added to ethyl 3-ketocyclobutane-1-carboxylate yielding a product whose infrared spectrum is as follows: ν_{max} 3460 strong and broad (OH), 2980, 2950 and 2840 (CH), 1725 strong (C=O), 1600 strong doublet, 1590, 1510, 1500, 1450 broad, 1375, 1345, 1295, 1240 broad, 1175 broad, 1095, 1030 strong, 830 strong, 780, 750, and 690 cm^{-1}.

Hydrogenolysis, with 1 drop of $HClO_4$ added (by procedure B), yielded ethyl 3-(*p*-methoxyphenyl)cyclobutanecarboxylate, bp 114–115° (0.15 mm), 3.0 g (25% over-all).

Saponification (by procedure C) yielded the title compound, bp 129–150° (0.3–0.4 mm), which upon crystallization followed by two recrystallizations from ether at −80° gave the product, mp 70.5–72.0°, with the following infrared spectrum: ν_{max}^{mull} 1700 strong (C=O), 1610, 1580, 1515, 1460 strong, 1430, 1380, 1355, 1295, 1260, 1230, 1205, 1175, 1030, 930 broad, 805, and 750 cm^{-1}. The pmr spectrum of the product is as follows: a singlet at δ 12.0 (1 H, CO_2H), simplified AA'BB' four-line multiplet with halves centered at 6.96 and 6.60 (4 H, aromatic), singlet at 3.59 (3 H, OCH_3), two adjacent quartetlike multiplets centered at 3.17 (1 H) and 2.88 (1 H), another multiplet centered at 2.34 (4 H).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut equiv, 206.2. Found: C, 69.45; H, 6.80; neut equiv, 205.1, 207.3.

Instrumentation.—pK_a determinations in 50.0% (v/v) aqueous ethanol were carried out as previously reported.[6] Pmr spectra (100 mc) were run in CCl_4 solution containing 6% tetramethylsilane.

Registry No.—Ethyl 3-phenyl-3-hydroxycyclobutane-1-carboxylate, 16204-46-9; ethyl 3-phenylcyclobutanecarboxylate, 16204-47-0; 3-phenylcyclobutanecarboxylic acid, 16204-48-1; 3-(*p*-fluorophenyl)cyclobutanecarboxylic acid, 16204-49-2; 3-[*m*-(trifluoromethyl)phenyl]cyclobutanecarboxylic acid, 16204-50-5; 3-(*m*-fluorophenyl)cyclobutanecarboxylic acid, 16204-51-6; 3-(*m*-tolyl)cyclobutanecarboxylic acid, 16204-52-7; 3-(*p*-methoxyphenyl)cyclobutanecarboxylic acid, 16204-53-8.

Cyclopropanes. XXIII. An Optically Active Cyclopropylsodium[1]

JAMES B. PIERCE AND H. M. WALBORSKY

Chemistry Department, Florida State University, Tallahassee, Florida 32306

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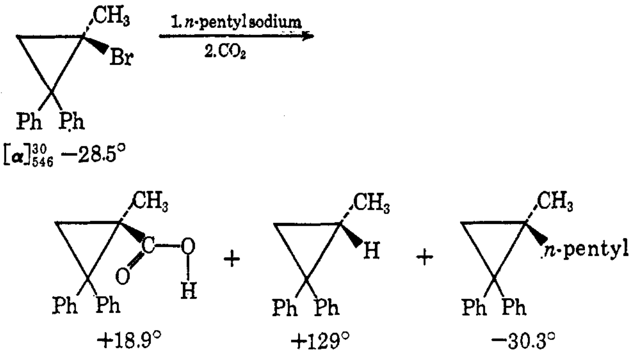
Halogen–metal exchange between (−)-(*R*)-1-bromo-1-methyl-2,2-diphenylcyclopropane and *n*-amylsodium yielded upon carbonation (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (optical purity, 46%), (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane (optical purity, 83%), and (−)-(*R*)-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane (optical purity, 66%) with over-all retention of configuration. In an ancillary study to the determination of the absolute configuration of (−)-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane it was found that the most effective method for the reduction of a vinylcyclopropane intermediate was by the use of diimide.

It has recently been established that organolithium[2] and magnesium[3] reagents derived from 1-bromo-1-methyl-2,2-diphenylcyclopropane are capable of maintaining their optical activity and configuration. In connection with our current studies on the reduction of this compound with sodium in liquid ammonia, we were interested in determining the effect on the optical stability of replacing lithium or magnesium by the less covalently bonded sodium. There was some evidence that 1-methyl-2,2-diphenylcyclopropylsodium would have at least some degree of optical stability since previous studies had shown that the reaction of the corresponding bromide with metallic sodium in benzene or toluene yielded 1-methyl-2,2-diphenylcyclopropane (optical purity 60–70%) with net retention of configuration.[2] Since carbonation, under these conditions, did not yield the corresponding acid and since the mechanism of direct metallation is still under investigation,[4] it was thought desirable to produce the intermediate organosodium derivative by halogen–metal exchange reaction.

Optically active 1-methyl-2,2-diphenylcyclopropylsodium has now been prepared by the reaction of *n*-pentylsodium with (−)-(R)-1-bromo-1-methyl-2,2-diphenylcyclopropane in pentane solution. Carbonation followed by hydrolysis of the reaction mixture gave three main products, (+)-(R)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid in 10% yield (optical purity, 46%), (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane, 45% yield (optical purity, 83%), and (−)-(*R*)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane in 25% yield (optical purity, 66%).



All products were produced with over-all retention of configuration. The relative[2,5] and absolute configurations[6] of the cyclopropyl bromide, carboxylic acid and hydrocarbon have previously been established and the configuration of 1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane was established by an independent synthesis starting from an alcohol of known absolute configuration.[6] Since none of the above reactions affect the optically active center in the starting carbinol, the configuration of the resulting (−)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane must be identical with that of the starting material. Furthermore, in that the (−)-carbinol has been shown to have the same configuration

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(1) The support of this work by grants from the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

(2) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964).

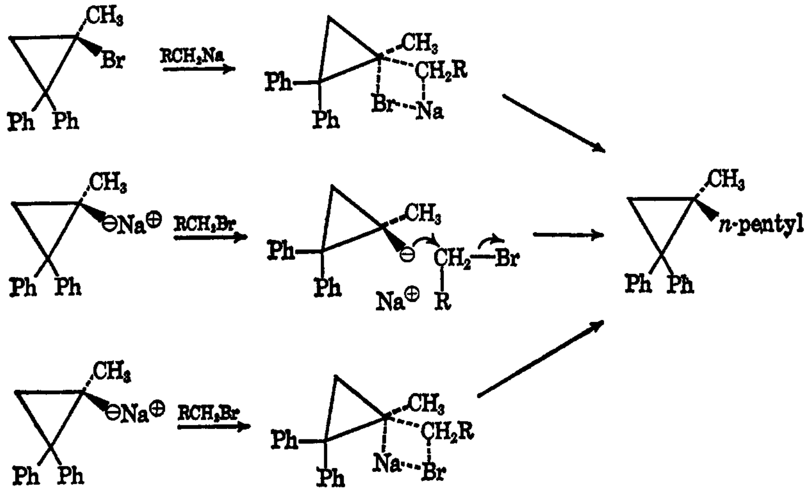
(3) H. M. Walborsky and A. E. Young, *ibid.*, **86**, 3288 (1964).

(4) H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **4**, 418 (1965).

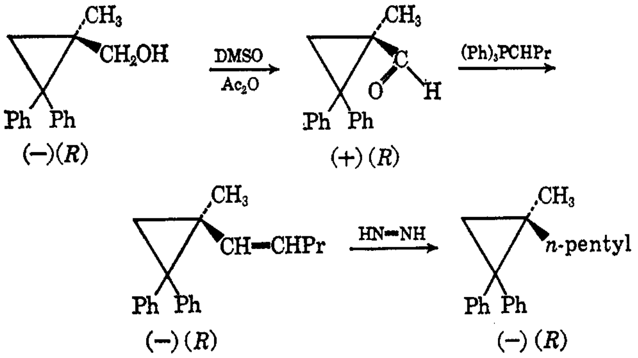
(5) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato *J. Amer. Chem. Soc.* **83**, 2517 (1961).

(6) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).

Scheme I



as (−)-1-bromo-1-methyl-2,2-diphenylcyclopropane,[2,6] it follows that (−)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane has the (*R*)-configuration and was produced in the original halogen–metal interchange reaction with retention of configuration.



Since carbonation of the mixture resulting from the reaction of *n*-pentylsodium with (−)-(*R*)-1-bromo-1-methyl-2,2-diphenylcyclopropane gives the corresponding (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, it is clear that some halogen–metal exchange must be occurring to give optically active 1-methyl-2,2-diphenylcyclopropylsodium. Using pentane as solvent, in contrast to more acidic solvents, the lifetime of the organosodium intermediate is long enough to permit it to be trapped with carbon dioxide. The over-all retention of configuration found is analogous to the stereochemistry of the reaction of *n*-butyllithium with the same bromide in ether solution. However, the optical purity of the resulting acid is only about 46% as compared to 100% in the case of the corresponding lithium compound. This may reflect the fact that the carbon–metal bond is less covalent in the organosodium intermediate and therefore leads to more rapid racemization.

The formation of the other products in the exchange reaction can be rationalized in several ways. Some of the 1-methyl-2,2-diphenylcyclopropane may be formed by hydrolysis of the cyclopropylsodium intermediate, but since the carbonation was carried out under anhydrous conditions it would seem unlikely that the bulk of it could result in this manner. Other possibilities for its formation are an E2 elimination by 1-methyl-2,2-diphenylcyclopropylsodium of bromide ion either from the amyl bromide formed in the exchange reaction or from starting material. A careful search of the reaction products did not reveal any of the known unsaturated cyclopropyl compounds, and therefore the latter reaction is considered improbable. The observation that the 1-methyl-2,2-diphenylcyclopropane that is formed has an optical purity considerably greater than the 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (83% *vs.* 46%) probably reflects the fact that the former is formed during the period that the halogen–metal exchange reaction is still going on, whereas the latter is not formed until the end of the reaction when carbon dioxide is added.

The formation of 1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane is an example, in the formal sense, of a Wurtz type reaction occurring on a cyclopropane ring. Wurtz reactions are generally believed to occur by an S_N2 displacement mechanism and are therefore unlikely with cyclopropyl halides since in this system displacement reactions of this type are energetically unfavorable. Moreover, such a displacement would lead to an inversion of configuration. In the case at hand and in some other recently reported examples,[7] the reaction proceeds with retention of configuration. At present there is no way of deciding which of the three possibilities in Scheme I is operative, but the first does not seem to allow for any racemization in the product and since the product is found to be only 66% optically pure, it would appear that either the second or third is a more probable pathway.

Perhaps worthy of comment are the attempts made to reduce the double bond in 1-(1-methyl-2,2-diphenylcyclopropyl)pentene without opening the cyclopropane ring in the synthesis of 1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane. Reduction with hydrogen using palladium on charcoal as catalyst gave the ring-opened product entirely. A similar observation has been made previously in an attempt to reduce the double bond of vinylcyclopropanes under these conditions.[8] An attempt to reduce the double bond by hydroboration followed by treatment of the intermediate organoboranes with propionic acid, according to the method of

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[7] R. M. Magid and J. G. Welch, *Tetrahedron Lett.*, 2613 (1967); K. Sisido, S. Kozima, and K. Takizawa, *ibid.*, 33 (1967).

[8] M. Yu Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).

Brown,[9] gave a mixture of starting material, ring-opened product, and the desired cyclopropane. The opening of a cyclopropane ring, under these general conditions, appears to be a function of the particular substituent on the ring since the cyclopropane rings in vinylcyclopropane and spiro[2.5]oct-4-ene do not appear to be cleaved by the hydroboration procedure[10] and yet cyclopropane itself is opened.[11]

Very good results can be obtained in saturating a double bond adjacent to a cyclopropane ring without concurrent ring opening by the use of diimide as the reducing agent. The reaction has been carried out both by the method of Corey[12] with copper ion catalyst and by the procedure of Van Tamelen[13] using dipotassium azodicarboxylate. No cleavage of the cyclopropane ring was observed and the only materials isolated were the saturated hydrocarbon and occasionally some starting material.[14]

Experimental Section[15]

Reaction of *n*-Pentylsodium with 1-Bromo-1-methyl-2,2-diphenylcyclopropane.—*n*-Pentylsodium was made according to the method described by Schlosser[16] from 1.79 ml (0.0148 mol) of *n*-pentyl chloride in 45 ml of dry pentane and 0.68 g (0.0296 g-atom) of sodium. The sodium was first dispersed in hot decalin, and, after cooling, the dispersed particles were washed several times with dry pentane. To the deep blue solution of *n*-pentylsodium was added 0.984 g (0.00343 mol) of racemic 1-bromo-1-methyl-2,2-diphenylcyclopropane in 20 ml of dry pentane at −25 to −15°. The mixture became yellow. After stirring for 5 min, the mixture was carbonated by bubbling in dry CO_2 gas until the yellow color disappeared and then for an additional 5 min. Finally, 5 ml of isopropyl alcohol and then water were added and the mixture was extracted with ether from a 5% NaOH aqueous phase. Both the aqueous and organic phases were retained.

The basic aqueous phase was acidified and then reextracted with ether. After drying and removal of the solvent, a residue smelling strongly of hexanoic acid was isolated. This was pumped down under high vacuum at 70° to remove most of the hexanoic acid which was caught in a cold trap and identified by its infrared spectrum. The residue consisted of a semicrystalline material, which on washing with a little hexane gave crystal, mp 183–187°. As a check on the purity of this 1-methyl-2,2-diphenylcyclopropanecarboxylic acid, the crystals were recombined with the hexane washings and the entire material was converted into the methyl ester with diazomethane. Gas chromatography showed that only one product was present and the retention time of this product was identical with that of methyl-1-methyl-2,2-diphenylcyclopropanecarboxylate.[17] The material was crystallized from hexane to give 0.073 g or 8.1% of the methyl ester: mp 92–93°; nmr (CCl_4), δ 6.75 to 7.50 (10 H, envelope), 3.20 (3 H, singlet), 2.19 (1 H, doublet, J = 5 cps), 1.32 (1 H, doublet, J = 5 cps), 1.13 (3 H, singlet).

The ether phases from the original extraction were dried and the solvents were then removed. Gas chromatography of the residue on a 4-ft column of ethylene glycol isophthalate on acid-washed Chromosorb P at 200° indicated the presence of four products, two of which were very minor. One of the major products appeared (from its retention time) to be 1-methyl-2,2-diphenylcyclopropane, and the other, which had a considerably longer retention time, was not identified at this point, but later was shown to be 1-pentyl-1-methyl-2,2-diphenylcyclopropane. The gas chromatograph indicated that the total weight of 0.820 g of nonacidic residue consisted of 25% low boilers (residual decalin), 37.5% 1-methyl-2,2-diphenylcyclopropane, 28.4% 1-pentyl-1-methyl-2,2-diphenylcyclopropane, and 3.5 and 5.3% of two unidentified minor products. From these data it could be deduced that the over-all yields of 1-methyl-2,2-diphenylcyclopropane and 1-pentyl-1-methyl-2,2-diphenylcyclopropane were 43.3 and 24.5%, respectively, based on the cyclopropyl bromide used as starting material.

Some of the two major components were separated and collected by gas chromatography. The material with retention time corresponding to that of 1-methyl-2,2-diphenylcyclopropane gave infrared and nmr spectra identical with those of the authentic material: nmr (CCl_4), δ 7.01 and 7.18 (10 H, both singlets), 1.00 to 1.83 (3 H, complex), 0.91 (3 H, doublet, J = 6 cps). The material with longer retention time crystallized after collection, mp 56–56.8°, and gave infrared and nmr spectra identical with those of authentic 1-pentyl-1-methyl-2,2-diphenylcyclopropane whose synthesis is described below.

In a second experiment *n*-pentylsodium was prepared from 0.216 g of sodium and 0.50 g of *n*-pentyl chloride. To this blue suspension in pentane was added 0.301 g of (−)-1-methyl-1-bromo-2,2-diphenylcyclopropane, $[\alpha]^{30}_{\mathrm{Hg}}$ +128.5°, in 10 ml of dry pentane. Work-up as before yielded an acidic and nonacidic residue. The hexanoic acid was removed from the acidic residue and the 1-methyl-2,2-diphenylcyclopropanecarboxylic acid was then distilled under high vacuum onto a cold finger: mp 175–185°, $[\alpha]^{30}_{\mathrm{Hg}}$ +18.9° (*c* 0.911, $CHCl_3$). The major products in the nonacidic residue were again collected by gas chromatography. The 1-methyl-2,2-diphenylcyclopropane, identified by its retention time and nmr and infrared spectra, had $[\alpha]^{30}_{\mathrm{Hg}}$ +129° (*c* 0.667, $CHCl_3$) or 83% optical purity. The 1-pentyl-1-methyl-2,2-diphenylcyclopropane, mp 53–55°, was again identified by its retention time and infrared and nmr spectra and had $[\alpha]^{30}_{\mathrm{Hg}}$ −30.3° (*c* 0.760, $CHCl_3$) or 66% optical activity.

(+)-1-Methyl-2,2-diphenylcyclopropanecarboxaldehyde.—A solution consisting of 3.048 g (0.0128 mol) of 1-methyl-2,2-diphenylcyclopropylcarbinol ($[\alpha]^{30}_{\mathrm{Hg}}$ −43.3), 40 ml of DMSO, and 25 ml of acetic anhydride was stirred overnight at room temperature. After this time, about one-half the acetic anhydride and DMSO was removed by distillation under reduced pressure. The remaining material was stirred with dilute NaOH for 5 min and then was extracted several times with ether. The ether phases were combined, washed twice with water, and then dried with $MgSO_4$. Evaporation of the solvents left a crystalline residue, mp 94–105°. Recrystallization from methanol failed to improve the melting point range and spectral data suggested that a mixture had been obtained. The crystalline material was chromatographed on alumina using hexane as an eluent and by collecting 75-ml fractions. A total of 1.20 g or 31.5% of α-(2,2-diphenyl-1-methylcyclopropyl)-1-thiomethyl dimethyl ether (mp 115–117°, $[\alpha]^{30}_{\mathrm{Hg}}$ −0.28° (*c* 0.454, $CHCl_3$)) was isolated in the first ten fractions. Recrystallization from 95% ethanol gave an analytical sample.

Anal. Calcd for $C_{19}H_{22}OS$: C, 76.47; H, 7.43. Found: C, 76.46; H, 7.53.

Both infrared and nmr spectra were consistent with the proposed structure. The nmr spectrum (CCl_4) showed peaks at δ 7.1–7.7 (10 H, complex), 2.1 (3 H, singlet), 1.1 (3 H, singlet) and three AB double doublets[18] at 4.58 and 4.42 (J = 11 cps), 3.44 and 3.03 (J = 9.5 cps), and 1.17 and 1.28 (J = 5 cps).

After removal of the above material, elution with 30% benzene in hexane gave 1.29 g or 42.5% of the desired aldehyde: mp 119–122°; $[\alpha]^{30}_{\mathrm{Hg}}$ +93.8° (*c* 0.210, $CHCl_3$). Infrared and nmr spectra were identical with those of material prepared by another method.[6] Nmr signals (CCl_4) were at δ 8.93 (1 H, singlet), 7.05 to 7.60 (10 H, complex), 2.12 (1 H, doublet, J = 5 cps), 1.72 (1 H, doublet, J = 5 cps), and 1.07 (3 H, singlet).

***cis*- and *trans*-1-(2,2-Diphenyl-1-methylcyclopropyl)pentene.**—The Wittig reagent from *n*-butyltriphenylphosphonium bromide was prepared according to the method of Mechoulam and

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[9] H. C. Brown and K. Murray, *J. Amer. Chem. Soc.*, **81**, 4108 (1959).

[10] S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).

[11] W. A. G. Graham and F. G. A. Stone, *Chem. Ind.* (London), 730 (1957).

[12] E. J. Corey, W. L. Mock, and J. Pasto, *Tetrahedron Lett.*, 347 (1961).

[13] E. E. Van Tamelen, R. S. Dewey, and R. J. Timmono, *J. Amer. Chem. Soc.*, **83**, 3725 (1961).

[14] Professor D. N. Kursanov has informed me that his procedure for ionic hydrogenation may be used to reduce double bonds conjugated with a cyclopropane ring: D. N. Kursanov, *Tetrahedron*, **23**, 2235 (1967).

[15] All melting points are uncorrected. Rotations at the 5461-Å mercury line were measured on a Bendix-Ericcson Model 987 ETL/NPL polarimeter.

[16] M. Schlosser, *Angew. Chem., Intern. Ed. Engl.*, **3**, 362 (1964).

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

[18] Reported as true chemical shifts $\nu_0\delta$ (ppm), see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. I, Pergamon Press, Inc., New York, N. Y., 1965, p 319.

Sondheimer[19] by suspending 3.4 g (0.00850 mol) of butyltriphenylphosphonium bromide in 50 ml of dry ether and then adding 5.3 ml (0.00850 mol) of a 1.617 *M* solution of *n*-butyllithium in hexane to this suspension over *ca.* 10 min. The mixture was stirred for 2 hr under argon and gradually became deep red. To this red solution was added 1.0 g (0.00425 mol) of (±)1-methyl-2,2-diphenylcyclopropanecarboxaldehyde in 15 ml of dry ether. The mixture became hot and as the red color faded a large quantity of white solid precipitated. The mixture was stirred overnight at room temperature and then the ether was gradually distilled off under argon and replaced by an equivalent amount of THF. The mixture was then refluxed for 3 hr, and after cooling, water and ether were added. The water layer was washed once with ether and the combined ether extracts were washed with dilute HCl and then with sodium bicarbonate solution. The ether layers were dried and the solvent was then removed to leave a residue which crystallized from hexane to give some rather impure triphenylphosphine oxide. Some of this material also remained in the hexane-soluble residue so this material was chromatographed on alumina using hexane as eluent. The desired hydrocarbon was eluted in the first four 75-ml fractions free of triphenylphosphine oxide. This material was combined and distilled in a cold finger apparatus to give 1.16 g or 99% of the desired racemic 1-(2,2-diphenyl-1-methylcyclopropyl)pentene.

Anal. Calcd for $C_{21}H_{24}$: C, 91.24; H, 8.75. Found: C, 91.18; H, 8.85.

Nmr and infrared spectra were consistent with the proposed structure. Nmr signals (CCl_4) were at δ 6.68–7.50 (10 H, complex), 4.90–5.48 (2.1 H, complex), 0.50–2.48 (12.7 H, complex).

The optically active material was prepared in a manner identical with that above from 0.592 g (0.00251 mol) of optically active 1-methyl-2,2-diphenylcyclopropanecarboxaldehyde, $[\alpha]^{30}_{\text{Hg}}$ +93.8°. Obtained were 0.660 g or 95% of optically active (−)-1-(2,2-diphenyl-1-methylcyclopropyl)pentene, $[\alpha]^{30}_{\text{Hg}}$ −38.6° (*c* 0.247, $CHCl_3$).

Hydrogen, Palladium, Charcoal Reduction of (±)1-(2,2-Diphenyl-1-methylcyclopropyl)pentene—To 1.16 g (0.00421 mol) of racemic 1-(2,2-diphenyl-1-methylcyclopropyl)pentene in 50 ml of absolute ethanol was added 0.25 g of a mixture of 5% palladium on charcoal. The resulting mixture was shaken overnight under 40 psi of hydrogen gas. The catalyst was removed by filtration and the ethanol evaporated. Gas chromatography indicated that the material produced was quite pure (one sharp peak), but it was not the same material as that previously isolated and suspected of being 2,2-diphenyl-1-methyl-1-pentylcyclopropane. Infrared and nmr spectra confirmed this conclusion and, furthermore, the nmr strongly suggested that the product was probably 1,1-diphenyl-3-methyloctane, that is the product resulting from opening the cyclopropane ring, since a well-defined triplet signal occurred at δ 4.08 ppm. This signal can be assigned to the benzhydryl proton in the above substance but is inconsistent with the material being the desired 1-pentyl-1-methyl-2,2-diphenylcyclopropane.

Hydroboration of (±)1-(2,2-Diphenyl-1-methylcyclopropyl)-pentene.—To a solution of 0.256 g (0.000927 mol) of (±)1-(2,2-diphenyl-1-methylcyclopropyl)pentene in 4 ml of dry diglyme was added 200 mg (0.00529 mol) of sodium borohydride. The solution was stirred and 1 ml of borontrifluoride etherate in 6 ml of dry diglyme was added over a period of 10 min. Stirring was continued for 1 hr at room temperature and then an additional 3 hr at refluxing temperature. Finally, 3 ml of propionic acid was added and refluxing was continued for 3 hr more. The mixture was extracted from dilute aqueous base with ether and the ether layers were washed several times. Finally, the ether was removed and the residue was reextracted from an aqueous phase with hexane. The hexane layers were dried and the solvent was removed. Gas chromatography of the residue at 225° on a 6-ft column of 15% Carbowax on acid-washed Chromosorb P indicated that it consisted of a mixture of starting material, some of the desired 1-pentyl-1-methyl-2,2-diphenylcyclopropane, and a good deal of the corresponding ring-opened product whose retention time was identical with that of the material obtained from reduction of 1-(2,2-diphenyl-1-methylcyclopropyl)pentene with hydrogen using palladium on charcoal catalyst. The gas chromatographic peaks were not well enough separated to get an accurate estimate of the percentage of each product present.

Reaction of (±)1-(2,2-Diphenyl-1-methylcyclopropyl)pentene with Hydrazine, Air, and Copper Catalyst—About 60 mg of the above hydrocarbon was mixed with 11 ml of 95% hydrazine and enough absolute ethanol was then added to affect solution. Air was bubbled in and a very dilute solution of copper sulfate in methanol was added dropwise, one drop about every 15 min. Reaction was continued for 3 hr and then water and ether were added and the organic material was extracted. The ether layers were washed with water and dried and the solvent was then removed. Gas chromatography at 225° on a 6-ft column of 15% Carbowax on acid-washed Chromosorb P indicated that the product consisted of about 30% 2,2-diphenyl-1-methyl-1-pentylcyclopropane and 70% starting material. An infrared spectrum was also consistent with this data. There was no indication of any ring-opened product.

Reaction of 1-(2,2-Diphenyl-1-methylcyclopropyl)pentene with Dipotassium Azodicarboxylate and Acetic Acid—Dipotassium azodicarboxylate was prepared according to the method of Thiele.[20] The yellow salt was stored in the cold under methanol until it could be used. To 0.189 g (0.000685 mol) of (±)1-(2,2-diphenyl-1-methylcyclopropyl)pentene dissolved in 10 ml of ethanol under nitrogen was added a 200-mg portion of the dipotassium salt and then about 0.2 ml of acetic acid. When the solution no longer showed the presence of the yellow salt, another 200-mg portion was added until a total of 4 g (0.0206 mol) of the salt had been added. Another 0.2 ml of acetic acid was also added after about one-half of the salt had been added. The total reaction took about 6 hr. Most of the ethanol was removed under reduced pressure and then water was added and the residue was extracted with hexane. The hexane layers were dried and the solvent was then removed to leave a residue whose gas chromatograph at 225° on a 6-ft column of 15% Carbowax on acid-washed Chromosorb P indicated it to be a mixture of about 75% of the desired (±)-1-pentyl-1-methyl-2,2-diphenylcyclopropane and 25% of the starting material. The residue was dissolved in 1 ml of methanol and allowed to stand at 0° for a few hours, crystalline (±)-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane was obtained, mp 53–55°. This material gave nmr and infrared spectra identical in every detail with those of the material isolated previously from the reaction of amylsodium with 1-bromo-1-methyl-2,2-diphenylcyclopropane. Nmr signals (CCl_4) were at δ 6.83–7.42 (10 H, complex), 0.50–1.60 (15.6 H, complex), 0.95 (sharp singlet superimposed on complex band).

Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.42. Found: C, 90.46; H, 9.44.

The optically active material was made in a similar manner to that described above from 0.354 g (0.00128 mol) of (−)-1-(2,2-diphenyl-1-methylcyclopropyl)pentene ($[\alpha]^{30}_{\text{Hg}}$ −38.6°), 10 g of dipotassium azodicarboxylate, and 1.0 ml of acetic acid. In this case gas chromatography of the product indicated it to consist of 87.5% of the desired saturated hydrocarbon and 12.5% starting material. Crystallization from methanol gave a white solid: mp 55–56°; $[\alpha]^{30}_{\text{Hg}}$ −43.3° (*c* 0.537, $CHCl_3$).

Registry No.—1-Methyl-2,2-diphenylcyclopropylsodium, 16299-35-7; (+)-(*R*)-methyl 1-methyl-2,2-diphenylcyclopropanecarboxylate, 16299-36-8; (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane, 16054-27-6; (−)-(*R*)-1-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane, 16109-74-3; (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, 4542-84-1; (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde, 16054-29-8; α-(2,2-diphenyl-1-methylcyclopropyl)-1-thiomethyldimethyl ether, 16299-37-9; (−)-(*R*)-1-(2,2-diphenyl-1-methylcyclopropyl)pentene, 16054-31-2; (±)-1-(2,2-diphenyl-1-methylcyclopropyl)pentene, 16054-21-0; (±)-*n*-pentyl-1-methyl-2,2-diphenylcyclopropane, 16054-32-3.

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