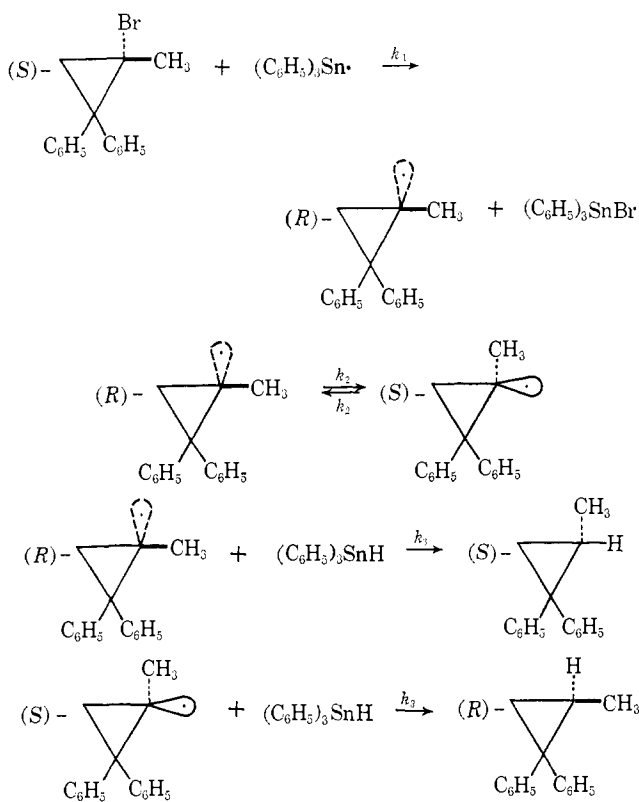
Table I. Reduction^a of Optically Active Cyclopropyl Bromides

Starting bromide	Temp, °C	Product ^b	Rotation, ^c deg	% enantiomeric excess
	80°		+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
	65		-4.44 ± 0.08	2.28 ^g

^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 CHCl₃. ^d [α]_D²⁰ +108 ± 1° (c 0.80, CHCl₃) (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 [α]_D²⁴ -117 ± 4° (c 0.73, CHCl₃) (Walborsky, *et al.*, footnote d). ^h Based on a comparison of the saponified product [α]_D²³ -4.87 ± 0.24° with enantiomerically pure acid [α]_D²⁴ -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 dihydronaphthalide 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 $3.1 \times 10^6 M^{-1} \text{sec}^{-1}$ for k_3 ,³ we calculate a value at 40° of $3.3 \times 10^8 \text{sec}^{-1}$ 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 inversion⁵ 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.

(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

(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 Leermakers, *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. Rugh, *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).