black precipitate separated. The precipitate was washed with ether. The combined ether extracts were washed once with 150 ml of saturated NH_4Cl solution, three times with 150 ml of saturated K_2CO_3 solution, and twice with 150 ml of saturated NaCl solution, and dried over Na_2SO_4. The solvent was evaporated through a Vigreux column. The residue was fractionated through a 20 × 0.6 cm vacuum-jacketed column containing a 0.4 cm o.d. tube. The fraction collected at 100–130° was purified by preparative glc (25 ft Carbowax 20M at 112°) to give 2.6 g (20.2%) of **1a** which was ≥98% chemically pure by glc: pmr spectrum (in $CHCl_3$, ~80%) cis-2 (-3) *H*, s, δ 0.17, 1 H; trans-2 (-3) *H*, δ 0.43, 0.09 H; 1 H, broad, δ 1.00, 0.12 H; 1′-*H*, s, δ 3.38, 0.02 H; O*H*, s, δ 4.3, 1 H.

Cyclopropylcarbinyl-*1,1′,1′-trans*-2,3,3-d_6 methanesulfonate (1b), prepared from **1a** by a previously reported procedure[5] in 78% yield, was ~96% chemically pure by pmr (the major impurity was pyridine): pmr in $CDCl_3$—cis-2 and -3 *H*, broad s, δ 0.37, 1 H; trans-2 and -3 *H*, broad, δ 0.65, ~0.1 H; C*H*, broad, δ 1.2, ~0.1 H; CH_3, s, δ 2.98, 3 H.

Solvolysis of Cyclopropylcarbinyl-*1,1′,1′-trans*-2,3,3-d_6 Methanesulfonate (1b). **1b** (3.3 g, 21.1 mmol) was solvolyzed in a vigorously stirred suspension of $CaCO_3$ (1.6 g, 16 mmol) in 84 ml of 60% aqueous acetone at 40°. After 6 min (~10 half-lives), pH 6–7, 100 ml of pentane was added followed by anhydrous K_2CO_3 until a saturated water solution separated out. The aqueous layer was extracted twice with 30 ml of a 1:1 pentane–ether mixture. The combined extracts and the acetone solution were dried over Na_2SO_4. The solvents were evaporated (pentane and ether through a 60-cm Vigreux column, acetone through a 20 × 0.6 cm vacuum-jacketed column) and the residue (53% **2**, 44% **3**, and 3% **4** *via* glc on 20 ft 15% glycerol on Chromosorb P 45–60 at 80°) was fractionated by preparative glc (25 ft Carbowax 20M at 112°). Two fractions were collected: **4** (~90% chemically pure by glc analysis) and 1.2 g (78%) of a mixture of **2** and **3** (≥97% by glc; the major impurity was pyridine). The pmr spectrum of **4** (~30% in CCl_4; 25 μl tube) shows four broad singlets, =C*H*, δ 4.3, ~0.1 H; O*H*, δ 5.5, 1 H; CH_2, δ 7.81, ~0.3 H; CH_2OH δ 6.50, ~0.4 H, and a 1:1:1 triplet (J = 2.5 Hz) at δ 5.02 with a small shoulder (~10%, δ 4.94) which corresponds to the cis-1 and trans-1 hydrogen, respectively (~0.35 H). The pmr spectrum of the mixture of **2** and **3** (~90% in $CHCl_3$) is shown in Figure 2.

Control Experiment. Cyclopropylcarbinol was treated with an equivalent amount of methanesulfonic acid under the conditions described for the solvolysis of **1b**. No rearrangement was observed when $CaCO_3$ was present.

Acknowledgment. This research was supported by grants from the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. The authors appreciate exchanges of information with Professor K. Wiberg.

Cyclopropanes. XXIX. The Stereochemistry of the 1-Methyl-2,2-diphenylcyclopropyl Radical in and out of Solvent Cage[1]

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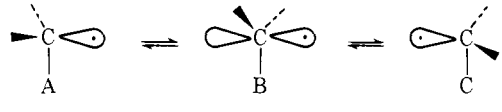
Abstract: The 1-methyl-2,2-diphenylcyclopropyl radical (**4**) has been generated in solution from a variety of optically active precursors to yield cyclopropyl derivatives which were largely if not entirely racemized. However, when the radical **4** disproportionates within the solvent cage, the 1-methyl-2,2-diphenylcyclopropane (**3a**) obtained was found to be 31–37% optically pure (66–68% retention of configuration). Evidence to support the contention that the disproportionation occurred within a solvent cage will be presented.

The stereochemistry of free radicals and the question of their geometry have been the subject of a number of reviews.[2] The question whether a radical is bent and is undergoing a rapid inversion from one pyramidal form to another (A ⇄ C) or whether it is a planar mole-



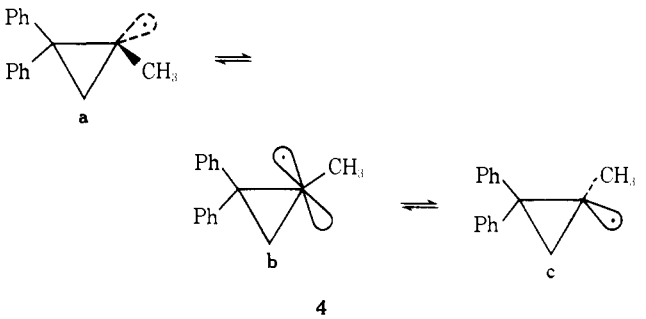
cule (B) is a difficult one to answer since B is a transition state in the inversion process. To decide whether B is a transition state or a true intermediate is a difficult question to answer chemically. If a radical is planar, it would have a plane of symmetry and could not exist in optically active form. Therefore, one approach used to determine whether or not it is planar has been to prepare a radical from an optically active starting material. A number of examples have been studied,[2] and every case gave a racemic product. This result, however, can be explained in two ways. In the first explanation, the loss of optical activity in the product is due to the planar radical which cannot exist in optically active form. In the second, the loss of optical activity is ascribed to the fact that the rate of inversion of the radical is more rapid than the rate at which it reacts to form product. Even where optically active products are obtained, the results are not subject to a clear-cut explanation of the geometry of a radical. Skell and coworkers[3] have found that the bromination of optically active 1-chloro- or 1-bromo-2-methylbutane leads to optically active products, and they interpret these results in terms of halogen-bridged radicals. If a bridged radical is formed directly without ever proceeding through an open-chain radical, then clearly the optical activity in the product has no bearing whatever on the geometry of the open-chain radical.

(1) The support of this work by Public Health Service Research Grant No. CA 04065 from the National Cancer Institute is gratefully acknowledged.

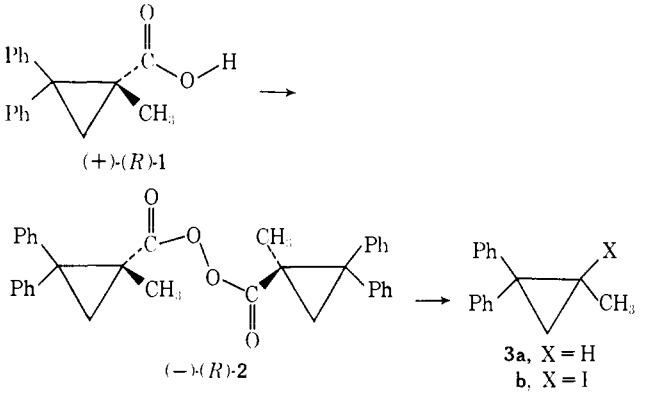
(2) E. L. Eliel, "Stereochemistry of Carbon Compound," McGraw-Hill, New York, N. Y., 1962; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(3) P. S. Skell, *Chem. Soc. Spec. Publ.*, **No. 19**, 131 (1965).

The geometry of radicals has also been investigated by physical and spectral methods. For the methyl radical, which has been studied in most detail, indications are that this radical is planar, or nearly planar. The possibility of the existence of the nonplanar cyclopropyl radical and nonlinear vinyl radicals has been demonstrated by esr studies.[4] However, failure to detect nonplanar cyclopropyl radicals generated by reactions involving acylhypohalide decompositions has been reported.[5] Evidence for nonlinear vinyl radicals has been obtained from decomposition of α-substituted cinnamyl peroxy[6] esters and cinnamoyl peroxides,[7] from reduction of 3-chloro-3-hexenes with sodium naphthalenide,[8] from reduction of α-bromostilbenes[9] and 2-bromo-2-butenes[10] with tin hydrides, and also from electrolytic reduction of stereoisomeric 3-iodo-3-hexenes.[11] There



is evidence, summarized by Smith,[5c] that the C–H bonds in cyclopropane resemble sp^2 hybrid bonds, in almost all respects, more than they resemble sp^3 hybrid bonds. On this basis, the geometry of the cyclopropyl radical might be expected to be bent rather than planar.



Optically pure (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (**1**), $[\alpha]^{24}_{Hg}$ +43.5° (*c* 2.24, $CHCl_3$), was converted to the corresponding (−)-(*R*)-1-methyl-2,2,-diphenylcyclopropanoyl peroxide (**2**), $[\alpha]^{24}_{Hg}$ −7.13° (*c* 4.0, $CHCl_3$), by the method of Greene and Kazan[12] which was used to prepare the racemic peroxide.[13] The decomposition of the diacyl peroxide **2** can lead to, *inter alia*, the hydrocarbon, 1-methyl-2,2-diphenylcyclopropane (**3a**), or if a good radical trap, such as iodine, is available then 1-iodo-1-methyl-2,2-diphenylcyclopropane (**3b**) would be formed. The absolute and relative configurations of the reactants and products have also been established[14,15] and this enables one to determine the stereochemical course of the reaction.

The results of decomposition of (−)-(*R*)-**2** in various solvents are summarized in Table I. In the case of tetrahydrofuran (run 1) and chromous ion catalyzed[16] decompositions (run 6) of optically active **2** in ethanol, the product **3a** resulting from hydrogen abstraction by the intermediate 1-methyl-2,2-diphenylcyclopropyl radical (**4**) was found to be racemic. These results support the proposed mechanism for the formation of Grignard reagents[17] and other organometallics[18] in which it has been suggested that the cyclopropyl radical is an intermediate.

Table I. Results of the Decomposition of Optically Active **2**[a]

Run	Reagent	Products 3a	Products 3b
1	Tetrahydrofuran	Racemization	
2	Benzene + I_2[b]		Racemization
3	CCl_4 + I_2		Racemization
4	Thiophenol	3.22% retention	
5	CCl_4		Racemization[c]
6	C_2H_5OH + $CrSO_4$	Racemization	

[a] At 64–65° for 24 hr. [b] Reaction was carried out at 80°. [c] The product is 1-chloro-1-methyl-2,2-diphenylcyclopropane.

Decomposition of (−)-(*R*)-**2** in carbon tetrachloride resulted in the formation of racemic 1-chloro-1-methyl-2,2-diphenylcyclopropane. The addition of a good radical trap such as iodine (runs 2 and 3) resulted in the formation of the corresponding iodide **3b** but it, too, was racemic. These reactions presumably involve the formation of an intermediate acyl hypoiodide which decomposes by a radical pathway to the iodide. Another reaction which probably involves a similar intermediate is the lead tetraacetate–iodine procedure for the decarboxylation of carboxylic acids.[19] When this reaction was used with (+)-(*R*)-**1**, a 45% yield of >98% racemic iodide **3b** was obtained.[5a]

In run 4, in a further attempt to trap the cyclopropyl radical **4** before inversion, thiophenol was used as a solvent. Even with this excellent radical trapping agent as a solvent, essentially racemic **3a** was obtained from the decomposition of (−)-(*R*)-**2**.[20] Another solvent

(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); E. L. Cochran, R. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).
(5) (a) H. M. Walborsky, Chen-Jong Chen, and J. L. Webb, *Tetrahedron Lett.*, 3551 (1964); (b) D. E. Applequist and A. H. Peterson, *J. Amer. Chem. Soc.*, **82**, 2372 (1960). (c) For reviews on the stereochemistry of the cyclopropyl radical see M. Smith ("Rodd's Chemistry of Carbon Compounds," S. Coffey, Ed., 2nd ed, Elsevier, New York, N. Y., 1967) and W. G. Bentrude (*Annu. Rev. Phys. Chem.*, **18**, 283 (1967)).
(6) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967); R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966).
(7) O. Simmamura, K. Takumusa, and H. Yui, *Tetrahedron Lett.*, 5141 (1956).
(8) G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967).
(9) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964).
(10) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 305 (1968).
(11) A. J. Fry and M. Mitnick, *J. Amer. Chem. Soc.*, **91**, 6207 (1969).
(12) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).
(13) H. M. Walborsky and Jong-Chen Chen, *J. Amer. Chem. Soc.*, **92**, 7537 (1970).
(14) H. M. Walborsky, L. Barrash, A. E. Young, and F. J. Impastato, *ibid.*, **83**, 2517 (1961).
(15) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).
(16) J. K, Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).
(17) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964).
(18) H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **4**, 418 (1965).
(19) D. H. R. Barton and E. P. Serebryakov, *J. Chem. Soc.*, 2438 (1965); see also J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

which is also reported to be an excellent radical scavenger is tri-*n*-butyltin hydride[21] and this solvent–reagent was used in the reduction of (−)-(*R*)-1-bromo-1-methyl-2,2-diphenylcyclopropane to **3a** which was found to be largely, if not entirely, racemic, $[\alpha]^{24}_{Hg}$ +0.14° (*c* 2.09, $CHCl_3$).[22] The stereochemical results were the same whether the reaction was run at room temperature or at −30°. These results are in contrast with those involving the vinyl radical, which can be intercepted by triphenyltin hydride before it can equilibrate, even at 30°.[20] These data suggest that the rate of inversion of the cyclopropyl radical is faster than that of a vinyl radical. Moreover, the cyclopropyl radical, in solution, is incapable of maintaining its configuration. In order to trap the cyclopropyl radical before complete racemization, it must react with the solvent at a rate equal to or greater than the inversion frequency of the cyclopropyl radical, which has been estimated to be 10^8–10^{10} sec^{-1} by an esr study.[4] Since the average time required for diffusion from a cage has been estimated[23] to be 10^{-11} sec, the most likely place to intercept a rapidly inverting radical would be within a solvent cage.

Cage Reaction in Carbon Tetrachloride

Frank and Rabinowitch[24] were the first to point out that molecules (or fragments) undergoing a bimolecular collision in a liquid medium are confined to a cage formed by the solvent molecules. This "cage effect"[25] is responsible also for the recombination process, and such a reaction should be distinguished from ordinary bimolecular recombination. While the latter reaction takes place between free fragments which undergo random recombination, the cage recombination involves the two original fragments produced by the dissociation of a single molecule. Extensive studies have been made on the reaction of acetyl peroxide,[26] acyclic,[27] and cyclic[28] azoalkanes,[29,30] and in a number of other systems[31] which involve radical recombination within the solvent cage. We wish to report on the stereochemistry of a *solvent-cage radical-disproportionation reaction*.[32]

Evidence for Cage. There are a number of operational tests for cage reactions. First, they do not occur in the gas phase. Second, the amount of the cage product formed is independent of concentration of the initial peroxide. Third, the cage products are not retarded or eliminated by radical scavengers. As can be seen in Table II of our previous paper[13] a 2% yield of

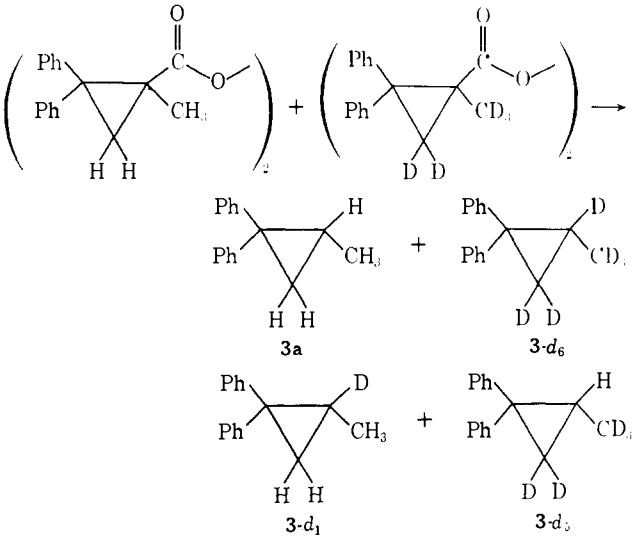
Table II. Decomposition of (+)-(*S*)-, (−)-(*R*)-, and (±)-1-Methyl-2,2-diphenylcyclopropanecarbonyl Peroxide in CCl_4

Run	2		3a	
	$[\alpha]^{25}_{Hg}$, deg	Concn, *M*	Yield	$[\alpha]^{25}_{Hg}$, deg
1	(±)	0.02	2.13 ± 0.07	
2	(±)	0.01	2.12 ± 0.02	
3	+5.1[a]	0.015		−40.0[c]
4	−6.9[b]	0.016		+46.2[d]

[a] Optical purity of (−)-(*R*)-**2**, 72%. [b] Optical purity of (−)-(*R*)-**2**, 98%. [c] Optical purity of (−)-(*R*)-**3a**, 37.4%. [d] Optical purity of (+)-(*S*)-**3a**, 31.4%.

3a was obtained in pure carbon tetrachloride (run 17). It is felt that **3a** results, in this case, from a disproportionation of **4** within the solvent cage. The evidence for this supposition is based not only on the formation of **3a** in a completely halogenated solvent, but also on the fact that the yield of **3a** was not decreased when a good radical trap such as iodine was added (run 18, Table II).[13] In agreement with the second criterion for a cage reaction, the yield of **3a** was found to be independent of concentration of the initial peroxide. As can be seen from Table II, the yield of **3a** was the same whether one started with a 0.02 *M* solution of **2** or a 0.01 *M* solution.

Finally, the most definitive evidence for a cage reaction was the observation (by mass spectral analysis) that only **3a** and **3**-d_6 were formed from the decomposition of an equimolar mixture of **2** and **2**-d_{10}[33] and none of the crossover products, **3**-d_1 and **3**-d_5. This reaction was



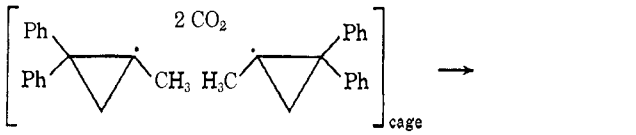
designed after the elegant work of Taylor and Martin who established a cage recombination reaction in the decomposition of acetyl peroxide.[26]

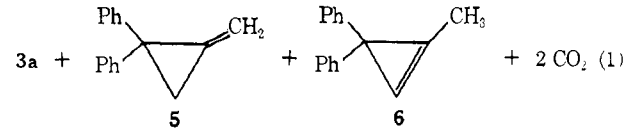
(20) The 3.22% optical purity found in **3a** represents a net retention of configuration.
(21) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 305 (1968).
(22) This represents less than 1% retention of optical activity with a small net *retention* of configuration. A similar optical result has been obtained by K. Sisido and coworkers (*Tetrahedron Lett.*, 33 (1967)) using our bromide and trimethyltin hydride. L. J. Altman and B. W. Nelson (*J. Amer. Chem. Soc.*, **91**, 5163 (1969)) using the same bromide and triphenyltin hydride found **3a** to be essentially racemized in agreement with our result but the small rotation and sign indicates a *net inversion* of configuration.
(23) S. W. Benson, "Foundation of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.
(24) N. H. Frank and H. Rabinowitch, *Trans. Faraday Soc.*, **38**, 120 (1934).
(25) For an excellent discussion see, E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968.
(26) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966); **89**, 6904 (1967).
(27) P. D. Bartlett and J. D. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).
(28) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968); C. G. Overberger, R. E. Zangaro, and J. P. Anselme, *J. Org. Chem.*, **31**, 2046 (1966); T. V. Von Auken and K. L. Rinehart, *J. Amer. Chem. Soc.*, **84**, 3736 (1964).
(29) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).
(30) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).
(31) References 28–30 cite a number of additional systems that have been studied, and also contain excellent reviews of the literature.
(32) A preliminary report of this work has been published: H. M. Walborsky and Jong-Chen Chen, *J. Amer. Chem. Soc.*, **89**, 5499 (1967).
(33) The synthesis of **2**-d_{10} may be found in the Experimental Section.

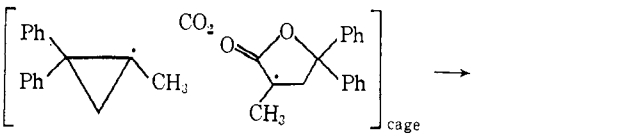
The mass spectra of the cyclopropyl hydrocarbon products from the crossover experiment showed the same intense peak (also a base peak) corresponding to a molecular ion m/e 208 ($C_{16}H_{16}^+$) and 214 ($C_{12}H_{10}D_6^+$) at 70 and also at 10 eV. This indicates that an equal amount of **3a** and **3**-d_6 was obtained from the decomposition of an equimolar mixture of **2** and **2**-d_{10} in carbon tetrachloride, and is consistent with a β-hydrogen transfer resulting in disproportionation.

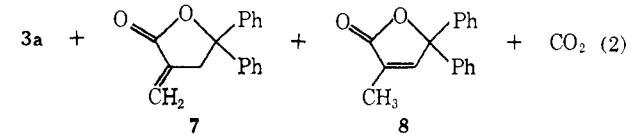
Disproportionation Reaction

One can envisage two conceivable cage disproportionation reactions (eq 1 and 2).



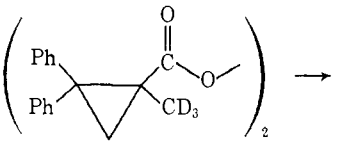




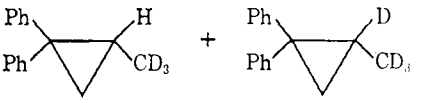


Assuming disproportionation by the process 1, either **5** or **6** or a mixture of both compounds would be expected to be present in the reaction products, but no such products could be detected in the reaction mixture. However, in a separate experiment, it was found that **5** and **6** were not stable under the conditions of the decomposition of the peroxide. If disproportionation occurs by process 2, **7** and **8** would be expected to be found in the products. However, **7** was absent in the reaction mixture. The evidence for the absence of **7** was based on the fact that after removing **8** from the reaction mixture, the residue showed no carbonyl absorption characteristic of a γ-lactone between 1750 and 1800 cm^{-1}. Exomethylene γ-lactone **7**, if present, would probably rearrange to the more stable endocyclic α,β-unsaturated γ-lactone **8** during the reaction.[34]

There are two kinds of β-hydrogens, methyl hydrogens and ring hydrogens, in **4**. In order to clarify which was transferred in the disproportionation and, hopefully, to ascertain whether reaction 1 or 2 obtains, the peroxide **2**-CD_3 was prepared (see Experimental Section) and decomposed in carbon tetrachloride. The cyclopropyl hydrocarbon was isolated and found to be a mixture of **3**-d_3 and **3**-d_4 in a ratio of 3:2, respectively. This shows that both the methyl and ring hydrocarbons are transferred in the cage disproportionation, and that ring hydrogen transfer is slightly favored. This would not be expected based on reaction 1 since radicals have been shown to preferentially abstract cyclopropylcarbinyl hydrogens rather than ring hydrogens.[35] In the absence of a large deuterium isotope effect one would have expected **3**-d_4 to have predominated. On the other hand, if disproportionation occurs by reaction 2 then one might expect the ring hydrogen to be abstracted preferentially leading to a predominance of **3**-d_3, as observed. Our data do not permit the exclusion of either reaction 1 or 2.



2-CD_3



3-d_3 3-d_4

Stereochemistry of 4 within Solvent Cage. It has been recently established by the work of Bartlett,[27] Greene,[28] and Kopecky[29] that cage recombination reactions can lead to from 17 to 100% retention of configuration depending on temperature and reaction conditions. The systems studied involved the formation of a benzylic type of radical which may well be planar. The results were interpreted on the basis of a planar rotating radical rather than a rapidly inverting pyramidal radical. It is doubtful that the question of whether a radical is a planar intermediate or whether it is a rapidly inverting species in which the planar form is a transition state can be answered by chemical reactivity or stereochemical data. The answer to this type of question can be obtained by physical measurements such as esr. The work of Fessenden and Schuler[4] has provided esr evidence for the cyclopropyl radical being a rapidly inverting radical (10^8–10^{10} sec^{-1}). Based on this datum, we have considered the radical we have generated as behaving similarly to the cyclopropyl radical and have assumed a nonplanar configuration for it. Moreover, it should be recognized that if the radical is inverting rapidly it would necessitate an extremely fast reaction in order to account for the 31–37% optical purity observed. It is questionable whether a disproportionation type of reaction would be a sufficiently fast reaction to account for such a high retention of optical activity and configuration. If on the other hand the cage imposes a further restriction on the radical, in that it makes it difficult for the radical to rotate (180° or more) while in the cage,[29,30] then even a rapidly inverting radical may be able to maintain its configuration for a sufficiently long time to react by a disproportionation reaction.

In summary, when the radical **4**, which is probably of a rapidly inverting pyramidal structure, has sufficient lifetime so that it can diffuse out of the solvent cage in which it was formed, the product formed by the radical reacting with substrate will be essentially racemic. If the radical is constrained in a solvent cage and reacts within that cage it will maintain its configuration to a large extent.

(34) N. H. Fischer and T. J. Mabry, *Tetrahedron*, **23**, 2529 (1969).

(35) H. C. Brown and M. Borkowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952); J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 3940 (1969), and references cited therein.

Experimental Section

(−)-(*R*)-1-Methyl-2,2-diphenylcyclopropanoyl Peroxide (2). Repeating[14] the procedure described for (±)-**2** and starting with (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (**1**), maximum rotation $[\alpha]^{24}_{Hg}$ +43.5° (*c* 2.24, $CHCl_3$), mp 188–189°, gave (−)-**2** with $[\alpha]^{24}_{Hg}$ −7.13° (*c* 4.0, $CHCl_3$), mp 130° dec. On further recrystallization from ether, the rotation remained the same.

Decomposition of 2 in Carbon Tetrachloride. The procedures for decomposition, separation of the neutral fraction, isolation of **3a**, and quantitative analysis of the products by vpc were the same as previously described in the general procedure.[14] 1-Chloro-1-methyl-2,2-diphenylcyclopropane was isolated by the following procedure: the neutral portion of the reaction mixture was chromatographed on alumina column using low boiling petroleum ether (bp 30–60°) as eluent. Upon evaporation of the petroleum ether, the residue solidified to yield 19.3% of the chloride, mp 65–65.5°. The infrared and nmr spectra were identical with those of an authentic sample.[15] A mixture melting point gave no depression. Decomposition of (+)-(*R*)-**2**, $[\alpha]^{23}_{Hg}$ 5.1° (70% optical purity) gave (−)-(*R*)-1-chloro-1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{23}_{Hg}$ 1.05° (*c* 2.85, $CHCl_3$).

Decomposition of (−)-(*R*)-2 with Iodine in Carbon Tetrachloride. The procedure for the decomposition of (−)-**2**, $[\alpha]_{Hg}^{24}$ 7.13° (100% optical purity) in the presence of an equimolar amount of iodine in carbon tetrachloride was the same as described in the general procedure.[14] The neutral portion was chromatographed on alumina column using low boiling petroleum ether as eluent. The solvent was evaporated, and further purification of the residue by sublimation gave 1-methyl-2,2-diphenylcyclopropyl iodide (**3b**): 22.6% yield; mp 85–86°; $[\alpha]_{Hg}$ +1.02° (*c* 6.6, $CHCl_3$). The infrared and nmr spectra were identical with those of an authentic sample.[15] A mixture melting point gave no depression.

Decomposition of (−)-(*R*)-2 with Iodine in Benzene. The decomposition was carried out at 80° and the iodide **3b** was isolated by the method described above. The yield of **3b** was 18.8%, $[\alpha]_{Hg}^{25.5}$ +1.25° (*c* 1.4, $CHCl_3$). The acid **1** which was isolated from the acidic portion gave mp 179–183°, $[\alpha]^{24}_{Hg}$ +42.3° (*c* 1.3, $CHCl_3$).

Decomposition of (−)-(*R*)-2 in THF. Optically pure **2** was used. The neutral portion from the reaction mixture was chromatographed on an alumina column using low boiling petroleum ether as eluent. The solvent was evaporated and **3a** was isolated from the residue by vpc, $[\alpha]^{24}_{Hg}$ +0.148° (*c* 12.5, $CHCl_3$). The infrared spectrum was identical with that of an authentic sample.[15]

Decomposition of (−)-(*R*)-2 in Thiophenol. Optically pure **2** was used. After decomposition, the reaction mixture was extracted with aqueous sodium bicarbonate. Crude **1** was isolated from the basic extract and gave mp 167–174°, $[\alpha]^{24}_{Hg}$ +33.3° (*c* 0.3, $CHCl_3$). The thiophenol solution was diluted with ether and then extracted with 10% cold potassium hydroxide solution until the thiophenol was completely removed. The ethereal solution was washed with water and dried over magnesium sulfate. The ether was removed by distillation and the residue subjected to thin-layer chromatography on silica gel using hexane as the developing solvent. The main broad band between R_f 0.28 and 0.53 was extracted and vpc analysis, using the EGIP column at 200°, showed two peaks.

Two compounds were collected from the column. One was a liquid which corresponded to **3a**, $[\alpha]^{24}_{Hg}$ +4.84° (3.22% optically pure) and its infrared spectrum was identical with that of an authentic sample.[15] The other compound was a solid which was identified as phenyl disulfide, mp 59.5–60° (reported mp 61°). The infrared spectrum was identical with that of an authentic sample and the nmr spectrum was consistent with the structure.

Reduction of (−)-(*R*)-1-Bromo-1-methyl-2,2-diphenylcyclopropane with Tri-*n*-butyltin Hydride. The bromide (1.0 g), $[\alpha]_{Hg}$ −128.5°, and 7 g of tri-*n*-butyltin hydride were mixed together at room temperature under an argon gas atmosphere with stirring for 1 hr. Thin-layer chromatography on silica gel and vpc analysis showed no starting bromide in the reduction mixture. The reduction product **3a** was isolated by thin-layer chromatography using pentane as developing solvent to give 0.704 g (97% yield), $[\alpha]^{24}_{Hg}$ +0.14° (*c* 2.09, $CHCl_3$). The product **3a** which was isolated from thin-layer chromatography showed only one peak by vpc. The infrared spectrum was identical with that of an authentic sample.[15]

The reaction was repeated at low temperature (−26 to −29°) with the addition of 0.05 g of azobisisobutyronitrile to a mixture of 0.158 g of bromide ($[\alpha]_{Hg}$ −128.5°) in an excess amount of tri-*n*-butyltin hydride (1 g) under an argon atmosphere. The solution was irradiated with a short-wave ultraviolet source (115 V) for 5 hr with stirring. After the reaction, 20 ml of ether and dilute hydrochloric acid were added until hydrogen gas ceased to be evolved. The ethereal layer was separated, washed with aqueous sodium bicarbonate and water, and dried over molecular sieves. Thin-layer chromatography and vpc analysis showed no starting bromide in the ethereal solution. The product **3a** was isolated by preparative thin-layer chromatography to give 0.108 g (94.5% yield), $[\alpha]^{24}_{Hg}$ +0.294° (*c* 1.7, $CHCl_3$).

Chromous Ion Catalyzed Decomposition of (−)-(*R*)-2. Optically pure (−)-(*R*)-**2** was used. The procedure for the decomposition of **2** in the presence of 2 equiv of chromous sulfate in ethanol was that described by Kochi.[16] The yield of **3a** was 3.5%, $[\alpha]^{25}_{Hg}$ +2.5° (*c* 1.05, $CHCl_3$).

Preparation and Decomposition of 1-Methyl-d_3-2,2-diphenylcyclopropanoyl Peroxide (2-CD_3). The procedure for preparation of 1-methyl-d_3-2,2-diphenylcyclopropyl cyanide was similar to that for 1-methyl-2,2-diphenylcyclopropyl cyanide[36] except that methyl iodide-d_3 was used: mp 142–143.5°; the infrared spectrum ($CHCl_3$) showed 2220 (s) cm^{-1}; nmr ($CDCl_3$) 7.7–7.2 (10 H, multiplet, aromatic), two doublets at 2 and 1.6 (2 H, 5.5 cps, ring), and a 1-ppm trace amount (singlet, methyl hydrogen).

A solution of 1.0 g of the above cyanide, 1 g of potassium hydroxide, and 30 ml of ethylene glycol was refluxed for 3 days. The reaction mixture was diluted with 30 ml of water, extracted with ether, acidified with hydrochloric acid, and extracted with ether. The etheral solution was washed with water and dried over magnesium sulfate. The ether was removed by distillation leaving 0.9 g (99% yield) of product, mp 135–165°. Two recrystallizations from acetone–water solution gave mp 176–178°: nmr ($CDCl_3$) 7–7.55 (10 H, multiplet, aromatic), two doublets at 2.24 and 1.5 (2 H, 5.5 cps, ring), and 1 ppm (3.2 % D, singlet, methyl hydrogen).

The method for preparation of 2-CD_3 from 1-CD_3 was the same as that for preparation of **2** from **1**. The procedure for the decomposition of 2-CD_3 and the isolation of the cyclopropyl hydrocarbon fraction was the same as described in the general procedure.[14] The mass spectrum of the products shows that the relative intensity at *m/e* 212 ($C_{16}H_{12}D_4^+$) to 211 ($C_{16}H_{13}D_3^+$) was 39:61%, and at *m/e* 194 ($C_{16}H_{12}D_4^+$–CH_3) to 193 ($C_{16}H_{15}D_3^+$–CH_3) was 38:62%. Based upon the 96.8 atom % D of 2-CD_3, the reaction gave a mixture of 39.4% of **3**-d_4 and 60.6% of **3**-d_3.

Preparation of 1-Methyl-d_3-2,2-diphenyl-3,3-dideuteriocyclopropanoyl Peroxide (2-d_{10}). The method used for the synthesis of a crude acetone cyanohydrin-d_6 from acetone-d_6 was similar to that previously described for acetone cyanohydrin.[37]

In a three-necked flask with a magnetic stirrer, and cooled by means of an ice bath, was placed 21.6 g of a pure acetone cyanohydrin-d_6 and 56.2 g of anhydrous pyridine, and then 28.4 g of thionyl chloride was added slowly with stirring under a nitrogen atmosphere. After all the thionyl chloride had been added, the stirring was continued for 1 hr at 0° and then at room temperature for 6 hr. A cold saturated solution of sodium chloride (300 ml) was added to the reaction mixture and the oily layer was separated, washed with a saturated sodium chloride solution, and dried over molecular sieves to yield 14.9 g of crude 1-methylacrylonitrile-d_5.

The solution of 14.9 g of the crude 1-methylacrylonitrile-d_5 and 9 ml of a saturated petroleum ether solution of diphenyldiazomethane was refluxed overnight. The solvent was removed under reduced pressure and recrystallization of the residue from ether gave 0.4 g of 1-methyl-d_3-2,2-diphenyl-3,3-dideuteriocyclopropyl cyanide, mp 142–144°. The infrared spectrum (CCl_4) of the cyanide showed 2240 (m) cm^{-1} and no absorption between 2300 and 3000 cm^{-1}; nmr ($CDCl_3$) 7.8–7.2 (multiplet, aromatic). The mass spectrum showed the molecular ion at *m/e* 238.

The procedure for preparation of 2-d_{10} from 1-methyl-d_3-2,2-diphenyl-3,3-dideuteriocyclopropyl cyanide was the same as that of 2-CD_3 from 1-methyl-d_3-2,2-diphenylcyclopropyl cyanide. The nmr spectrum ($CDCl_3$) of 2-CD_3 showed absorption only at 7.1–8.7 ppm (multiplet, aromatic).

Decomposition of an Equimolar Mixture of 2 and 2-d_{10} in Carbon Tetrachloride. The procedures for decomposition of an equimolar mixture of **2** and 2-d_{10} for isolation of the cyclopropyl hydrocarbon fraction were the same as described in the general procedure.[14] The mass spectrum of the product showed *m/e* 208 ($C_{16}H_{16}^+$, relative intensity 100%), 209 ($C_{16}H_{16}^+ + 1$, 17.7%), 214 ($C_{16}H_{10}D_6^+$, 100%), 215 ($C_{16}H_{10}D_6 + 1$, 17%).

(36) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, 77, 6026 (1955).

(37) R. F. B. Cox and R. T, Stormont, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 7.