

Cyclopropanes XVIII. The Stereochemistry and Isomerization
of the 1-Methyl-2,2-diphenylcyclopropyl
Radical¹

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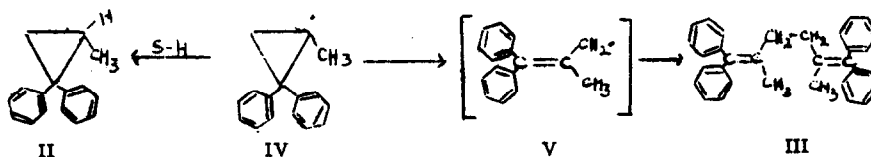
(Received 18 September 1964)

In connection with our work concerning the mechanism of formation of Grignard reagents² as well as other organometallics it became necessary to determine the optical and structural fate of the 1-methyl-2,2-diphenylcyclopropyl radical. The method chosen to generate this radical was the decomposition of the diacyl peroxide of (+)-(R)-1-methyl-2,2-diphenylcyclopropane-carboxylic acid(I). Of the procedures available for the preparation of diacyl peroxides, the one that produced the best results was that of Greene and Kazan³ which gave a 43-68% yield of peroxide I, m.p. 129° (dec.), I.R. 1775, 1780 cm⁻¹ (C=O), 90-98% purity (iodometric titration), and $[\alpha]_{5461}^{25} -71^{\circ}$

- (1) This investigation was supported by Public Health Service Research Grant No. CA 04065-07 from the National Cancer Institute.
- (2) H. M. Walborsky and E. A. Young, J. Am. Chem. Soc., 0000 (1964).
- (3) F. D. Greene and J. Kazan, J. Org. Chem., 28, 2168 (1963).

(c. 4.0, CHCl_3) starting with optically pure (+)-(R)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, m.p. 188-189° and $[\alpha]_{5461}^{25} + 43^\circ$ (c. 2.0, CHCl_3).

A 1% solution of (-)-(R)-I in tetrahydrofuran was refluxed for 24 hours under an argon atmosphere. The products isolated consisted of 2.7% yield of the starting acid, 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, a 29% yield of II which was purified by preparative gas chromatography² and was found to be essentially racemic, $[\alpha]_{5461}^{25} + 0.17^\circ$ (c. 1.2, CHCl_3 , 0.1% optical purity) and an 8% yield of III, m.p. 140-143° (lit.⁴ m.p. 145°)⁵. The remainder of the product consisted of a complex mixture containing esters and lactones which we have not completely identified.



(4) G. Wittig and H. Pook, Ber., 70, 2490 (B 37).

(5) Although our m.p. is slightly lower than that reported⁴ for III our other data which includes, elemental analysis (C, 92.75; H, 7.41), U.V. $\left. \begin{array}{l} \text{EtOH} \\ \text{max.} \end{array} \right\} 245 \text{ m}\mu$ (ϵ , 23,900) and n.m.r. at 60Mc in CCl_4 showing singlets at 97 cps ($=\text{C}-\text{CH}_3$) and 136 cps ($=\text{C}-\text{CH}_2$) and phenyl absorption at 422 cps with integrated peak ratios of 3:2:9.9, are consistent with the proposed structure.

Of significance is the finding that hydrocarbon II is racemized. This shows that the tertiary 1-methyl-2,2-diphenyl-cyclopropyl radical (IV), which was generated from the decomposition of the optically active diacyl peroxide, is like the secondary cyclopropyl radical⁶, incapable of maintaining its configuration.

The formation of III from IV is of major interest. To our knowledge this is the first example of the isomerization in solution of a cyclopropyl radical to an allyl radical⁷. It seems that in the systems previously studied⁷ the energy barrier to isomerization was sufficiently high so that in spite of the relief of steric strain and the gain of resonance energy in going to the allylic system, the cyclopropyl radicals still retained their structural integrity. Apparently the phenyl rings in the 2-position markedly lowers the energy barrier to

(6) D. E. Applequist and A. H. Peterson, J. Am. Chem. Soc., 82, 23772 (1960).

(7) We will not review the previous work bearing on this point at this time. Critical reviews of the literature and discussions of this question can be found in the following articles:

H. Hart and D. P. Wyman, J. Am. Chem. Soc., 81, 4891 (1959);

D. I. Schuster and J. D. Roberts, J. Org. Chem., 27, 51 (1962).

isomerization as well as leading to a more resonance stabilized allylic system.

The solvent plays an important role in determining the product ratios of II to III. In THF the yield of II is 29% and the yield of III is 8%. If, however, one goes to a solvent such as benzene, which does not have a propensity for donating hydrogen atoms and thereby allows the cyclopropyl radical IV to have a longer lifetime, then the yield of II is reduced to a mere trace and the yield of III goes up to 36%. On the other hand, using benzene as a solvent but adding a good radical trap such as iodine⁸ prevents the formation of isomerized product III and 19% yield of 1-iodo-1-methyl-2,2-diphenylcyclopropane² (VI) is obtained. When the optically active diacyl peroxide I is used the iodo derivative VI formed, is racemic. This reaction presumably involves the formation of an intermediate acyl hypoiodite which decomposes to radical IV. Another reaction which probably involves an acyl hypoiodite is the lead tetraacetate-iodine procedure for the decarboxylation of carboxylic acids⁹. When this reaction is used with optically active 1-methyl-2,2-diphenylcyclopropanecarboxylic acid a 45%

(8) G. S. Hammond, J. Am. Chem. Soc., **72**, 3737 (1950).

(9) D. H. R. Barton and E. P. Serebryakov, Proc. Chem. Soc., 309 (1962).

yield of >98% racemized iodide VI is obtained. Acyl hypobromites react similarly since the Cristol-Firth reaction¹⁰ (HgO/Br₂ in CCl₄) gave a 5% yield of product consisting of 99% 1-bromo-1-methyl-2,2-diphenylcyclopropane and 1% 1-chloro-1-methyl-2,2-diphenylcyclopropane. The product mixture was racemic.

The decomposition of diacyl peroxide I to produce radical IV which can either react with solvent to yield II or isomerize to III, provides a useful tool to evaluate the ability of various solvents to donate atoms to tertiary cyclopropyl radicals. We are currently engaged in such a study.

(10) S. Cristol and W. C. Firth, Jr., J. Org. Chem. 26 280 (1961)