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[21] Alfred P. Sloan Foundation Research Fellow.
[22] Goodyear Foundation Fellow, 1963–1964.

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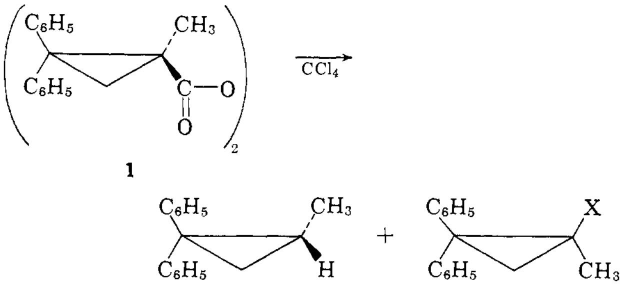
Cyclopropanes. XXII. Cage Disproportionation of Optically Active 1-Methyl-2,2-diphenylcyclopropyl Radical[1]

Sir:

In our previous studies[2] on the decomposition of the diacyl peroxide (**1**) of (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, we found that, in hydrogen atom donating solvents, the 1-methyl-2,2-diphenylcyclopropane (**2**) formed was racemic. This was interpreted to mean that the 1-methyl-2,2-diphenylcyclopropyl radical was incapable of maintaining its configuration, a conclusion which had also been reached for radicals generated at a trigonally hybridized carbon[3] as well as for those produced at a tetrahedrally hybridized carbon.[4] Although the latter radicals have been shown to be planar, the vinyl and cyclopropyl radicals are believed to be bent and to possess inversion frequencies of 10^8–10^{10} sec^{-1}.[5] In order for the vinyl or cyclopropyl radical to be able to maintain its configuration to any appreciable extent, it must react with another substrate at a rate equal to or greater than this inversion frequency. The most likely place to find such a rapid reaction would be within a solvent cage. At this time, we wish to report on the stereochemistry of what we believe to be a reaction occurring in a solvent cage.



1

2

3a, X = Cl
b, X = I

The diacyl peroxide **1** of (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid when decomposed in hydrogen atom donating solvents (*i.e.*, toluene, ether, THF, etc.) leads to the formation, *inter alia*, of 1-methyl-2,2-diphenylcyclopropane (**2**) which is racemic. When the decomposition is carried out in pure (vpc) carbon tetrachloride one obtains, besides the expected essentially racemic 1-chloro-1-methyl-2,2-diphenylcyclopropane (**3a**), a 2% yield of **2**. We feel that **2** results from a disproportionation of the 1-methyl-2,2-diphenylcyclopropyl radical within the solvent cage.

Our evidence for the above supposition is based not only on the formation of **2** in a completely halogenated solvent such as carbon tetrachloride but also on the fact that **2** is also formed in a 3% yield when a good radical trap such as iodine[6] is added. Under these conditions no **3a** is formed, only **3b**. Another criterion for cage product is that the amount of product formed is independent of concentration of the initial substrate. As can be seen from Table I the yield of **2** was the same whether one started with a 0.02 *M* solution of **1** or a 0.01 *M* solution. Finally, the best evidence is the stereochemical result. Decomposition of (−)-(*S*)-**1**- yielded (−)-(*R*)-**2** with an optical purity of 37% and with over-all retention of configuration.[7] Starting with the enantiomer, (+)-(*R*)-**1**, the hydrocarbon (+)-(*S*)-**1** was obtained with an optical purity of 31%.

Table I. Decomposition of (+)-, (−)-, and (±)-Diacyl Peroxides of 1-Methyl-2,2-diphenylcyclopropanecarboxylic Acid in CCl$_4$ at 67°

Run	**1** $[\alpha]^{25}$ Hg, deg	Concn, *M*	% yield (**2**)	**2** $[\alpha]^{25}$ Hg, deg
1	(±)	0.02	2.13 ± 0.07	. . .
2	(±)	0.01	2.12 ± 0.02	. . .
3	−30.0[a]	0.015	. . .	−40.0[c]
4	+40.0[b]	0.016	. . .	+46.2[d]

[a] Optical purity of **1** 72%. [b] Optical purity of **1** 98%. [c] Optical purity of **2** 37.4%. [d] Optical purity of **2** 31.4%.

To our knowledge the only other example of retention of configuration in a cage reaction is the example provided by Bartlett,[8] who demonstrated that the photolyses of *meso*- and (±)-azobis(3-methyl-2-phenyl-2-butane) in frozen solvents (−196°) yield pure *meso*- and (±)-2,3,4,5-tetramethyl-3,4-diphenylhexane, respectively. At temperatures greater than 0° the stereospecificity is lost. This contrasts the stereochemical behavior of a tetrahedrally hybridized radical[9] with the bent cyclopropyl radical which was able to maintain its configuration to a large extent in a cage reaction at 67°.

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[1] This investigation was supported by Public Service Research Grant No. CA 04065-09 from the National Cancer Institute, and in part by the National Science Foundation.
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Structure and Infrared Spectrum of the Solvated Proton in Dimethyl Sulfoxide

Sir:

In the course of other work we have recently found that the equilibrium constant for reaction 1[1] in di-

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