based on starting dione **1b**) of **4b**-7-d_1 after triturating the initial residue with 2-methylbutane, separating, distilling, and combining distillates. A 5.03-g portion of deuterated dienone was reduced with lithium aluminum deuteride, using the procedure described for the undeuterated case, and afforded 5.0 g (98%) of **5**-1,7-d_2, mp 75–77.5°. This was converted to 6.4 g (70%) of **5**-1,7-d_2 *p*-nitrobenzoate, mp 73–78°, which was solvolyzed in buffered acetic acid for 19 hr at room temperature. Work-up gave 4.09 g of product which yielded 0.36 g (5.6%) of dideuterated **8b** after addition of 2-methylbutane and filtration. The remaining oil was subjected to preparative tlc (development with 1:9 ether–hexane), giving 1.53 g of dideuterated **7** and 2.20 g of cloudy yellow oil which afforded 2.0 g of dideuterated acetate **8a** as a clear oil after treatment with Norit in 2-methylbutane (<1% *p*-nitrobenzoate present). Pyrolysis of a 0.528-g portion of acetate yielded 0.279 g (72%) of a mixture of dienes which was separated by preparative glpc on column 2 (120°) into two fractions, the second of which (69 mg) was, by analytical glpc, a 90:10 mixture of **9b** and dideuterated **7**, respectively: nmr (CCl_4) τ 7.47 (triplet of septuplets, J = 5.8 and 1.3 Hz) and 4.56 (triplet of quartets, J = 5.8 and 1.4 Hz).

Registry No.—**2b** tosylate, 30783-60-9; **4a**, 30783-61-0; **4b**, 30783-62-1; **5**, 30783-63-2; **5** methyl ether, 30783-64-3; **5** acetate, 30783-65-4; **5** *p*-nitrobenzoate, 30783-66-5; **7**, 30783-67-6; **8a**, 30783-68-7; **8b**, 30783-69-8.

Cyclopropanes. XXX. Haller–Bauer Cleavage of Phenyl Cyclopropyl Ketones[1]

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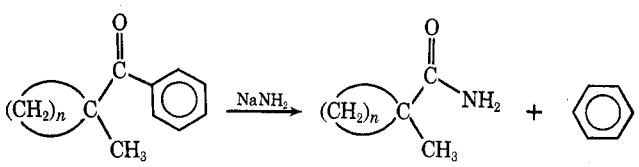
The syntheses and the establishment of the absolute configurations of 1-chloro-, 1-fluoro-, and 1-methoxy-2,2-diphenylcyclopropyl phenyl ketones are described. The optically active ketones were cleaved with sodium amide to yield optically active 1-chloro-, 1-fluoro-, and 1-methoxy-2,2-diphenylcyclopropane, respectively.

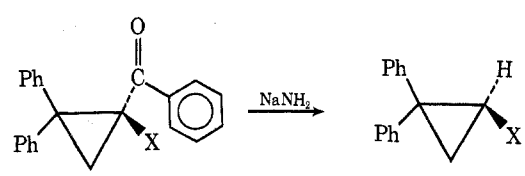
The Haller–Bauer cleavage of nonenolizable ketones such as 1-alkylcyclohexyl phenyl,[3] 1-alkylcyclopentyl phenyl,[3] 1-alkylcyclobutyl phenyl,[3] and 1-alkylcyclopropyl phenyl[4] ketones with sodium amide proceeds in the direction to produce largely the 1-alkylcycloalkanecarboxamide and benzene.



n = 2-5

A notable exception was observed in the case of 1-alkylcyclopropyl phenyl ketones in that certain 2-substituted cyclopropyl ketones such as 1-methyl-2,2-diphenylcyclopropyl phenyl ketone[5] (**1**) and *Z*-2-phenylcyclopropyl phenyl ketone[6] cleaved predominantly in the reverse manner. These observations were rationalized[6] on the basis that relief of steric interaction between the phenyl group in the 2 position and the carbonyl in the 1 position provided the driving force for the reverse cleavage.

Moreover, it was demonstrated that cleavage of **1** was stereospecific in that the hydrocarbon, 1-methyl-2,2-diphenylcyclopropane (**5**) formed by cleavage of optically active **1**, was optically pure and its configuration was retained. In connection with some other work it became necessary to prepare optically active 1-chloro-2,2-diphenylcyclopropane (**6**), 1-fluoro-2,2-diphenylcyclopropane (**7**), and 1-methoxy-2,2-diphenylcyclopropane (**8**). Based on our previous experience, the Haller–Bauer cleavage reaction seemed a promising route for accomplishing this. It was not clear, however, what the effect of an α-halo or methoxyl substituent would have on the course of the reaction.



X = CH_3 = **1**-(−)-(*R*) X = CH_3 = **5**-(+)-(*S*)
Cl = **2**-(+)-(*S*) Cl = **6**-(+)-(*S*)
F = **3**-(−)-(*S*) F = **7**-(−)-(*S*)
CH_3O = **4**-(+)-(*S*) CH_3O = **8**-(+)-(*S*)

Syntheses and Absolute Configurations.—The synthesis and absolute configuration of (−)-(*R*)-**1** has previously been described.[5] Optically active (+)-(*S*)-**2** was prepared by the addition of phenyllithium to known[7] (+)-(*S*)-1-chloro-2,2-diphenylcyclopropanecarboxylic acid. The syntheses of **3** and **4** were achieved in an analogous manner to that of **1** and **2**. This involved the addition of diazodiphenylmethane to α-fluoro and α-methoxy acrylate, which yielded after saponification the 1-fluoro- and 1-methoxy-2,2-diphenylcyclopropanecarboxylic acids, respectively. The acids were resolved using an appropriate alkaloid and the optically active acids were treated with phenyllithium to obtain **3** and **4** (see Experimental Section).

The absolute configuration of **3** was established by relating its precursor, 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid, to 2,2-diphenylcyclopropanecarboxylic acid. The absolute configuration of the latter

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

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(3) K. E. Hamlin and V. Biermacher, *J. Amer. Chem. Soc.*, **77**, 6376 (1955); for a review see K. E. Hamlin and A. W. Weston, *Org. React.*, **9**, 1 (1957).

(4) F. J. Piehl and W. G. Brown, *J. Amer. Chem. Soc.*, **75**, 5023 (1953); C. L. Bumgardner, *J. Org. Chem.*, **29**, 767 (1964).

(5) F. J. Impastato and H. M. Walborsky, *J. Amer. Chem. Soc.*, **84**, 4838 (1962); H. M. Walborsky and F. J. Impastato, *Chem. Ind. (London)*, 1690 (1958).

(6) C. L. Bumgardner and K. G. McDaniel, *J. Amer. Chem. Soc.*, **91**, 6821 (1969).

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

acid had previously been established.[8] Of the many methods available for relating configurations one of the most convenient, when applicable, is the infrared analysis of quasiracemates.[7-9] The solid-state (KBr disks) spectrum (Table I) of the equimolar mixture of

TABLE I

THE INFRARED ABSORPTION BANDS (cm^{-1}) ASSOCIATED WITH CARBOXYL GROUP

Compd[a]	Bonded OH	COOH dimer sub-maxima	Carbonyl stretching	Broad in-plane COH	Broad out-of-plane COH
(+)-A	3235		1741, 1708	1226	821
(±)-A		2624 2538 2474	1714		852
(+)-B	3200		1733, 1696	1163	820
(+)-B		2685 2615 2550	1696		939
(+)-A–(+)-B	3230		1730, 1696	1153 1169	826
(+)-A–(−)-B		2710 2633 2573	1714		946

[a] A = 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid; B = 2,2-diphenylcyclopropanecarboxylic acid.

(+)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid and (−)-2,2-diphenylcyclopropanecarboxylic acidshows clearly quasiracemate compound formation and the molecules are therefore of opposite configuration. Moreover, the equimolar mixture of (+)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid and (+)-2,2-diphenylcyclopropanecarboxylic acid gave a solid solution spectrum.[10] On the basis of these results it can be concluded with confidence that the acids of like sign of rotation have the same configuration. Since the absolute configuration of (+)-2,2-diphenylcyclopropanecarboxylic acid has been established as *S*, then the absolute configuration of (+)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid is *R* and the (−) enantiomer is *S*.

The method of quasiracemates was not amenable to the determination of the absolute configuration of 1-methoxy-2,2-diphenylcyclopropanecarboxylic acid, since the infrared spectra (KBr disk) of the racemic acid and the optically pure enantiomer were virtually identical.

We had previously shown[10] that optical rotatory dispersion of the aldehydes derived from the configurationally related acids, (+)-2,2-diphenylcyclopropanecarboxylic acid and (−)-1-methyl-2,2-diphenycyclopropanecarboxylic acid, gave similar negative Cotton effects. Optical rotatory dispersion is then another method available for relating configuration.[11]

(+)-(*R*)-1-Fluoro-2,2-diphenylcyclopropanecarboxylic acid was converted to (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropylcarboxaldehyde (see Experimental Section). The aldehyde exhibited the expected negative Cotton effect and thereby provided additional evidence for the assignment of the (+)-(*R*) configuration to its precursor acid.

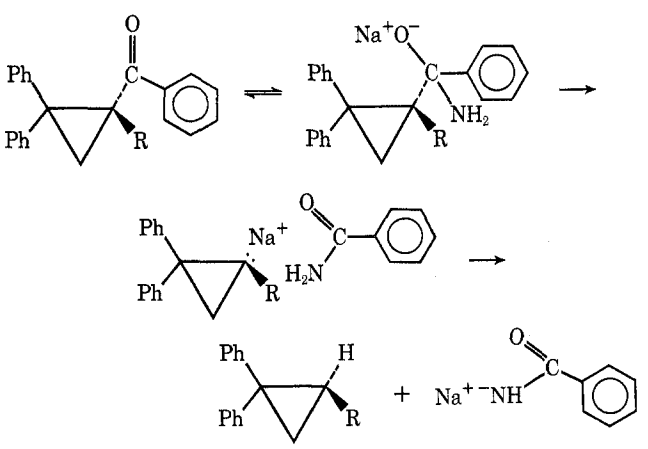
The configuration of (+)-1-methoxy-2,2-diphenylcyclopropanecarboxylic acid was obtained by converting it to the (+)-1-methoxy-2,2-diphenylcyclopropanecarboxaldehyde, which exhibited a negative Cotton effect very similar in shape to the other aldehydes in this series. The dextrorotatory 1-methoxy acid and aldehyde as well as the (−)-phenyl ketone derived from the (+) acid have therefore been assigned the *R* configuration.

Discussion

In our earlier work[5] it was shown that the cleavage of **1** resulted in the formation of **5** in a stereospecific manner. The cleavage of **2**, **3**, and **4** produced the cyclopropyl hydrocarbons **6**, **7**, and **8**, respectively. We have assigned absolute configurations based on the retention of configuration previously demonstrated for this reaction.[5] The optical rotations of the hydrocarbons (**6**, **7**, and **8**), in the absence of authentic samples, can only be viewed as minimum values. Although based on our previous work they would be expected to be of high optical purity.

The results obtained are consistent with the mechanism proposed earlier[5] (Scheme I). Both steric and

SCHEME I



electronic effects would favor the cleavage in the direction shown. Although the electronic effect to be expected is by no means entirely clear,[12] it is felt that the inductive effect of Cl, F, and methoxy groups would facilitate the formation of the carbanion intermediate,[12] since the cyclopropyl anion has been shown to be pyramidal.[13]

Experimental Section[14]

(±)-1-Methoxy-2,2-diphenylcyclopropanecarboxylic Acid.—A solution of 32.0 g (0.25 mol) of ethyl α-methoxy acrylate[15] and

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

(9) A. Rosenberg and L. Schotte, *Ark. Kemi*, **7**, 347 (1954).

(10) Thermal analysis (A Fredga, "The Suedberg Anniversary Volume," Almquist and Wiksells, Uppsala, 1945) confirms the observations of the infrared analysis. The phase diagrams of the quasiracemates may be found in the Dissertation of E. J. Powers, Florida State University, June 1969.

(11) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, N. Y., 1960.

(12) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967); A. Streitwieser, Jr., and F. Mares, *ibid.*, **90**, 2444 (1968).

(13) H. M. Walborsky and J. M. Motes, *ibid.*, **92**, 2445 (1970), and references cited therein.

(14) The infrared spectra were obtained with a Perkin–Elmer infrared spectrophotometer, the nmr spectra with a Varian A-60 analytical spectrometer, and optical rotations with a Bendix automatic polarimeter using a 1.0-cm cell. All melting points are uncorrected.

(15) N. Ogata, S. Nazakura, and S. Murahashi, *Bull Chem. Soc. Jap.*, **43**, 2987 (1970); V. Auwers, *Ber.*, **44**, 3523 (1911).

49.0 g (0.25 mol) of diazodiphenylmethane dissolved in 200 ml of cyclohexane was refluxed until the C=C stretching band at 1628 cm^{-1} was no longer present. The solvent was removed *in vacuo* and the residue was distilled to yield 60.8 g (80%) of ethyl 1-methoxy-2,2-diphenylcyclopropanecarboxylate: bp 146–148° (1 mm); ir (neat) 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.7–7.0 (m, 10, phenyl), 3.8 (q, 2, CH_2O), 3.2 (s, 3, CH_3O), 2.3 (d, 1, J = 6 Hz, ring CH), 1.7 ppm (d, 1, J = 6 Hz, ring CH).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.81; H, 6.97.

Ethyl 1-methoxy-2,2-diphenylcyclopropanecarboxylate (49 g) was added to a solution of 200 ml of 25% aqueous potassium hydroxide and 300 ml of methanol and refluxed for 4 hr. Acidification with 2 N hydrochloric acid yielded 36.9 g (85%) of the acid which, after recrystallization from chloroform–hexane (1:1), gave white needles: mp 178–179°; ir 1705 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.5–7.0 (m, 10, phenyl), 3.25 (s, 3, CH_3O), 2.22 (d, 1, ring), 1.80 ppm (d, 1, ring).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.21; H, 5.89.

(+)-(*R*) and (−)-(*S*)-1-Methoxy-2,2-diphenylcyclopropanecarboxylic Acid. A.—A mixture of 13.4 g (0.05 mol) of (±) acid and 19.7 g of brucine was added to 500 ml of acetone and the mixture was refluxed for 1 hr. The hot solution was filtered and evaporated to one-half its volume, and water was added until the solution became slightly cloudy. The solution was allowed to remain overnight at ambient temperature. The first crop of crystals (15 g) was dried in a vacuum oven at 50° (12 mm). The dried crystals (12.1 g) were recrystallized twice from acetone to yield 8.1 g of brucine salt.

The brucine salt was dissolved in acetone, acidified with 30 ml of concentrated hydrochloric acid, and diluted with water. The solid was filtered and recrystallized from chloroform–hexane (1:1) to yield 3.3 g of acid: mp 179°; $[\alpha]_{Hg}^{25}$ −84° (*c* 1.0, $CHCl_3$); ir and nmr were identical with those of (±) acid.

Anal. Calcd for $C_{17}H_{16}O_3$: 76.10; H, 7.31. Found: C, 75.81; H, 6.95.

B.—The combined filtrates from the above resolution were acidified with 30 ml of concentrated hydrochloric acid and diluted with water to yield 9.8 g of acid, $[\alpha]_{Hg}^{25}$ +12°. The partially resolved acid was added to 11.8 g of quinine dissolved in 500 ml of acetone. The solution was filtered and concentrated to one-half its volume, and water was added until the solution was slightly cloudy. After the solution had remained overnight at ambient temperatures, 10.4 g of quinine salt was obtained which after two recrystallizations from acetone and hydrolysis with hydrochloric acid gave 4.3 g of (+)-(*R*)-1-methoxy-2,2-diphenylcyclopropanecarboxylic acid. A further crystallization from chloroform–hexane (1:1) gave mp 179°, $[\alpha]_{Hg}^{25}$ +84.5° (*c* 1.0, $CHCl_3$).

(+)-(*S*)-1-Benzoyl-1-methoxy-2,2-diphenylcyclopropane.—To a stirred cooled (0°) solution of 1.07 g (0.0025 mol) of (−)-(*S*)-1-methoxy-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]_{Hg}^{25}$ −84.5°, was added, over a period of 30 min, 6 ml of a 1.35 M ethereal solution of phenyllithium. Stirring was continued for an additional 30 min and the mixture was then hydrolyzed with 100 ml of saturated ammonium chloride. The ether solution was washed three times with water and saturated sodium chloride and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was crystallized from methanol to yield 1.2 g (85%) of ketone: mp 154–155°; $[\alpha]_{Hg}^{25}$ +34.2° (*c* 1.0, $CHCl_3$); ir (CCl_4) 1684 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 9.0 7.0 (m, 15, phenyl), 3.10 (s, 3, CH_3O), 2.61 (d, 1, ring), 1.72 ppm (d, 1, ring).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.30; H, 6.02.

(−)-(*R*)-1-Methoxy-2,2-diphenylcyclopropylcarbinol.—To a cooled (0°) solution of 2.68 g (0.01 mol) of (+)-(*R*)-1-methoxy-2,2-diphenylcyclopropanecarboxylic acid ($[\alpha_{Hg}^{25}$ +84°) dissolved in 100 ml of ether was slowly added an ether solution of 0.02 mol of lithium aluminum hydride. After the addition was completed the mixture was refluxed for 1 hr and then hydrolyzed with 20 ml of saturated ammonium chloride. The clear supernatant was filtered from the solids and dried over molecular sieves, and the solvent was removed to yield an oil which crystallized from ether–chloroform (3:1) to give a 75% yield of carbinol: mp 82–83°; $[\alpha]_{Hg}^{25}$ −12.5 (*c* 1.0, $CHCl_3$); nmr (CCl_4) δ 7.6–7.1 (m, 10, phenyl), 3.7–3.4 (m, 2, CH_2O), 3.18 (s, 3, CH_3O), 2.6–2.5 (s, 1, OH), 1.65 (d, 1, ring), 1.32 ppm (d, 1, ring).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.08. Found: C 80.18; H, 6.95.

(+)-(*R*)-1-Methoxy-2,2-diphenylcyclopropanecarboxaldehyde.—A solution of 2.0 g (0.008 mol) of (−)-(*R*)-1-methoxy-2,2-diphenylcyclopropylcarbinol, $[\alpha]_{Hg}^{25}$ −12.5°, in 11 ml of acetic anhydride and 17 ml of dimethyl sulfoxide was allowed to remain at ambient temperature for 18 hr[16] and then poured onto a mixture of 4.5 g of sodium hydroxide dissolved in 50 ml of water and 200 g of ice. The gummy precipitate was taken up in ether and washed three times with water and saturated sodium chloride, and the ether solution was dried over molecular sieves. The solvent was removed and the residue was crystallized from hexane–chloroform (5:1) to yield 1.2 g (54%) of the aldehyde: mp 128–129°; $[\alpha]_{Hg}^{25}$ +49° (*c* 5.0, dioxane); uv (dioxane) 304 nm (ϵ_{max} 130); ir 2750 and 1728 cm^{-1} (CHO). A sample, mp 117–118°, $[\alpha]_{Hg}^{26}$ −40° (*c* 1.0, $CHCl_3$), gave ORD (*c* 0.011 g/cm^3, dioxane) $[\Phi]_{500}$ −86.1°, $[\Phi]_{450}$ −96.9°, $[\Phi]_{400}$ −161°, $[\Phi]_{375}$ −184°, $[\Phi]_{350}$ −75.1°, $[\Phi]_{340}$ +129°, $[\Phi]_{330}$ +786°, $[\Phi]_{323}$ +852°, $[\Phi]_{320}$ +388°, $[\Phi]_{315}$ −214°, $[\Phi]_{311}$ −1032°, CD (*c* 0.043 M, dioxane) $[\theta]_{340}$ 0, $[\theta]_{306}$ 5500, $[\theta]_{278}$ 0.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.82; H, 6.26.

(±)-1-Methoxy-2,2-diphenylcyclopropane.—A solution of 19.4 g (0.9 mol) of diazodiphenylmethane in 100 g of methyl vinyl ether was irradiated with a Hannovia medium pressure mercury lamp using a Pyrex filter until the solution was decolorized. The excess ether was removed and the oily residue was distilled to yield 11.2 g (50%) of product, bp 106–108° (0.25 mm). An analytical sample was obtained by vpc using a CES 4-ft column: nmr ($CDCl_3$) δ 7.5–7.1 (m, 10, phenyl), 3.51 (q, 1, Hx), 3.08 (s, 3, CH_3O), 1.60–1.14 ppm (m, 2, H_aH_b).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.41; H, 7.29.

Ethyl α-Fluoroacrylate.[17]—Two drops of ethanol and 179 g (1.22 mol) of ethyl oxalate were added to 48 g (1.11 mol) of sodium hydride (56% dispersion in mineral oil) stirred in 1100 ml of benzene. While the reaction temperature was maintained between 40 and 60°, 118 g (1.11 mol) of ethyl fluoroacetate was added over a period of 1 hr. Ethanol was distilled off and after cooling to 40°, 33.5 g (1.12 mol) of trioxymethylene (anhydrous powder) was added to the stirred reaction mixture. After 20 min the benzene solution was decanted from the precipitated solids. This solution was usually submitted to further reaction without separation, hydroquinone being added to retard polymerization. A minimum yield of 75% was obtained based on the formation of 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid from the subsequent addition of diazodiphenylmethane to the benzene solution of acrylate.

To obtain analytical data, a reaction was run in decalin and the product was distilled from the reaction mixture, since in benzene and even in xylene an azeotrope was formed. The reaction in decalin yielded 25% product: ir (neat) 1750 (C=O), 1180 and 1160 (d, CO), 1655 (C=C), 898 (=CH_2), and 1025 cm^{-1} (CF); nmr (benzene) δ 5.66 (dd, 1, J_{FH} = 32, J_{HH} = 3.5 Hz, *trans*-HC=CF), 5.19 (dd, 1, J_{FH} = 7.1 Hz, J_{HH} = 3.5 Hz, *cis*-HC=CF), 4.22 (q, 2, J = 7.2 Hz), and 1.23 (t, 3, J = 7.2 Hz).

Ethyl (±)-1-Fluoro-2,2-diphenylcyclopropanecarboxylate.—A pentane solution (900 ml) containing 0.86 mol of diazodiphenylmethane was added to the above benzene solution of ethyl α-fluoroacrylate and heated to reflux.

After decolorization of the diazodiphenylmethane a sample of the crude ester was precipitated from ether at Dry Ice–acetone temperatures and crystallized from pentane yielding cubic crystals: mp 59–60°; ir (CCl_4) 1750 (C=O), 1140 (CO), 1020 and 1060 cm^{-1}; near ir (CCl_4) 1.627 μ (ring CH_2); nmr (CCl_4) 7.56–7.00 (m, 10, phenyl), 3.85 (q, 2, J = 7.5 Hz, CH_2O), 2.13 (dd, 1, J_{FH} = 11.4, J_{HH} = 6.8 Hz, *trans* ring H), 2.07 (dd, 1, J_{FH} = 38.5, J_{HH} = 6.8 Hz, *cis* ring H), 0.82 (t, 3, = 7.5 Hz).

Anal. Calcd for $C_{18}H_{17}O_2F$: C, 76.04; H, 6.03. Found: C, 75.96; H, 6.11.

(±)-1-Fluoro-2,2-diphenylcyclopropanecarboxylic Acid.—The above ester was saponified with 100 g of potassium hydroxide in 1 l. of aqueous methanol, and the acidified product was taken up in ether after removal of a neutral fraction which was discarded. Crude product was realized in 75% yield based on the starting ethyl α-fluoroacetate. Crystallization from benzene gave fine needles: mp 174–175°; ir (KBr) 1714 (C=O), 2624, 2538, and

(16) J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, **87**, 4215 (1965).

(17) E. D. Bergman and I. Shahak, *J. Chem Soc.*, 4033 (1961).

2475 (OH submaxima), 852 (γ, COOH), and 710 and 695 cm^{-1} (d, phenyl); the ir spectrum was run on a Perkin–Elmer 541 spectrophotometer; near ir ($CHCl_3$) 1.627 μ; nmr ($CDCl_3$) δ 7.6–7.0 (m, 10, phenyl), 2.20 (dd, 1, J_{FH} = 4.2, J_{HH} = 6.6 Hz, *trans* ring CH to F), and 2.13 ppm (dd, 1, J_{FH} = 30.6, J_{HH} = 6.6 Hz, *cis* ring CH to F).

Anal. Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11. Found: C, 75.00; H, 5.13.

(+)-(*R*)- and (−)-(*S*)-1-Fluoro-2,2-diphenylcyclopropanecarboxylic Acid.—The salt obtained by adding 52.6 g (0.212 mol) of the above racemic acid to 99.0 g (0.212 mol) of brucine in acetone was crystallized from acetone to constant rotation (six times). Hydrolysis with hydrochloric acid yielded acid, $[\alpha]_{Hg}^{25}$ −155 ± 1° (*c* 1.2, acetone), and an additional crystallization of the acid from dimethylformamide did not change the rotation.

The mother liquors from the first two of the above crystallizations yielded on hydrolysis 39.7 g of acid, $[\alpha]_{Hg}^{25}$ +13°, which was combined with 52 g (0.16 mol) of quinine in acetone. One crystallization of the salt afforded on hydrolysis acid of the above maximum, but opposite, rotation. A second crystallization of the acid from acetone and another from ethanol produced no change in rotation.

The resolved acid crystallized from chloroform as cubes: mp 181–183°; $[\alpha]_{Hg}^{25}$ +155° (*c* 1.0, acetone); ir (KBr) 3235 (ν, OH), 1741, 1708 (d, C=O), 1226 (β, COH), and 821 cm^{-1} (γ, C=OH–); the nmr ($CDCl_3$) was identical with that of the racemic acid.

Anal. Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11. Found: C, 75.12; H, 5.25.

(±)-1-Fluoro-2,2-diphenylcyclopropylcarbinol.—A solution of 9.2 g (0.0368 mol) of 1-fluoro-2,2-diphenylcyclopropanecarboxylic acid in 150 ml of anhydrous ether was added slowly to 2.6 g (0.068 mol) in lithium aluminum hydride. After the mixture was stirred for 4.5 hr, 25 ml of saturated ammonium bromide was added.

A clear ether solution was filtered from the coagulated solids, dried over molecular seives, and evaporated to yield 83% product which was crystallized from 25% chloroform in low-boiling petroleum ether: mp 83.5–85.0°; ir (Nujol) 3300 (bonded OH), 1060 (CO), and 762, 748, 735, 708, and 694 cm^{-1} (phenyl); near ir ($CHCl_3$) 1.633 μ; nmr (CCl_4) δ 7.55–7.05 (m, 10, phenyl), 3.82 (s, 1, 1/2 CH_2O), 3.44 (d, 1, J = 5 Hz, 1/2 CH_2O), 2.58 (s, 1, OH) (the signal shifted upfield on dilution), 1.73 (dd, 1, J = 14, J = 7 Hz), ring CH), 1.44 ppm (s, 1, ring CH); nmr (benzene) δ 3.83 (s, 1, 1/2 CH_2O), 3.44 (s, 1, 1/2 CH_2O), 2.98 (s, 1, OH), 1.79, 1.46, 1.42, and 1.24 (d, 1/2 H each, J = 7 Hz, ring CH_2).

Anal. Calcd for $C_{16}H_{15}OF$: C, 79.32; H, 6.24. Found: C, 79.32; H, 6.19.

(+)-(*R*)-1-Fluoro-2,2-diphenylcyclopropylcarbinol.—The optically active carbinol (85% yield) was prepared from acid of maximum rotation (*i.e.*, $[\alpha]_{Hg}^{25}$ +155°) in a manner similar to the racemic carbinol except for an increase of the reaction period to 7.5 hr. Crystallization from high-boiling petroleum ether gave fine needles: mp 105.2–106.0°; $[\alpha]_{Hg}^{25}$ +146 ± 2° (*c* 0.48, methanol); the ir, near ir, and nmr spectra were identical with those of the racemic material.

Anal. Calcd for $C_{16}H_{15}OF$: C, 79.32; H, 6.24. Found: C, 79.51; H, 6.05.

(±)-1-Fluoro-2,2-diphenylcyclopropanecarboxaldehyde.—To 4.85 g (0.02 mol) of 1-fluoro-2,2-diphenylcyclopropylcarbinol dissolved in 2 ml of dimethyl sulfoxide (stored over molecular sieves) was added 12.3 g (0.06 mol) of dicyclohexylcarbodiimide. After the mixture was cooled to 0°, 3.0 g (0.003 mol) of crystalline orthophosphoric acid was added. The mixture was stirred overnight at room temperature with a calcium chloride drying tube venting the flask.

The reaction mixture was diluted with four volumes of ether and filtered. The ether layer was separated and washed successively with saturated sodium bicarbonate, water, and finally saturated sodium chloride. The ether solution was dried over molecular seives and the solvent was stripped to yield a gummy residue. Triturating with pentane produced 2.1 g (44%) of a granular white solid which crystallized from hexane: mp 96–98.5°; ir (CCl_4) 1735 (C=O), 2780, 2770, 2930 (O=CH), and 1195 and 1205 cm^{-1} (d, CO); near ir 1.631 and 2.229 μ; uv max (CCl_4) 298 mμ; nmr (CCl_4) δ 9.17 (d, 1, J = 11 Hz, O=CH), 7.84–7.05 (m, 10, phenyl), 218 (d, 1, J = 7 Hz, 1/2 ring CH_2) and 2.11 ppm (dd, 1, J_{FH} = 26, J_{HH} = 7 Hz, 1/2 ring CH_2).

Anal. Calcd for $C_{16}H_{13}OF$: C, 79.98; H, 5.45. Found: C, 80.13; H, 5.70.

(+)-(*R*)-1-Fluoro-2,2-diphenylcyclopropanecarboxyladehyde.—In a 50-ml flask, 0.900 g (0.0037 mol) of (+)-1-fluoro-2,2-diphenylcyclopropanecarbinol (maximum rotation), 16 ml of dimethyl sulfoxide, and 10 ml of acetic anhydride were mixed and allowed to stand for 18 hr at room temperature.[16] The reaction mixture was added, with stirring, to 4.5 g of sodium hydroxide in 50 ml of water and 200 g of ice. The gummy precipitate which resulted was dissolved in ether, and the ether solution was washed with water several times, lastly with aqueous sodium chloride, and then dried over molecular sieves. After the solvent was removed on a rotary evaporator, the resulting oil was crystallized from hexane. After three more crystallizations from hexane, 0.150 g (57%) of product was obtained: mp 116–117°; $[\alpha]_{Hg}^{25}$ +164° (*c* 0.56, dioxane); the ir and nmr spectra were identical with those of the racemic material; uv (dioxane) 305 (ϵ_{max} 63); ORD $[\alpha]_{550}^{25}$ +168, $[\alpha]_{400}$ +496, $[\alpha]_{350}$ +638°, $[\alpha]_{332}$ +708°, $[\alpha]_{323}$ +594°, $[\alpha]_{320}$ +673°, $[\alpha]_{315}$ +710°, $[\alpha]_{300}$ +4070°, $[\alpha]_{277.5}$ +11,860°, $[\alpha]_{275}$ +13,100°, $[\alpha]_{272}$ +118,860°, $[\alpha]_{267}$ +13,980°, $[\alpha]_{264}$ +12,730°, and $[\alpha]_{254}$ +17,700° (*c* 0.056, dioxane).

Anal. Calcd for $C_{16}H_{15}OF$: C, 79.98; H, 5.45. Found: C, 79.20; H, 5.30.

(−)-(*S*)-1-Benzoyl-1-fluoro-2,2-diphenylcyclopropane.—To a cooled (0°) and stirred solution of 2.5 g (0.01 mol) of (−)-(*S*)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]_{Hg}^{25}$ − 155°, was added, over a 30-min period, 25 ml of 1.5 *M* phenyllithium solution in ether. Stirring was continued for an additional hour and the reaction mixture was then hydrolyzed with ice water. The ether extract was washed with water and saturated sodium chloride and dried over magnesium sulfate. The solvent was evaporated and the residue was crystallized from ethanol to yield 2.8 g (90%) of ketone: mp 147–148°; $[\alpha]_{Hg}^{25}$ −38° (*c* 1.0, $CHCl_3$); ir (neat) 1683 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.3–7.0 (m, 15, phenyl), 2.72 (q, 1, ring), 2.12 ppm (q, 1, ring).

Anal. Calcd for $C_{22}H_{17}OF$: C, 81.40; H, 6.11; F, 6.77. Found: C, 81.51; H, 5.90; F, 6.4.

(±)-1-Chloro-2,2-diphenylcyclopropanecarboxaldehyde.—To a solution of 5.7 g (0.022 mol) of (±)-1-chloro-2,2-diphenylcyclopropylcarbinol[7] in 95 ml of dimethyl sulfoxide was added to 60 ml of acetic anhydride and allowed to stir at ambient temperature for 16 hr. The solution was poured into a mixture of 200 ml of 15% sodium hydroxide and 100 g of ice and stirred until the oil solidified. The supernatant liquid was decanted and the solid was recrystallized from hexane to give 3.0 g (53%) of crystals: mp 124–125°; ir (CCl_4) 2740 and 2840 (aldehyde CH), 1720 cm^{-1} (C=O); nmr (CCl_4) δ 2.20 (d, 1, J = 5 Hz, ring H), 2.66 (d, 1, J = 5 Hz, ring H), 7.50 (complex, 10, phenyl), 9.36 (s, 1, aldehyde).

Anal. Calcd for $C_{16}H_{14}ClO$: C, 74.85; H, 5.10; Cl, 13.83. Found: C, 74.95; H, 5.17; Cl, 13.98.

(+)-(*S*)-1-Chloro-2,2-diphenylcyclopropanecarboxyaldehyde.—Optically pure carbinol,[7] $[\alpha]_{Hg}^{24}$ +74.1° (*c* 1.0, $CHCl_3$), prepared from acid, $[\alpha]_{Hg}^{24}$ +87.7° (*c* 1.1, $CHCl_3$), was oxidized by the above procedure to produce aldehyde, mp 106–108°, $[\alpha]_{Hg}^{24}$ +153° (*c* 1.0, $CHCl_3$). The ORD and CD curves were obtained using a sample of aldehyde: $[\alpha]_{Hg}^{24}$ −71° (*c* 1.0, $CHCl_3$); ORD (*c* 0.0096 g/cm^3, dioxane) $[\Phi]_{500}$ −195°, $[\Phi]_{450}$ −268°, $[\Phi]_{400}$ −346°, $[\Phi]_{375}$ −450°, $[\Phi]_{350}$ −651°, $[\Phi]_{340}$ −868°, $[\Phi]_{330}$ −1170°, $[\Phi]_{326}$ −1600°, $[\Phi]_{315}$ −1532°, $[\Phi]_{310}$ −1450°, $[\Phi]_{300}$ −544°, $[\Phi]_{290}$ +1409°; CD (*c* 0.0375 *M*, dioxane) $[\theta]_{343}$ 0°, $[\theta]_{294}$ −5100°, $[\theta]_{259}$ 0°. The ir, nmr, and uv spectra were identical with those of the racemic aldehyde.

(−)-(*R*)-1-Benzoyl-1-chloro-2,2-diphenylcyclopropane.—To a solution of 1.2 g (4.4 mmol) of (−)-(*R*)-1-chloro-2,2-diphenylcyclopropanecarboxylic acid,[7] $[\alpha]_{Hg}^{24}$ −84° (*c* 0.98, $CHCl_3$), 96% optically pure, in 100 ml of ether was added 17 ml of 1.0 *M* phenyllithium in ether under nitrogen at 0°. The solution was allowed to stir for 40 min while warming to room temperature. The reaction was quenched with ice water and the solution was washed with saturated sodium chloride until the washings were neutral and dried, and the ether removed to give an oil which crystallized upon trituration with hexane. Crystallization from ethanol gave 0.59 g (40%) of white crystals: mp 123–124°; ir (CCl_4) 1680 cm^{-1}; nmr (CCl_4) δ 2.02 (d, 2, J = 6.5 Hz, ring), 3.10 (d, 2, J = 6.5 Hz, ring), 7.48 (complex, 13, aromatic), 8.24 (complex, 2, benzoyl ortho H); $[\alpha]^{25}D$ −66.1° (*c* 1.0, $CHCCl_3$). The analytical sample had mp 125–127°.

Anal. Calcd for $C_{22}H_{17}ClO$: C, 79.39; H, 5.15; Cl, 10.65. Found: C, 79.12; H, 5.17; Cl, 10.74.

Cleavage of (−)-(*R*)-1-Benzoyl-1-chloro-2,2-diphenylcyclopropane.—A mixture of 231 mg (0.69 mmol) of (−)-(*R*)-1-benzoyl-1-

chloro-2,2-diphenylcyclopropane, $[\alpha]^{25}D$ −64.8° (*c* 1.0, $CHCl_3$), prepared from acid, $[\alpha]^{25}_{Hg}$ −82.1°, 93.9% optically pure, 150 mg of sodium amide, and 9 ml of benzene was stirred at reflux under nitrogen for 20 hr. Ice water was added and the solution was washed with water until the washings were neutral, dried, concentrated, and subjected to preparative tlc on silica gel using benzene–hexane (1:1). The band with the highest R_f value weighed 18 mg and proved to be (−)-(*R*)-1-chloro-2,2-diphenylcyclopropane based on nmr spectrum and elemental analysis: $[\alpha]^{23}_{Hg}$ −202° (*c* 0.16, $CHCl_3$); nmr (CCl_4) δ 1.71 (d, 2, *J* = 6 Hz, $-CH_2-$), 3.70 (t, 1, *J* = 6 Hz, –CHCl–), 7.37 (m, 10, phenyl).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.80; H, 5.73. Found: C, 78.69; H, 5.69.

Cleavage of (−)-(*S*)-1-Benzoyl-1-fluoro-2,2-diphenylcyclopropane.—A mixture of 1.65 g (0.005 mol) of (−)-(*S*)-1-benzoyl-1-fluoro-2,2-diphenylcyclopropane ($[\alpha]^{25}_{Hg}$ −38°), 1 g of sodium amide, and 50 ml of toluene was stirred and refluxed for 12 hr. The reaction mixture was hydrolyzed by pouring onto ice water and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue was distilled to yield 580 mg (55%) of 1-fluoro-2,2-diphenylcyclopropane whose ir and nmr spectra were identical with those of an authentic sample.[18]

Cleavage of (+)-(*S*)-1-Benzoyl-1-methoxy-2,2-diphenylcyclopropane.—A mixture of 1.1 g (0.03 mol) of ketone, 1.2 g of sodium amide, and 100 ml of xylene was stirred and refluxed for 12 hr. The reaction mixture was hydrolyzed by pouring onto ice, the organic layer was separated, washed with water, and dried over molecular sieves, and the solvent removed *in vacuo*. The residue (0.95 g) was distilled to yield 0.37 g (40%) of 1-methoxy-2,2-diphenylcyclopropane, $[\alpha]^{25}_{Hg}$ +75°. Ir and nmr spectra were identical with those of the racemic sample synthesized.

(18) C.-J. Chen, Ph.D. Dissertation, Florida State University, 1969.

Registry No.—(−)-(*R*)-2, 30724-74-4; (−)-(*S*)-3, 30724-75-5; (+)-(*S*)-4, 30724-76-6; (−)-(*R*)-6, 30724-77-7; (±)-8, 30724-78-8; (±)-A, 30788-13-7; (+)-(*R*)-A, 30724-79-9; (−)-(*S*)-A, 30745-01-8; (±)-1-methoxy-2,2-diphenylcarboxylic acid, 30724-80-2, 30724-81-3 [(±)-(*R*) isomer], 30745-02-9 [(−)-(*S*) isomer]; ethyl 1-methoxy-2,2-diphenylcyclopropanecarboxylate, 30724-82-4; (−)-(*R*)-1-methoxy-2,2-diphenylcyclopropylcarbinol, 30724-83-5; (+)-(*R*)-1-methoxy-2,2-diphenylcyclopropanecarboxaldehyde, 3074 5-03-0; ethyl (±)-1-fluoro-2,2-diphenylcyclopropanecarboxylate, 30724-84-6; (±)-1-fluoro-2,2-diphenylcyclopropanecarbinol, 30724-85-7, 30745-04-1 [(+)-(*R*) isomer]; (±)-1-fluoro-2,2-diphenylcyclopropanecarboxaldehyde, 30788-14-8; 30788-15-9 [(+)-(*R*) isomer]; (±)-1-chloro-2,2-dephenylcyclopropanecarboxladehyde, 30724-86-8, 30724-87-9 [(+)-(*S*) isomer].

The Tricyclo[5.1.0.0^{3,5}]octan-2-ols

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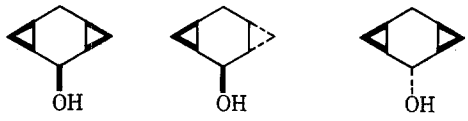
The cis,cis-, cis,trans-, and *trans,trans*-tricyclo[5.1.0.0^{3,5}]octan-2-ols have been prepared and the structures assigned by chemical correlations and nmr spectroscopy. Solvolysis of the *p*-nitrobenzoate of the cis,cis isomer has been carried out in formic acid, acetic acid, and aqueous 1,4-dioxane (85%) for kinetic and product studies. The latter two solvents produce only isomers of the starting material, but formic acid produces a complex reaction mixture that arises from cyclopropyl participation. Some solvolytic studies of the cis,trans *p*-nitrobenzoate in aqueous dioxane have been carried out.

Tricyclo[5.1.0.0^{3,5}]octan-2-ol may exist in three isomeric forms, *cis,cis*-**1** (*cc*-**1**), *cis,trans*-**1** (*ct*-**1**), and

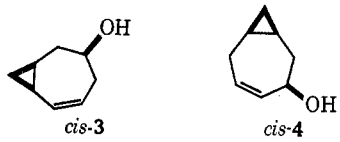


cis,cis-**1** *cis,trans*-**1** *trans,trans*-**1**

trans,trans-**1** (*tt*-**1**), from which are derived only two ketones, *cis*-**2** and *trans*-**2**. We became interested in

cis-**2** *trans*-**2**

the various isomers of **1** as solvolytic models for the related *cis*-bicyclo[5.1.0]oct-5-en-3-ol (*cis*-**3**) and *cis*-bicyclo[5.1.0]oct-4-en-3-ol (*cis*-**4**).[2] The carbonium ions from the sulfonic or carboxylic esters of **1**, **3**, and **4** are

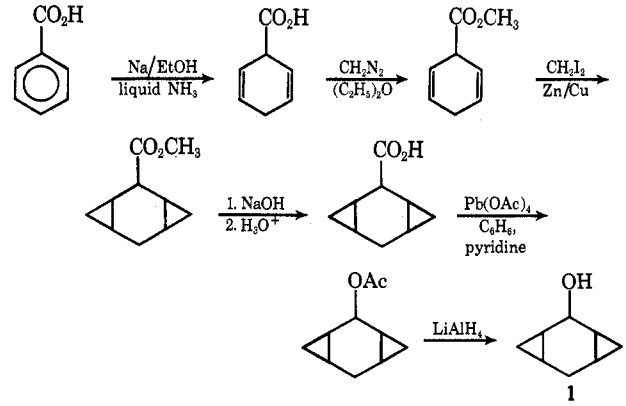


cis-**3** *cis*-**4**

valence tautomeric. We have consequently prepared each of the isomers of **1**, proved their structures, and examined the solvolytic behavior of the *p*-nitrobenzoates of *cc*-**1** and *ct*-**1**.

Synthesis and Structure.—The synthesis of *cis,cis*-**1** followed the procedures developed by Sims[3] and Winstein[4,5] (Scheme I). The stereochemistry of the Sim-

SCHEME I



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(1) National Institutes of Health Predoctoral Fellow, 1968–1970.

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