and the product was extracted with ether. The combined ether extracts were washed with dilute sulfuric acid, aqueous sodium hydroxide and water, and then dried over sodium sulfate. Unchanged acid (1.0 g.) was recovered from the alkaline extract. Removal of the solvent and fractional crystallization of the residue from petroleum ether gave 0.8 g. of (−)-3-methyl-4,4-diphenyl-2-butanone, m.p. 79–80°, $(\alpha)^{26}D$ −31.5 ± 2.2° ($CHCl_3$, *c* 1.170); λ_{max} (isoöctane) 286 mμ, ε 38.6; R.D. (*c* 0.54) in isoöctane: $(\alpha)_{700}$ +7°, $(\alpha)D$ +3°, $(\alpha)_{600}$ +1°, $(\alpha)_{350}$ +33°, $(\alpha)_{315}$ +215° (peak), $(\alpha)_{310}$ +166° (shoulder), $(\alpha)_{300}$ 0°, $(\alpha)_{290}$ −226°.

Only a plain dispersion curve was observed in methanol and in dioxane. The carbonyl absorption was observed as a shoulder on the larger benzenoid absorption (1st maximum 270 mμ). That this shoulder was actually the carbonyl absorption was demonstrated by observing the shifts of the absorption bands on changing the polarity of the solvent. In determining the maxima and extinction coefficients of the ketone and (−)-2-methyl-3,3-diphenylpropionaldehyde it was necessary to extrapolate the absorption curves.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.65; H, 7.61. Found: C, 85.71; H, 7.41.

(−)-S-2-Methyl-3,3-diphenylpropionaldehyde.—To a solution of 3.0 g. of chromic anhydride[40] in pyridine (30 ml.) was added 3.0 g. of 2-methyl-3,3-diphenylpropanol ($[\alpha]D$ +23.7°) in pyridine (30 ml.). The combined solutions were allowed to stand at room temperature for 22 hours, and then poured into an excess of water. The product was obtained by extraction with ether. The combined ether extracts were washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate and water, before drying over sodium sulfate. The residual oil, after removal of the solvent, was distilled to give 1.25 g. of the desired aldehyde, b.p. 113–114° (0.15 mm.), $(\alpha)^{26.5}D$ −14.3 ± 2.2° ($CHCl_3$, *c* 1.430); λ_{max} (isoöctane) 290 mμ, ε 50; R.D. (*c* 1.04) in isoöctane: $(\alpha)_{700}$ −38°, $(\alpha)D$ −46°, $(\alpha)_{400-390}$ −69° (plateau), $(\alpha)_{350}$ −50°, $(\alpha)_{340}$ −19° (peak), $(\alpha)_{335}$ −42°, $(\alpha)_{330}$ −65° (shoulder), $(\alpha)_{315}$ −194° (shoulder), $(\alpha)_{310}$ −218°. In the presence of air and light the aldehyde underwent rapid autoxidation, and it was necessary to use freshly prepared material for determination of physical constants.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.93; H, 7.32.

Morpholinothiocarbamide[41] of (−)-2-Methyl-3,3-diphenylpropionic Acid.—A mixture of thionyl chloride (2.2 g.) and (−)-2-methyl-3,3-diphenylpropionic acid (1.5 g., $[\alpha]D$ −52.6°) was allowed to stand at room temperature for 2 days. Excess of thionyl chloride was then distilled from the reaction product under reduced pressure. Without further purification the acyl chloride was dissolved in anhydrous acetone (40 ml.) and added to freshly dried potassium thiocyanate (0.6 g.). This mixture was refluxed for 1 hour, when 10 g. of dry morpholine was added. After refluxing for a further 10 minutes, the reaction mixture was allowed to stand overnight. The acetone was evaporated under reduced pressure, and the residue was dissolved in chloroform. The chloroform solution was washed with dilute hydrochloric acid and water, before drying over sodium sulfate. Removal of the solvent and crystallization of the solid residue from chloroform–petroleum ether gave 2.0 g. of the desired product, m.p. 171–172°, $(\alpha)^{26}D$ +36.1 ± 2.1° ($CHCl_3$, *c* 1.545); λ_{max} (MeOH) 275 and 342 mμ, log ε 4.15 and 2.61; R.D. in methanol (*c* 0.64): $(\alpha)_{700}$ +35°, $(\alpha)D$ +30°, $(\alpha)_{510}$ 0°, $(\alpha)_{400}$ −697°; (*c* 0.064): $(\alpha)_{380}$ −1820°, $(\alpha)_{372}$ −2100° (trough), $(\alpha)_{353}$ 0°, $(\alpha)_{320}$ +6060.

Anal. Calcd. for $C_{21}H_{24}O_2N_2S$: C, 86.44; H, 6.56. Found: C, 86.37; H, 6.75.

1,1-Dimethyl-2,2-diphenylethylene.—Triphenylisopropylphosphonium iodide[42] (10.8 g., 0.025 mole) was added to a solution of butyllithium (0.25 mole) in anhydrous ether (70 ml.) at 0° and under an atmosphere of nitrogen. The reaction mixture was stirred at this temperature for 2 hours and at room temperature for 4 hours. Benzophenone (6.0 g., 0.033 mole) was then added to the red colored solution and, after refluxing for 4 hours, the mixture was stirred overnight. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in petroleum ether, and again filtered. The precipitates were digested with hot petroleum ether and the washings were combined with the filtrate. Unreacted benzophenone was removed by elution of the petroleum ether solution from an alumina column; distillation of the partially purified product gave 2.8 g. (54%) of 1,1-diphenyl-2,2-dimethylethylene, b.p. 80° (0.08 mm.), $n^{21}D$ 1.5886; λ_{max} (95% ethanol) 244 mμ, ε 13000; reported for 1,1-diphenyl-2,2-dimethylethylene, $n^{23.5}D$ 1.586,[43] λ_{max} (heptane) 248 mμ, ε 11700.[44]

1,1-Diphenylbutene.—1,1-Diphenylbutene was prepared by the acid-catalyzed dehydration of 1,1-diphenylbutanol.[45] Gas–liquid chromatography showed that the product was homogeneous; b.p. 80–82° (0.1 mm.), $n^{20}D$ 1.5865°; λ_{max} (EtOH) 250 mμ, ε 12,700; reported[46] for 1,1-diphenylbutene, $n^{20}D$ 1.5898.

4,4-Diphenyl-1-butene.—Diphenylmethane (0.05 mole, 8.4 g.) in dry ether (100 ml.) was added to a solution of potassium amide (0.05 mole) in liquid ammonia (250 ml.). After stirring for 30 minutes, allyl chloride (0.05 mole, 4.0 g.) in dry ether (40 ml.) was added to the reaction mixture. The red color of the potassium diphenylmethide disappeared as the addition was completed. Excess of potassium amide was neutralized with ammonium chloride, and the ammonia was allowed to evaporate. The residual ether solution was filtered and, after removal of the solvent, was distilled under reduced pressure. The fraction b.p. 82–84° (0.12 mm.) was collected to yield 7.9 g. (76%), $n^{21.5}D$ 1.5739, infrared 995 and 920 $cm.^{-1}$ ($CH{=}CH_2$).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.74. Found: C, 92.16; H, 7.80.

(40) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(41) C. Djerassi and K. Undheim, *ibid.*, **82**, 5755 (1959).

(42) G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

(43) W. J. Hickenbottom and G. E. M. Moussa, *J. Chem. Soc.*, 4195 (1957).

(44) H. Suzuki, *Bull. Chem. Soc. (Japan)*, **33**, 619 (1960).

(45) R. Lagrave, *Ann. Chim. (France)*, **8**, 391 (1910).

(46) K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **74**, 365 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Cyclopropanes. XIV. The Haller–Bauer Cleavage Reaction[1,2]

BY F. J. IMPASTATO AND H. M. WALBORSKY

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The cleavage of (−)-(R)-1-benzoyl-1-methyl-2,2-diphenylcyclopropane by sodium amide in toluene produced (+)-(S)-1-methyl-2,2-diphenylcyclopropane. Under these conditions the reaction proceeds with complete retention of activity and configuration. The mechanism of the reaction is discussed.

Introduction

Evidence for at least a certain lack of geometric stability for the cyclopropyl carbanion exists in the base-catalyzed *cis–trans* conversions of the isomers of 1-benzoyl-2-nitro-3-phenylcyclopropane.[3] A sim-

(1) This work was supported by a grant from the Research Corporation.

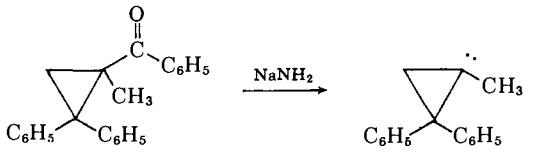
(2) For a preliminary communication see H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1958); H. M. Walborsky, *Rec. Chem. Prog.*, **23**, 75 (1962).

(3) E. P. Kohler and L. I. Smith, *J. Am. Chem. Soc.*, **44**, 624 (1922)

ilar study of the *cis–trans* isomerization of cyclopropyl esters by Julia and co-workers[4] gave similar results, with the additional finding that the rate of the transformation increased with increasing base strength of the reagent employed. It has also been demonstrated[5] that optically active 2,2-diphenylcyclopropyl cyanide was racemized by methoxide ion, although about one-fiftieth as fast as the acyclic methylethylacetonitrile. When the active cyclopropyl cyanide was alkylated, using lithium diisopropyl amide and methyl iodide in ether, the product was found to be racemic.[6]

In each of the above experiments, the cyclopropyl carbanions generated were adjacent to an unsaturated group, which by virtue of its electron delocalizing influence would undoubtedly be instrumental in lowering the energy requirements for the achievement of planarity (the rehybridization of the electron pair from a hybridized orbital into a p-orbital) and thereby give rise to racemization or *cis–trans* interconversion. On the other hand, such delocalization is somewhat disfavored by stereoelectronic factors causing the bond exocyclic to the cyclopropane ring to have a high energy (I-strain). Apparently, the strain involved is not sufficient to prevent passage of the molecule through such a high energy planar structure. That such an energy barrier to planarity does indeed exist is supported by the observation that the rate of deuterium exchange in 2,2-diphenylcyclopropyl cyanide was about 8×10^3 faster than the rate of racemization.[7] The question now arises as to whether a cyclopropyl carbanion, lacking substituents capable of delocalizing the pair of electrons, would be able to maintain its spatial configuration.

The Haller–Bauer cleavage of 1-benzoyl-1-methyl-2,2-diphenylcyclopropane was chosen for investigation since it has been postulated[8] that this cleavage reaction proceeds through a carbanion intermediate which would in this case give rise to the 1-methyl-2,2-diphenylcyclopropylcarbanion.

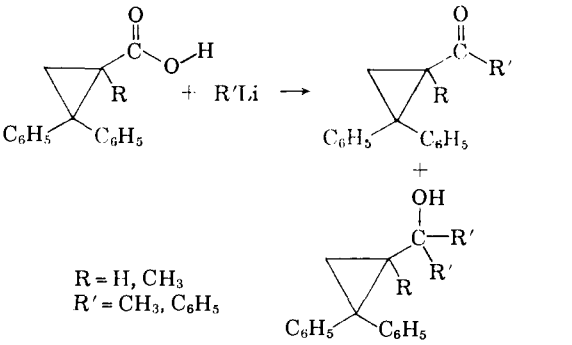


Since this carbanion contains no unsaturated groups adjacent to the negative charge, its formation from an optically active ketone should yield the desired information concerning the optical stability of the carbanion. Moreover, such information will provide a further insight into the mechanism of the Haller–Bauer cleavage reaction.

Results and Discussion

Syntheses.—Several procedures for the preparation of ketones were evaluated in order to determine the most convenient method. Treatment of 2,2-diphenylcyclopropylnitrile with phenylmagnesium bromide at room temperature resulted in a 20% yield of the corresponding ketone. The analogous reaction with 1-methyl-2,2-diphenylcyclopropylnitrile was abortive. An 81% yield of 1-methyl-1-benzoyl-2,2-diphenylcyclopropane was realized by the reaction of diazodiphenylmethane with isopropenyl phenyl ketone. The 1-benzoyl-2,2-diphenylcyclopropane was prepared in 51% yield by the addition of α-diazoacetophenone to 1,1-diphenylethylene at 140° in the presence of copper powder.

In the above cases, where the yields were satisfactory, the ketones obtained were racemic. Since the resolution of an acid is generally more convenient than resolution of a ketone, the method of Tegnér[9] was employed. The addition of phenyllithium and methyllithium to 2,2-diphenylcyclopropanecarboxylic acid and 1-methyl-2,2-diphenylcyclopropanecarboxylic acid provided the desired methyl and phenyl ketones in good yields. The main side product of the reaction is the corresponding tertiary alcohol. Ordinarily the alcohol and the ketone can be separated by either fractional crystallization or column chromatography. However, in the case of the 1-methyl-1-benzoyl-2,2-diphenylcyclopropane and (1-methyl-2,2-diphenylcyclopropyl)-diphenylcarbinol mixture, these substances were not separable by conventional methods. The mixture was treated with *p*-toluenesulfonic acid in order to convert the carbinol into 1,1,4,4-tetraphenylisoprene,[10] in the hopes that the ketone could be separated from the hydrocarbon by column chromatography. This turned out to be the case, but unfortunately the ketone was also acid sensitive[11] and was in turn converted to 1,1,4-triphenyl-3-methyl-1-butene-4-one. This problem was solved by heating the mixture with *p*-toluenesulfonyl chloride in *pyridine*. Under these reaction conditions the carbinol was converted to the isoprene derivative which was separated quite readily from the ketone which under the basic conditions employed was unaffected. Treatment of (+)-(R)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid with phenyllithium produced (−)-(R)-1-methyl-1-benzoylcyclopropane and (−)-(R)-(1-methyl-2,2-diphenylcyclopropyl)-diphenylcarbinol. Although the active carbinol was not



(4) M. Julia, S. Julia, B. Bemont and G. Tchernoff, *Compt. rend.*, **248**, 242 (1959).

(5) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **78**, 872 (1956).

(6) H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6026 (1955).

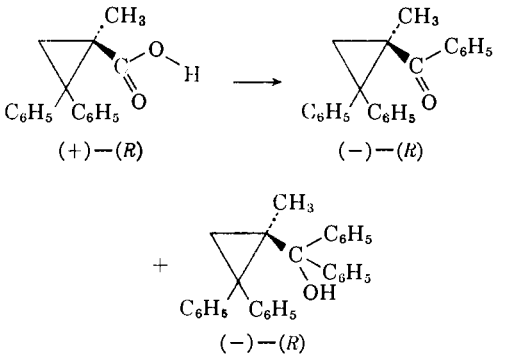
(7) H. M. Walborsky, A. A. Youssef and J. M. Motes, *ibid.*, **84**, 2465 (1962).

(8) For a review see K. E. Hamlin and A. W. Weston, *Org. Reactions*, **9**, 1 (1957).

(9) C. Tegnér, *Acta Chem. Scand.*, **6**, 782 (1952); K. Mislow and C. L. Hamermesh, *J. Am. Chem. Soc.*, **77**, 1590 (1955).

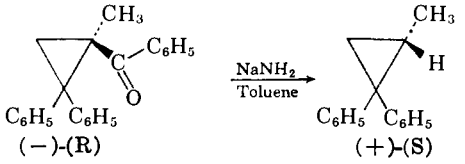
(10) H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6396 (1955); H. M. Walborsky and F. M. Pendleton, *ibid.*, **83**, 1405 (1960).

(11) H. M. Walborsky and L. Plonsker, *ibid.*, **83**, 2138 (1961).



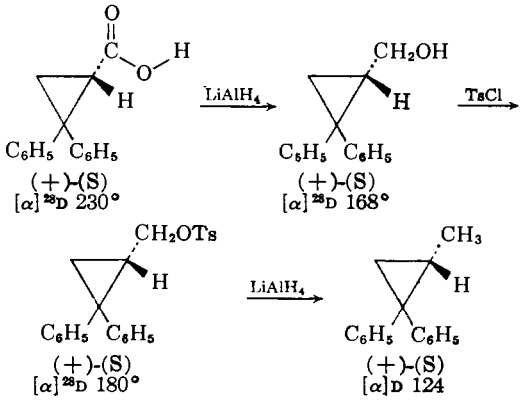
isolated from the reaction mixture it has the (−)-R-configuration since it has been independently prepared from the (+)-(R)-acid.[11]

Haller–Bauer Cleavage.—Since there was conflicting evidence[8,12] concerning the direction that this cleavage might take, a sample of racemic ketone was subjected to the Haller–Bauer reaction conditions. Fortunately, the product formed in good yield was 1-methyl-2,2-diphenylcyclopropane showing that it was the cyclopropyl moiety that cleaved. Cleavage of the optically active ketone, $[\alpha] -33 \pm 1°$, gave rise to the hydrocarbon 1-methyl-2,2-diphenylcyclopropane, which was also optically active $[\alpha] +127 \pm 1°$.

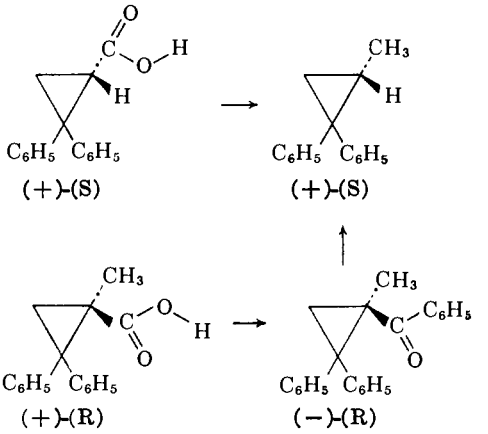


The formation of the optically active hydrocarbon in this reaction raises two questions: 1. To what extent has the optical activity been maintained? 2. Does the reaction proceed with inversion or retention of configuration?

The first question was answered by converting optically pure (+)-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]_D$ 230°, to the hydrocarbon. (+)-1-methyl - 2,2 - diphenylcyclopropane, $[\alpha]_D$ 127°. This clearly demonstrates that the *Haller–Bauer cleavage proceeds with complete retention of optical activity.*



In order to determine whether the reaction proceeds with inversion or retention of configuration, it is only necessary to relate the configuration of 2,2-diphenylcyclopropanecarboxylic acid and 1-methyl-2,2-diphenylcyclopropanecarboxylic acid. It has recently been shown[13] that (−)-2,2-diphenylcyclopropanecarboxylic acid is related in configuration to (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid. Since the *enantiomer* of the former acid was converted by unambiguous reactions to (+) - 1 - methyl - 2,2 - diphenylcyclopropane (*vide supra*), and since the latter acid was converted to the (−)-1-benzoyl-1-methyl-2,2-diphenylcyclopropane which was cleaved by sodium amide in toluene to the (+)-hydrocarbon, it follows that the *Haller–Bauer cleavage occurs with retention of configuration.* The configurational relationship is summarized as



The absolute configuration of 1-methyl-2,2-diphenylcyclopropane has been established by a direct chemical correlation with (+)-propylene oxide.[14] The (+)-hydrocarbon was shown to possess the *R*-configuration and therefore the absolute configurations of all substances that have been related to this hydrocarbon have been established.[15]

The final question that remains concerns itself with the possible mechanism of the reaction, including whether or not one is dealing with a discrete carbanion intermediate.

A cyclic concerted mechanism, such as depicted below (path A), has been suggested.[2] This mechanism would account for the observed stereochemistry of the reaction. Alternatively, the intermediate I can dissociate into a carbanionic species and a benzamide molecule (path B). That the latter mechanism is the more probable one is suggested by the recent work of Cristol and Freeman,[16] in which it was shown that the cleavage of dehydronorcamphor produced Δ^3-cyclopentenylacetamide rather than the Δ^2-isomer. If the concerted mechanism (path A) was operative, then one would have expected the exclusive formation of the Δ^2-isomer.

Further evidence in support of the carbanion or ion-pair intermediate is found in the following

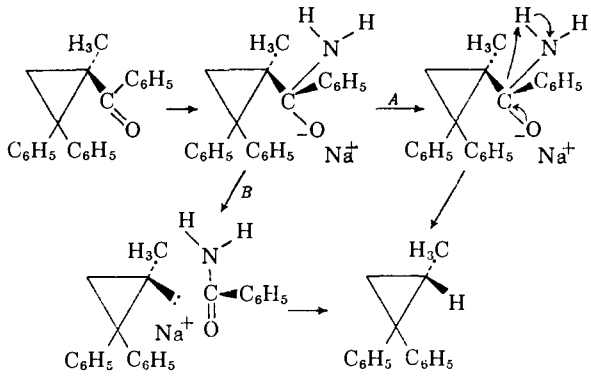
(12) A. Haller and E. Benoist, *Ann. Chim.*, **17**, 25 (1921); F. J. Piehl and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 5023 (1953).

(13) H. M. Walborsky, L. Barash, A. E. Young and F. J. Impastato, *ibid.*, **83**, 2517 (1961).

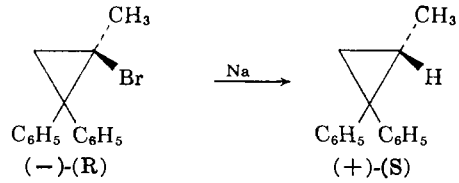
(14) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).

(15) In this article all structural formulas are drawn in their absolute configuration.

(16) S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).



experiments. When optically active (−)-(R)-1-bromo - 1 - methyl - 2,2 - diphenylcyclopropane[17] was treated with sodium in refluxing toluene, the hydrocarbon (+)-(S)-1-methyl-2,2-diphenylcyclopropane was produced and found to be 61% optically pure.[18] A similar result was obtained when the Haller–Bauer cleavage was carried out



using sodium piperidide in refluxing piperidine. Under these conditions the hydrocarbon was produced with an optical purity of 66%. The roughly 34–39% racemization (17–20% inversion) would not be unusual when one considers that under these reaction conditions no benzamide as a proton source is available at the immediate reaction site, and therefore the protons must come from the solvent shell. A similar stereochemical result was observed by Cram[19] in which the cleavage of (−)-1,2-diphenyl-2-methyl-1-butanone by potassium N-methylanilide in N-methylaniline produced (+)-2-phenybutane of 63% optical purity.

Experimental

1-Benzoyl-2,2-diphenylcyclopropane. Procedure A—A 100-ml. three-neck round-bottom flask was equipped with pressure-equalized dropping funnel, ball joint-sealed mechanical stirrer, and condenser. An excess of 1,1-diphenylethylene (20 ml.) and a catalytic amount of copper powder were placed in the flask, and a solution of 2.9 g. (0.02 mole) of α-diazoacetophenone[20] in 5 ml. of the same olefin was placed in the dropping funnel. The contents of the flask were brought to a temperature of 140° by means of an electrically heated oil-bath, and, when equilibrium was attained, the system was connected to an inverted separatory funnel filled with water which served to measure the evolved nitrogen. A few drops of the diazo solution were added from the dropping funnel, and the stirrer set in motion. After gas evolution began, the remainder of the diazo solution was added at such a rate that a steady flow of nitrogen was maintained (15 min.). At the end of the reaction, a corrected volume of 404 ml. of nitrogen had been collected (90% of theory). The hot mixture was filtered to remove the copper catalyst, and the filtrate collected in a distilling flask. Almost all of the excess olefin was removed by distillation at reduced pressure. The residue, which set to a pasty mass on cooling, was dissolved in hot ethanol, partially decolorized with charcoal, filtered, and allowed to cool. The ketone was obtained as colorless plates and weighed 2.5 g. (46%), m.p. 133–134°. An additional 0.5 g. of product was obtained by evaporation of the mother liquor and chromatography of the residue, bringing the total yield to 51% of theory. The ketone did not react with aqueous permanganate, but slowly decolorized a solution of bromine in carbon tetrachloride; infrared spectrum, 1675 cm.$^{-1}$ (C=O); ultraviolet spectrum, $10^{-5}M$, isoöctane: λ_{max}, 242 mμ; ε, 18,600.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.88; H, 6.36.

Procedure B.—A slurry of 4.6 g. (0.015 mole) of 2,2-diphenylcyclopropanecarbonitrile[5] in 50 ml. of anhydrous diethyl ether was added over a period of 10 minutes to a well-stirred solution of 0.02 mole of phenylmagnesium bromide in 30 ml. of ether. The mixture was stirred for an additional 30 minutes and then hydrolyzed by the dropwise addition of 6 ml. of an aqueous solution containing 1.5 g. of ammonium chloride. The clear ethereal solution was decanted and the residual pasty mass washed thoroughly with four 20-ml. portions of ether. The washings and the solution were combined and the solvent evaporated at reduced pressure. After treatment with charcoal and four recrystallizations, the solid residue still retained a yellow color and melted over the range 133–139°. The product was then taken up in 1:1 benzene–ligroin, and the resulting solution passed through 30 g. of alumina contained in a 30-ml. sintered glass funnel. Evaporation of the solvent and recrystallization of the residue from ethanol yielded 0.9 g. of ketone (20%) identical with that obtained by procedure A, m.p. 134°.

Procedure C.—A solution of 4.7 g. (0.02 mole) of 2,2-diphenylcyclopropanecarboxylic acid[5] in 150 ml. of anhydrous ether was added to a solution of 0.06 mole of phenyllithium in 200 ml. of ether. The addition was completed in 20 minutes, and stirring was continued for another 20 minutes. The mixture was hydrolyzed by pouring into 250 ml. of water containing 5 g. of ammonium chloride. The ethereal layer was separated and washed with 50-ml. portions of saturated aqueous sodium chloride solution until the washings were neutral to litmus. The ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent removed at reduced pressure. The thick oily residue was solidified by trituration with petroleum ether. Recrystallization of the crude product from ethanol afforded 3 g. (51%) of the desired ketone. Concentration of the mother liquor gave an additional 1.5 g. of product, bringing the total yield to 73%. Again, the ketone was found to be identical with that prepared by procedures A and B.

1-Acetyl-2,2-diphenylcyclopropane.—Treatment of 24 g. (0.1 mole) of 2,2-diphenylcyclopropanecarboxylic acid[5] with 0.3 mole of methyllithium, as outlined in procedure C above, yielded 20.3 g. (87%) of the desired ketone, obtained as a colorless, viscous liquid boiling at 159–160° (2.5 mm.) and 168–170° (4 mm.) (bath temperature, 200°). The 1-acetyl-2,2-diphenylcyclopropane thus obtained gave a positive iodoform test, did not react with aqueous permanganate, and slowly decolorized a solution of bromine in carbon tetrachloride; spectra: infrared, 1695 cm.$^{-1}$ (C=O); ultraviolet ($10^{-5}M$, isoöctane), λ_{max}, 223 mμ, ε, 15,100; near-infrared, λ_{max}, 1.64 μ.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.19; H, 7.07.

1-Methyl-1-acetyl-2,2-diphenylcyclopropane was also prepared by procedure C above. Treatment of 5 g. (0.02 mole) of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid[5] with 0.06 mole of methyllithium resulted in a crude product, which after two recrystallizations from ethanol, yielded 2.5 g. (50%) of the desired ketone, m.p. 88.5–89°. The iodoform test was inconclusive. The ketone reacted slowly with bromine in carbon tetrachloride, but was not affected by aqueous potassium permanganate; spectra: infrared, 1690 cm.$^{-1}$ (C=O); ultraviolet ($10^{-5}M$, isoöctane), λ_{max}, 223 mμ, ε, 17,900; near-infrared, λ_{max}, 1.64 μ.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.19; H, 7.46.

1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—The attempted synthesis of this ketone by reaction of 1-methyl-2,2-diphenylcyclopropanecarbonitrile[5] and phenylmagnesium bromide at room temperature (procedure B, above) resulted in essentially complete recovery of unchanged

(17) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959).

(18) This experiment was performed by Mr. J. Webb.

(19) D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5740 (1959).

(20) M. S. Newman and P. F. Beal, *ibid.*, **71**, 1506 (1949).

starting material. When the reaction was conducted in tetrahydrofuran solvent at the reflux temperature, only an intractable tar resulted, from which no identifiable product could be obtained.

The treatment of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid with phenyllithium as in procedure C above produced the desired ketone in yields ranging from 65–71%, m.p. 105–107°. The ketone was unreactive toward aqueous permanganate solution, but slowly decolorized a solution of bromine in carbon tetrachloride; spectra: infrared, 1675 cm.$^{-1}$ (C=O); ultraviolet (10^{-5} *M*, isoöctane) λ_{max}, 240 mμ, ϵ, 16,700; near-infrared, λ_{max}, 1.64 μ.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.67; H, 6.60.

Optically Active 1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—Preparation of the optically active ketone by the phenyllithium procedure required minor modifications, in order to keep the formation of the corresponding tertiary carbinol at a minimum. In the racemic preparation, the carbinol was produced in negligible quantities, and was easily separated from the desired product by recrystallization. Using the same procedure for the preparation of the optically active ketone, however, resulted in the formation of copious quantities of carbinol (30–35%) and separation, in this case, could not be accomplished by physical methods.

The following procedure was found to be more advantageous. A solution of 0.1 mole of phenyllithium in 250 ml. of anhydrous ether was added rapidly (5 min.) to a stirred solution of 12.2 g. (0.05 mole) of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (having $[\alpha]^{23}D$ +34 ± 1°) in 500 ml. of anhydrous ether. Stirring was continued for 5 minutes after the addition. The mixture was hydrolyzed, and the product isolated as in the above procedure. After hydrolysis, 6 g. of unreacted acid was recovered from the aqueous phase. On evaporation of the solvent from the organic phase, an oil was obtained which could not be solidified. The infrared spectrum indicated that the crude product was the desired ketone contaminated with a small amount of carbinol. The mixture was dissolved in 20 ml. of pyridine and treated with an excess of *p*-toluenesulfonyl chloride (5 g.) for 2 hours on the steam-bath. The solution was poured onto 100 g. of cracked ice, and the organic product extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent evaporated, leaving an oily residue. Chromatography of the oil on an alumina column yielded a small amount of a white crystalline hydrocarbon, which proved to be 1,1,4,4-tetraphenyl-2-methylbutadiene[11] (by comparison with a sample prepared by an alternate method), and 5 g. of the desired ketone, as a colorless oil which solidified on standing overnight. The yield of ketone, based on unrecovered starting material, was 64% of theory. The 1-methyl-1-benzoyl-2,2-diphenylcyclopropane thus obtained had m.p. 75.5–77° and $[\alpha]^{23}D$ −33 ± 1° (*c* 1.733, $CHCl_3$), was unaffected by aqueous permanganate and slowly decolorized a solution of bromine in carbon tetrachloride. Its infrared spectrum in chloroform was identical with that of the racemic ketone.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.49; H, 6.49.

Alternate Preparation of Racemic 1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—A solution of 19.4 g. (0.1 mole) of diphenyldiazomethane in 15 ml. of isopropenyl phenyl ketone[21] was added to a fourfold excess of the unsaturated ketone, held at 120° by an electrically heated oil-bath. Nitrogen was given off immediately, and the addition was completed as rapidly as frothing (due to nitrogen evolution) would permit. After completion of the reaction, evidenced by the decolorization of the diphenyldiazomethane, most of the excess unsaturated ketone was removed by vacuum distillation. The viscous residue solidified on trituration with a small amount of methanol. Recrystallization from methanol yielded 25 g. (81%) of the racemic ketone, m.p. 104–106.5°, which did not depress the melting point of the previously prepared material.

1-Methyl-2,2-diphenylcyclopropyldiphenylcarbinol.—A solution of 13.3 g. (0.05 mole) of 1-methyl-2,2-diphenylcyclopropyl methylcarboxylate in 100 ml of anhydrous ether was added to a stirred solution of 0.2 mole of phenylmagnesium bromide in 300 ml. of anhydrous ether, and the mixture was stirred under reflux for 18 hours (previous reaction time of 2 hours resulted in recovery of unreacted ester). Hydrolysis was effected by the dropwise addition of saturated aqueous ammonium chloride solution, such that the magnesium halide separated as a pasty mass, from which the supernatant ethereal solution was cleanly decanted. The inorganic residue was washed with two 50-ml. portions of ether, and the washings combined with the ether solution. The solvent was evaporated with the water aspirator, and the crystalline residue was recrystallized from ethanol–ethyl acetate to yield 12.4 g. (62%) of the carbinol, m.p. 149–150°; spectra: infrared, 3540 cm.$^{-1}$ (free OH); near-infrared, λ_{max}, 1.64 μ.

Anal. Calcd. for $C_{29}H_{26}O$: C, 89.19; H, 6.68. Found: C, 89.42; H, 6.47.

1,1,4,4-Tetraphenyl-2-methylbutadiene.—1-Methyl-2,2-diphenylcyclopropyldiphenylcarbinol was dehydrated, by treatment with *p*-toluenesulfonyl chloride in pyridine, in a manner similar to that described by Walborsky and Hornyak,[10] to give the diene in yields of 80–90%. Recrystallization from ethanol gave the diene as needles which showed a blue-violet fluorescence, particularly when wet with solvent. This material had m.p. 137.5–138.5° and was identical with the hydrocarbon obtained in the preparation of optically active 1-methyl-1-benzoyl-2,2-diphenylcyclopropane, discussed earlier; spectra: ultraviolet, λ_{max}, 239,317 mμ; ϵ, 26,800, 19,400 ($10^{-5}M$, isoöctane). These data compare favorably with the ultraviolet absorption data obtained for 1,1,4,4-tetraphenylbutadiene[10] ($10^{-5}M$, isoöctane), λ_{max}, 245, 342 mμ; ϵ, 26,800, 31,400.

Anal. Calcd. for $C_{29}H_{24}$: C, 93.74; H, 6.60. Found: C, 93.51; H, 6.49.

The Haller–Bauer Cleavage. Sodium Amide Cleavage of 1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—A mixture of 3 g. (0.075 mole) of sodium amide, 9.3 g. (0.03 mole) of the 1-benzoyl-1-methyl-2,2-diphenylcyclopropane and 80 ml. of anhydrous toluene was refluxed for 5 hours, with stirring. During this time, the liquid phase gradually changed from colorless to a deep red-brown color. The mixture was cooled by immersing the reaction vessel in an ice-bath, and 50 g. of cracked ice was added to the contents. The two-phase mixture was transferred to a separatory funnel, and the aqueous lower layer drawn off. The toluene layer was washed with saturated aqueous sodium chloride solution, until the washings were neutral to litmus. The solution was filtered, and the toluene evaporated on the steam-bath, with the aid of an aspirator. The dark brown residual oil was vacuum distilled, and the fraction boiling at 106–107° (2.5 mm.) (bath temperature, 135°) was collected as a colorless liquid weighing 4.9 g. (79%). The product, methyl-2,2-diphenylcyclopropane, did not react with aqueous permanganate but slowly decolorized a solution of bromine in carbon tetrachloride. Its near-infrared spectrum showed an absorption at 1.64 μ, $n^{23}D$ 1.5788, d^{25}_{25} 0.977; M_D calcd. 69.27, found 70.78.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.52; H, 7.84.

Under identical conditions, 1.5 g. (0.005 mole) of optically active α-methyl ketone with $[\alpha]^{22}D$ −33 ± 1° (*c* 1.733, $CHCl_3$) and m.p. 75.5–77.5° yielded 676 mg. (68%) of optically active methyl-2,2-diphenylcyclopropane, which, after elution on alumina, boiled at 104–105° (2 mm.) (bath, 135°) and had $[\alpha]^{24}D$ +127 ± 0.7° (*c* 1.330, $CHCl_3$). The infrared spectrum of the optically active product was identical with that of the racemic hydrocarbon.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.71.

A small amount of petroleum ether-insoluble material was isolated from the crude reaction mixture, which proved to be optically active 1-methyl-2,2-diphenylcyclopropanecarboxamide. Its infrared spectrum was identical with that of an authentic sample. The optically active amide had $[\alpha]^{24}D$ +78 ± 3° (*c* 0.315, $CHCl_3$) and m.p. 177.5–178°.

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.18; H, 7.07; N, 5.68.

Sodium Piperidide Cleavage of 1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—A solution of sodium piperidide in piperidine was prepared by refluxing a mixture of 1 g. (0.025 mole) of sodium amide and 30 ml. of piperidine until ammonia ceased to be evolved (about 2 hours). To the reagent, thus prepared, was added a solution of 3.12 g. (0.01 mole) of the ketone in 20 ml. of piperidine, and the refluxing main-

(21) J. H. Burkhalter and R. C. Fuson, *J. Am. Chem. Soc.*, **70**, 4184 (1948).

tained for 5 hours. The hot reaction mixture was poured onto 400 g. of cracked ice, and the resulting mixture was extracted with four 50-ml. portions of ether. The combined ether extracts were washed with dilute hydrochloric acid until the washings were acid to litmus, and then with water. The excess water was removed by passage of the solution through a fluted filter containing 25 g. of anhydrous sodium sulfate. Evaporation of the solvent from the filtrate yielded a dark brown, viscous oil, which was eluted on a column of alumina with petroleum ether. The resulting clear liquid was evaporatively distilled to yield 1.2 g. (57%) of the expected hydrocarbon. The infrared spectrum of this product showed it to be identical with the hydrocarbon obtained *via* the sodium amide cleavage.

Under identical reaction conditions, 1.3 g. (0.004 mole) of optically active ketone having $[\alpha]^{24}D$ $-32 \pm 1.5°$ (*c* 0.843, $CHCl_3$) gave 471 mg. (54%) of pure hydrocarbon, which was shown to be identical with earlier preparations. This material, however, was only 66% optically pure, having $[\alpha]^{22}D$ $+85 \pm 2°$ (*c* 0.392, $CHCl_3$). Racemization to the extent of 34% had occurred during the course of the reaction.

2,2-Diphenylcyclopropylcarbinyl-*p*-toluenesulfonate.—To a solution of 3.8 g. (0.02 mole) of *p*-toluenesulfonyl chloride in 4 ml. of 2,6-lutidine (cooled to 0°) was added a solution of 2.1 g. (0.01 mole) of 2,2-diphenylcyclopropylcarbinol in 4 ml. of lutidine. The mixture was allowed to stand at room temperature for 2 hours, when it had set to a solid mass. Dropwise addition of 2 ml. of water caused the mass to liquefy, and its was poured into 75 ml. of water contained in a separatory funnel. The precipitated solid was extracted with three 50-ml. portions of ether, and the combined ether extracts were washed successively with water, 5% hydrochloric acid, water, 5% potassium hydroxide solution, and water. The ethereal solution was freed of excess water by passage through a fluted filter containing 30 g. of anhydrous sodium sulfate. The solvent was evaporated on the steam-bath, a stream of air being used to keep the temperature below 30°. When the first traces of solid appeared, the flask was removed from the steam-bath, and the residual solvent evaporated by the air stream. Recrystallization from petroleum ether containing a small amount of chloroform yielded 3.1 g. (90%) of the desired tosylate. The decomposition point varied from 58–80°, depending on the rate of heating. No satisfactory elemental analysis was obtained; however, the infrared spectrum showed bands (ascribed to the covalent sulfonate linkage) at 1365 and 1170 cm.$^{-1}$.

In the same manner, 1.2 g. (0.0054 mole) of active carbinol having $[\alpha]^{24}D$ $+167 \pm 3°$ (0.303, $CHCl_3$) gave a quantitative yield of optically active tosylate with $[\alpha]^{23}D$ $+98 \pm 4°$ (0.149, $CHCl_3$) and infrared absorption bands at 1365 and 1170 cm.$^{-1}$.

Methyl-2,2-diphenylcyclopropane.—Three grams of 2,2-diphenylcyclopropylcarbinyl tosylate (0.08 mole) was added rapidly (in the solid phase) to a well-stirred slurry of 3 g. of lithium aluminum hydride and 100 ml. of anhydrous ether. After 5 hours, 20 ml. of tetrahydrofuran was added, and the stirring continued for an additional 19 hours. The reaction was worked up in the usual manner. The liquid product obtained was distilled under vacuum, giving 1.12 g. (67%) of pure methyl-2,2-diphenylcyclopropane, boiling at 122.5° (4 mm.) (bath, 145°). Infrared spectra showed this hydrocarbon to be identical with the 1-methyl-2,2-diphenylcyclopropane obtained in the cleavage reactions.

Similarly, reduction of 1.7 g. (0.0045 mole) of optically active tosylate having $[\alpha]^{29}D$ $+98 \pm 4°$ (0.149 $CHCl_3$) by a weight-equivalent of lithium aluminum hydride, as outlined above, gave 607 mg. (65%) of pure, optically active 1-methyl-2,2-diphenylcyclopropane. Its identity was established by comparison with hydrocarbon prepared by the various procedures, and its specific rotation was $[\alpha]^{26}D$ $+127 \pm 2°$ (*c* 0.388, $CHCl_3$).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.82.

Metallation of (−)-(R)-1-Bromo-1-methyl-2,2-diphenylcyclopropane.[17]—To 0.7 g. of sodium sand dispersed in 25 ml. of toluene was added 2.0 g. of the bromide, and the mixture was refluxed, with stirring, for 7.5 hours. The reaction mixture was cooled and poured onto a Dry Ice and ether slurry. Upon workup, no acidic material was isolated, but the neutral fraction yielded an oil which was distilled *in vacuo* to give 0.67 g. (46%) of 1-methyl-2,2-diphenylcyclopropane, $[\alpha]^{26}D$ $+78 \pm 2°$ (*c* 5.8, $CHCl_3$), 61% optically pure. The infrared spectrum was identical in all respects with that of an authentic sample.

Repetition of the above using benzene as a solvent produced the hydrocarbon in 49% yield, $[\alpha]^{26}D$ $+89 \pm 2°$ (*c* 1.06, $CHCl_3$), 70% optically pure.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXVI. Synthesis and Stereochemistry of Bicyclo[5.1.0]octanols[1,2]

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endo- and *exo*-bicyclo[5.1.0]octan-3-ol and *endo-* and *exo*-bicyclo[5.1.0]octan-4-ol have been synthesized and their configurations have been established. In so doing, all six of the methylcycloheptanols were prepared and their configurations were established. Additional evidence for the assignment of configurations to *endo-* and *exo*-bicyclo[5.1.0]octan-2-ol also has been obtained.

endo- and *exo*-bicyclo[5.1.0]octan-2-ol have been obtained as the principal products of the solvolysis of 3-cycloöcten-1-yl brosylate.[3,4] However, *endo-* and *exo*-bicyclo[5.1.0]octan-3-ol and *endo-* and *exo*-bicyclo[5.1.0]octan-4-ol have not been described before, and their syntheses were undertaken in order to investigate the solvolysis of their derivatives. This paper describes the synthesis and stereochemistry of bicyclo[5.1.0]octan-3-ols and bicyclo[5.1.0]octan-4-ols. The stereochemistry of the bicyclo[5.1.0]octan-2-ols is also discussed. The solvolysis of suitable derivatives of the six bicyclo[5.1.0]octanols is described in the following paper.[5]

Preparation of *endo-* and *exo*-Bicyclo[5.1.0]-octan-3-ol.—*endo-* and *exo*-bicyclo[5.1.0]octan-3-ol have been synthesized in the following manner. Attempted mono-epoxidation of 1,3-cycloheptadiene[6] with monoperphthalic acid in ether, or with a 40% solution of peracetic acid in glacial acetic acid without additional solvent, yielded only polymeric material. However, when the diene dissolved in ether was treated with 40% peracetic acid solution, 3-cyclohepten-1-one was obtained directly.

The structure of 3-cyclohepten-1-one was first tentatively assigned on the basis of spectral data

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(2) Paper XXV, A. C. Cope and M. J. Youngquist, *J. Am. Chem. Soc.*, **84**, 2411 (1962).

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(4) A. C. Cope, S. Moon and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

(5) A. C. Cope, S. Moon and C. H. Park, *ibid.*, **84**, 4850 (1962).

(6) A. C. Cope, T. A. Liss and G. W. Wood, *ibid.*, **79**, 6287 (1957).