crystallization from water gave a pure sample, mp 206–207° (lit.[10] mp 200–201°).

Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.0; H, 5.04; N, 11.66. Found: C, 49.49; H, 5.17; N, 11.66.

***erythro*-N-Acetyl-2-methyl-3-(*p*-nitrophenyl)serine Methyl Ester (E-9b).**—The amino ester hydrochloride (8 g) was dissolved in 50 ml of water and neutralized with sodium bicarbonate solution. Ethyl acetate extracts provided 5.8 g of crude residue which was slurried in 60 ml of ether to which an ether solution of 2.5 ml of acetic anhydride was added. After stirring overnight the crystals were filtered and washed with ether. The crude product was recrystallized from 50 ml of methanol to provide 3.25 g (40%) of amido ester, mp 180–185° (lit.[10] mp 179°).

***threo*-4-Carbomethoxy-2,4-dimethyl-5-(*p*-nitrophenyl)oxazoline Hydrochloride (T-11b).**—An initial experiment in an nmr tube showed that more than 3 hr was required to approach complete reaction. To a solution of 1.5 g of amido alcohol E-9b in 40 ml of chloroform was added 4.5 ml of thionyl chloride. The crystals which deposited on stirring overnight (540 mg) were filtered and washed with chloroform, mp 178–181°.

Anal. Calcd for $C_{13}H_{15}N_2O_5Cl$: C, 49.61; H, 4.80; N, 8.91. Found: C, 50.15; H, 4.80; N, 8.75.

***threo*-N-Acetyl-2-methyl-3-(*p*-nitrophenyl)serine Methyl Ester (T-9b).**—The product and mother liquor residue of the above thionyl chloride reaction was stirred with 15 ml of water and 4 ml of saturated sodium bicarbonate solution for 2 hr. The crude product was filtered and washed with water. Chromatography on silica gel H (dry column) using chloroform–acetone (85:15) provided pure T-9b, 0.8 g, mp 168–171° (from ethyl acetate–ether).

Anal. Calcd for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.46. Found: C, 52.53; H, 5.58; N, 9.18.

***threo*-2-Methyl-3-(*p*-nitrophenyl)serine (T-14b).**—Hydrolysis of 500 mg of T-9b in methanol-6 *N* hydrochloric acid (as for the *erythro* isomer E-14b) provided after work-up 230 mg of the title amino acid, mp 202–203° (lit.[10] mp 195–196°). Recrystallization from water raised the melting point to 209–210°.

Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.0; H, 5.04; N, 11.66. Found: C, 49.44; H, 5.07; N, 11.53.

***erythro*-4-Carbomethoxy-2,4-dimethyl-5-(*p*-nitrophenyl)oxazoline Hydrochloride (E-11b).**—To 100 mg of T-9b, the *threo*-amido alcohol, in 5 ml of chloroform was added 20 drops of thionyl chloride. After stirring overnight, the crystals which had deposited were filtered and washed with chloroform. The dry product, 54 mg, showed mp 194–196°.

Anal. Calcd for $C_{13}H_{15}N_2O_5Cl$: C, 49.61; H, 4.80; N, 8.91. Found: C, 49.40; H, 4.71; N, 9.14.

When a portion of E-11b was stirred in water and sodium bicarbonate solution added, E-9b was recovered, indistinguishable (ir and tlc) from the sample described above.

Registry No.—*SR*-**2**, 16062-32-1; *RR*-**2**, 16096-48-3; *SR*-**3**, 13020-48-9; *RR*-**3**, 16062-34-3; *SS*-**3**, 16062-35-4; *RS*-**3**, 16062-36-5; *SR*-**4**, 16062-37-6; *RR*-**4**, 16062-38-7; *SR*-**5**, 16062-39-8; E-**5**, 16062-40-1; T-**5**, 16062-41-2; 2*S*-**6**, 16062-42-3; 2*R*-**6**, 16096-49-4; E-**9a**, 16047-64-6; T-**9a**, 16047-66-8; E-**9b**, 16062-44-5; T-**9b**, 16062-45-6; E-**11a**, 16062-46-7; T-**11a**, 16096-51-8; E-**11b**, 16062-47-8; T-**11b**, 16062-53-6; E-**12a**, 16062-48-9; E-**13a**, 16062-49-0; E-**14a**, 16047-68-0; T-**14a**, 16047-69-1; E-**14b**, 16062-52-5; T-**14b**, 16065-52-4; E-**15**, 16047-65-7; T-**15**, 16047-67-9; E-**16**, 16047-71-5; T-**16**, 16047-72-6; **18**, 16065-59-1; E-**19**, 16065-57-9; T-**19**, 16065-58-0.

Acknowledgment.—We wish to acknowledge with gratitude the constructive suggestions and discussions with Dr. Peter Pollak and Mr. N. Steinberg of these laboratories. Thanks also are due Messrs. B. Singleton and R. Zerfing for obtaining our nmr spectra.

Partial Asymmetric Synthesis in the Simmons–Smith Reaction. I[1]

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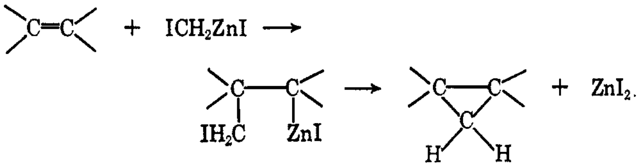
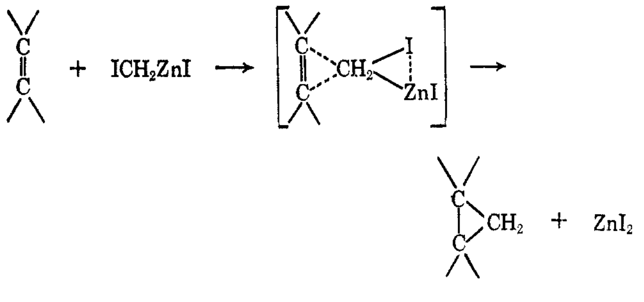
Partial asymmetric synthesis of cyclopropanes was obtained by reaction of the Simmons–Smith reagent with (−)-menthyl esters of α,β- and β,γ-unsaturated carboxylic acids. The steric course was interpreted as proceeding through an intermediate complex in which the Simmons–Smith reagent coordinates with ester carbonyl oxygen and the double bond in a twisted cisoidal conformation. Evidence for an effective coordination of the Simmons–Smith reagent with ester carbonyl oxygen was provided by the Simmons–Smith reaction with 2-cyclohexenyl acetate, leading exclusively to *cis*-2-bicyclo[4.1.0]heptanol.

A novel general stereospecific synthesis of cyclopropanes which involved the treatment of olefins with an active intermediate, iodomethylzinc iodide, prepared from methylene iodide and zinc–copper couple has been developed by Simmons and Smith[2a] and has been proved very useful in preparative applications.[2b–d]

As to the mechanism of the Simmons–Smith reaction, Hoberg[2c] postulated the cyclopropane formation as proceeding *via* addition of the active intermediate iodomethylzinc iodide to olefin and subsequent elimination of zinc iodide.



As an alternative, a three-center reaction involving a one-step displacement of zinc iodide from iodomethyl-



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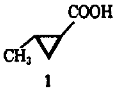
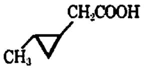
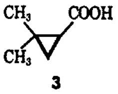
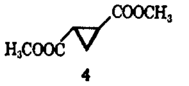
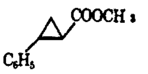
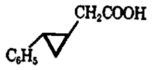
[1] (a) This work was supported by Grant 1240-A4 from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. (b) A short communication of this subject has appeared in *Bull. Inst. Chem. Res. Kyoto Univ.*, **44**, 203 (1966).

[2] (a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5323 (1958); **81**, 4256 (1959); **86**, 1337, 1347 (1964). (b) G. Wittig and K. Schwarzenbach, *Angew. Chem.*, **73**, 27 (1959); *Ann.*, **650**, 1 (1961); G. Wittig and F. Wingler, *Ber.*, **97**, 2139 (1964); G. Wittig and M. Jautelat, *Ann.*, **702**, 24 (1967). (c) H. Hoberg, *ibid.*, **656**, 1, 15 (1962); *ibid.*, **695**, 1 (1966). (d) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, 3353 (1966).

TABLE I

RESULTS OF THE SIMMONS–SMITH REACTIONS OF UNSATURATED (−)-MENTHYL ESTERS

Run	(−)-Menthyl ester	Cyclopropane product	Reagent	Yield, %	$[\alpha]^{20}D$ (neat), deg	Optical yield, %	Absolute confign
1	Crotonate	 1	Zn/Cu	21	+1.73	2.8[a]	1*S*:2*S*[a]
2			Zn	20	+4.3	7.0	
3			Zn, $AlCl_3$	35	+2.40	3.8	
4			Zn/Cu, Et_3N	12	+4.45	7.1	
5			Cd/Cu, BF_3	25	+0.80	1.3	
6	*trans*-3-Pentenoate	 2	Zn/Cu	54.5	+1.77	...	1*R*:2*S*[b]
7	Senecioate	 3	Zn/Cu	16.5	+6.6 (MeOH)	...	*S*[b]
8	Fumarate	 4	Zn/Cu	14	+12.8	6.4[c]	1*S*:2*S*[d]
9	Cinnamate	 5	Zn/Cu	33	−29.3	9.3[d]	1*R*:2*R*[e]
10			Zn	20	−21.8	7.0	
11			Zn/Cu, $AlCl_3$	12.5	−7.8	2.5	
12			Zn/Cu, CuCl	11	−13.5	4.3	
13			Cd/Cu, BF_3	7	−15.1	5.0	
14	*trans*-4-Phenyl-3-butenoate	 6	Zn/Cu	35	+4.1	1.4	1*R*:2*S*

[a] Based on the maximum rotation +61°: T. Sugita and Y. Inouye, *Bull. Chem. Soc. Jap.*, **39**, 1075 (1966). [b] Predicted by the Brewster calculation of conformational asymmetry. [c] Based on the maximum rotation +200°: Y. Inouye, *et al.*, *Tetrahedron*, **23**, 3237 (1967). [d] Based on the maximum rotation +311°: ref 14. [e] I. Tömösközi, *Tetrahedron*, **19**, 1979 (1963).

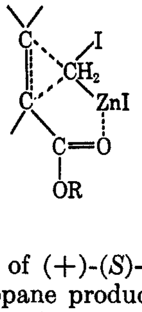
zinc iodide by olefin, *i.e.*, a methylene transfer mechanism, has also been suggested.[2a,b,3]

According to the former mechanism, therefore, the reagent would be expected to behave as a nucleophile in a rather ionic process, whereas in the latter it would be more "carbenelike" and therefore of electrophilic nature.

In connection with the unresolved mechanistic problem, it seemed of interest to undertake asymmetric synthesis in the Simmons–Smith reaction as a possible means of mechanistic solution.

With a molar ratio of olefinic ester/methylene iodide/zinc–copper couple[4] of 1:2:4 in absolute ether and a reflux period of 10–60 hr, (−)-menthyl α,β- and β,γ-unsaturated carboxylates stereospecifically afforded the corresponding cyclopropane compounds, which were isolated pure from the reaction mixture by the usual work-up, ozonolysis to remove unreacted olefinic esters, and subsequent alkaline hydrolysis.

As is seen from the data in Table I, all the (−)-menthyl esters except cinnamate, when treated with the Simmons–Smith reagent, afforded dextrorotatory cyclopropanecarboxylic acids of the *S*, 1*S*:2*S*, and 1*R*:2*S* configurations. This is in contrast to what should be expected from the transoidal coplanar model of the starting olefinic esters. It may be considered that the addition did take place in a two-step fashion[5] as Hoberg postulated and that the steric course was altered by the presence of a catalytic amount of copper as was encountered in the conjugate addition of Grignard reagent to α,β-unsaturated ester.[6] This possibility can be safely excluded, however, by the experimental fact that even in the absence of copper (runs 2 and 10) the reaction yielded cyclopropane acids of the same sign of rotation as those in the presence of copper. It seems more likely that the one-step methylene transfer mechanism operated through a three-center transition involving simultaneous coordination of the zinc atom of the reagent with ester carbonyl oxygen. This would necessitate a twisted cisoidal conformation of the α,β-unsaturated ester in order to attain a [3.1.0]bicyclic transition state complex and therefore should naturally



lead to the formation of (+)-(*S*)-, (+)-(1*S*:2*S*)-, and (+)-(1*R*:2*S*)-cyclopropane products in preponderance over the respective enantiomers.

(3) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

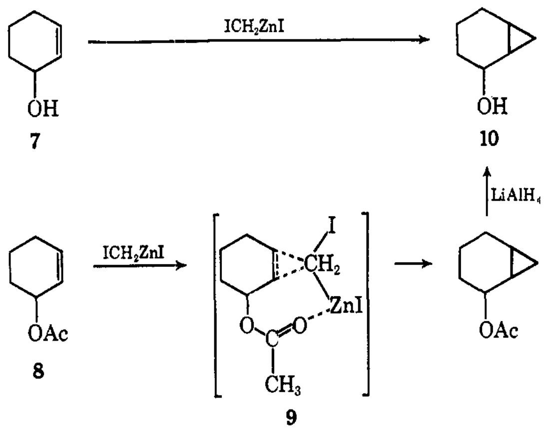
(4) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(5) If this were the case, the addition of the reagent to the double bond should take place from the less hindered side of the transoidal coplanar olefinic ester, say (−)-menthyl crotonate. This should be the stereochemical determining step and the absolute configuration of at least one of the α or β carbon, presumably the latter, should be *R* in the intermediate adduct. It then follows that the eventually resulting *trans*-cyclopropane is destined for the 1*R*:2*R* configuration, no matter what the mechanism is of the subsequent cyclization step. This is not what was found.

(6) Y. Inouye and H. M. Walborsky, *ibid.*, **19**, 1969 (1963).

The accelerating and directing influence of oxygen functions, such as hydroxyl,[2a,7] ether,[7b,8a] and carbonyl,[8b] has been pointed out in some cases. In contrast, the related esters (allyl acetates) were attacked from the less hindered side and formed cyclopropanes in lesser yields.[8a] However, Sims[9] indicated the possible interaction and directing effect of ester group in the Simmons–Smith reaction and more recently Wittig[10] also suggested a complex forming ability of carboxyl group with the Simmons–Smith reagent.

In the present work, the addition of the Simmons–Smith reagent to 2-cyclohexenyl acetate (**8**) yielded *cis*-2-bicyclo[4.1.0]heptanol (**10**), the same geometrical isomer as that resulted from 2-cyclohexen-1-ol, thereby supporting the possible coordination of the zinc atom in the complex with ester carbonyl oxygen.



As a test for the validity of the postulated bicyclic intermediate complex, in which the ethylenic ester is incorporated in a twisted cisoidal conformation, (−)-menthyl *trans*-3-pentenoate (run 6) was subjected to the same reaction. In this system, the double bond is removed by one methylene from carbomenthoxy group. The isolation of the double bond from the electron-withdrawing group would favor the electrophilic addition of the reagent to the double bond and would also accommodate the reagent in a less strained bicyclo[4.1.0] transition conformation. Consistent with this argument, the corresponding cyclopropane product of the same sign of rotation was obtained in a higher yield.

In the exceptional case of (−)-menthyl cinnamate (runs 9–13), the Cram–Prelog model was obeyed. In simpler olefinic systems, a phenyl group is often more effective than an alkyl group in releasing electron to the reaction sites,[11,12] so that the ester carbonyl oxygen of the cinnamate is expected to be more basic to coordinate the zinc atom of the reagent. However, the effective overlap energy of the fully conjugated system would inhibit the deviation from transoidal coplanarity of the system to attain the twisted cisoidal transition conformation. Consequently, the cinnamate system would be forced to adopt a transoidal coplanar conformation with one molecule of the Simmons–Smith reagent coordinated at ester carbonyl and thus would permit the electrophilic attack of another molecule of the reagent to the double bond. The addition from the less hindered side of the system should be more favored and this should naturally lead to the predominant formation of (−)-(1*R*:2*R*) enantiomer in cyclopropane product **5**, the Cram–Prelog model being thus obeyed. The relatively better optical yield found for these runs is consistent with this view, as is also revealed by model inspection.

In connection with both the anomaly in cinnamate system and the postulate of cisoidal coordination intermediate in others, the Simmons–Smith reaction of (−)-menthyl *trans*-4-phenyl-3-butenoate (run 14) is of particular interest. Here, the full conjugation in cinnamate system was intercepted by the introduction of one methylene between the double bond and carboxylate group and there would be no more reluctance of the system to undergo deviation from coplanarity. A similar situation to that of 3-pentenoate may now prevail in the present system: a twisted cisoidal conformation of bicyclo[4.1.0] pattern could now be readily accommodated in a less strained transition complex. The transition state geometry was reflected in the opposite sign of rotation (dextrorotation) and the 1*R*:2*S* configuration of the cyclopropane product **6**, thereby providing further evidence for the abovementioned cisoidal coordination complex as well as for the obedience of cinnamate system to the Cram–Prelog model.

Addition of a catalytic amount of Lewis acid such as aluminum chloride, boron trifluoride, and cuprous chloride or triethylamine (runs 3, 4, 5, 11, 12, 13, and 14) neither exerted any influence on the yield nor altered the steric course of the reaction. Thus the role of Lewis acid in this reaction may be considered as merely facilitating formation and enhancing the electrophilicity of the reagent, as demonstrated by the cadmium counterpart (*vide infra*). A viscous precipitate[13] formed upon addition of triethylamine to the preformed solution of the reagent may be responsible for the poorer reaction yield and the somewhat better optical yield (run 4), although its function is still obscure.

Zinc may be replaced by cadmium[2b] in the Simmons–Smith reaction (runs 5 and 13). The formation of cadmium complex from methylene iodide and metallic cadmium was effected only by the addition of boron trifluoride and the reaction of the cadmium complex with olefins differed little in yield and optical rotation of cyclopropane product from those with the zinc complex.

The dextrorotatory *trans*-2-phenylcyclopropaneacetic acid (**6**) was assigned the 1*R*:2*S* configuration by the unequivocal chemical transformation into (+)-*trans*-2-phenylcyclopropanecarboxylic acid of the established 1*S*:2*S* configuration.[14] An identical conclusion may be reached by the Brewster calculation of

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[7] (a) S. Winstein, T. Sonnenberg, and L. deVries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); (b) W. G. Dauben and D. G. Berezin, *ibid.*, **85**, 468 (1963); (c) E. J. Corey and E. Uda, *ibid.*, **85**, 1778 (1963); (d) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

[8] (a) A. C. Cope, S. Moon, and P. E. Petersen, *ibid.*, **84**, 1935 (1962); (b) J. M. Conia, *Tetrahedron Lett.*, 3151 (1965); Y. Armand, *Bull. Soc. Chim. Fr.*, 1893 (1965); M. Vidal, C. Durmont, and D. Arnaud, *Tetrahedron Lett.*, 5081 (1966).

[9] J. J. Sims, *J. Amer. Chem. Soc.*, **87**, 3511 (1965).

[10] G. Wittig and M. Jautelat, *Ann.*, **702**, 24 (1967).

[11] N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1957).

[12] P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

[13] E. P. Blanchard, H. E. Simmons, and J. S. Taylor, *J. Org. Chem.*, **30**, 4321 (1965).

[14] Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

TABLE II

PHYSICAL PROPERTIES OF STARTING MENTHYL ESTERS

Menthyl ester	Bp (mm) or mp, °C	$n^{20}D$	$[\alpha]^{20}D$ (EtOH), deg
Crotonate[a]	114–118 (5) 22.5	1.4662	−86.4[a]
trans-3-Butenoate[a]	88–89 (0.2)	1.4611	−72
Senecioate[b]	104–106 (0.2) 35–36		−80.4
Fumarate[c]	194–195 (0.1)	1.4824	−74
Cinnamate	140–141 (0.1)	1.5422	−71.2
trans-4-Phenyl-3-butenoate[d]	145–147 (0.06)	1.5195	−68.3 (MeOH)

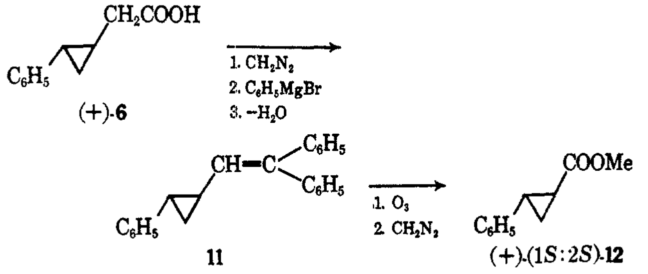
[a] H. Rupe, *Ann.*, **369,** 311 (1909). [b] H. M. Walborsky, T. Sugita, M. Ohno, and Y. Inouye, *J. Amer. Chem. Soc.*, **82,** 5255 (1960). [c] A. McKenzie and H. Wren, *J. Chem. Soc.*, **91,** 1215 (1907). [d] The structure was substantiated by uv analyses (λ_{max} 250 mμ, ϵ 16,800), ozonolysis to give benzoic and malonic acids, and correct elemental analysis (*Anal.* Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 80.68; H, 9.08.). *Cf.* R. P. Linstead and L. T. D. Williams, *J. Chem. Soc.*, 2741 (1926).

TABLE III

ANALYTICAL DATA OF DERIVATIVES OF CYCLOPROPANE PRODUCTS

Product	Bp, °C (mm)	$n^{20}D$	Derivative	Mp, °C	Molecular formula	Calcd, %		Found, %	
						C	H	C	H
1	98–100 (18)[a]	1.4374	*p*-Phenylphenacyl ester	107.5–108.5	$C_{19}H_{18}O_3$	77.53	6.16	77.76	6.42
2	109–112 (18)	1.4339	*p*-Phenylphenacyl ester	58.5	$C_{20}H_{20}O_3$	77.90	6.54	78.10	6.64
3	96–96.5 (17)[b]	1.4390	*p*-Phenylphenacyl ester	102	$C_{20}H_{20}O_3$	77.90	6.54	77.42	6.54
4	96–99 (16)[c]	1.4420	Acid	176	$C_5H_6O_4$	46.16	4.65	46.21	4.62
5	126–127 (9.5)[a]	1.5284	Acid	89–90	$C_{10}H_{10}O_2$	74.05	6.22	73.92	6.19
6	117–118 (0.1)	1.5329	Acid	41	$C_{11}H_{12}O_2$	74.97	6.86	74.68	7.01

[a] D. E. Applequist, *et al.*, *J. Amer. Chem. Soc.*, **82,** 2372 (1960). [b] E. R. Nelson, *et al.* [*ibid.*, **79,** 3467 (1957)], record bp 95–98° (12 mm) and $n^{20}D$ 1.4405. [c] M. Jacobson, *et al.* [*Science*, **147,** 748 (1965)], record bp 103–104° (24 mm) and $n^{24}D$ 1.4418.



conformational asymmetry ($[\phi]D_{calcd}$ +140°; $[\phi]D_{found}$ +476°).

Experimental Section[15]

Partial asymmetric synthesis in the present Simmons–Smith reactions is illustrated by a typical run for (−)-methyl crotonate to give *trans*-2-methylcyclopropanecarboxylic acid and the identical procedure was followed for others with small variations of additives.

***trans*-2-Methylcyclopropanecarboxylic Acid (1).**—A solution of methylene iodide (27 g, 0.1 mol) and zinc copper couple (13 g, 0.2 atom, in dust or granule) in 150 ml of ether was stirred for 0.5 hr and then (−)-menthyl crotonate (11 g, 0.05 mol) was added to the solution. After refluxed for 60 hr, the reaction mixture was poured into aqueous ammonium chloride. The ethereal layer was washed with water and aqueous thiosulfate and dried over anhydrous magnesium sulfate. Ether was removed and the residue was distilled to give a fraction boiling at 110–130° (17 mm), which was treated with crude ozone in carbon tetrachloride solution. The ozonide was decomposed with dilute sodium hydroxide solution and the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the residual oil was hydrolized with sodium hydroxide in boiling water–ethylene glycol (1:2) for 36 hr. The alkaline solution was thoroughly extracted with ether to remove menthol. The water layer was acidified with dilute hydrochloric acid and then extracted with ether. The combined extract was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. Distillation of the solvent-free residue gave **1**: bp 98–100° (18 mm); $n^{20}D$ 1.4374; yield 1.2 g (21%); $[\alpha]^{20}D$ +1.73° (neat); optical yield 2.8%. (See Tables II and III.)

Configurational Correlation of (+)-*trans*-2-Phenylcyclopropaneacetic Acid (6) to (+)-(1*S*:2*S*)-*trans*-2-Phenylcyclopropanecarboxylic Acid.—The dextrorotatory acid (0.9 g, $[\alpha]^{20}D$ +4.1°) was converted with diazomethane into the corresponding methyl ester: bp 150–152° (17 mm), $n^{20}D$ 1.5164. An excess of phenylmagnesium bromide (4 mol equiv) was added to the methyl ester (0.9 g) in absolute ether and the reaction mixture was refluxed for 4 hr. The resulted reaction mixture was worked up in a usual manner and then treated with phosphorus pentoxide in boiling benzene. The distillate [bp 130–140° (0.1 mm)] was ozonized to give, after treatment in conventional procedure and subsequent esterification, methyl (+)-*trans*-2-phenylcyclopropanecarboxylic acid (**12**): bp 133–134° (17 mm); $n^{20}D$ 1.5269; yield 0.3 g. The ir spectrum and R_t on vpc were identical with those of the authentic sample: $[\alpha]^{20}D$ +4.4° (*c*, 4.75, methanol).

***cis*-Bicyclo[4.1.0]heptan-2-ol (10).**—According to the Dauben procedure,[7b] the bicyclic alcohol was prepared in a 65% yield from 2-cyclohexenol (**7**): bp 75–76° (17 mm); $n^{20}D$ 1.4890. About 3% contamination of the *trans* isomer in the crude product was detected by vpc analysis. The phenylurethan had mp 109–109.5°.

***cis*-Bicyclo[4.1.0]heptan-2-ol (10) from 2-Cyclohexenyl Acetate (8).**—An identical procedure was followed for 2-cyclohexenyl acetate [bp 75–76° (17 mm), $n^{20}D$ 1.4590] and, after subsequent lithium aluminum hydride reduction of the reaction mixture, *cis*-bicyclic alcohol **10** was obtained in a 23% over-all yield. The product was contaminated by the *trans* isomer (5%) as detected by vpc analysis. The phenylurethan of *cis* **10** had mp 109.5° (*Anal.* Calcd for $C_{14}H_{17}O_2N$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.61; H, 7.45; N, 6.12.); the phenylurethan of the *trans* isomer had mp 97.5–98° (*Anal.* Found: C, 72.74; H, 7.41; N, 6.24.).

The identity of the *cis* isomer by this route was obtained by the comparison of ir spectrum, R_t on vpc, and physical properties and phenylurethan derivative with those of the authentic sample prepared by the Dauben procedure.

Registry No.—**1,** 14590-52-4; **1** *p*-phenylphenacyl ester, 16205-62-2; **2,** 16205-63-3; **2** *p*-phenylphenacyl ester, 16205-64-4; **3,** 14590-53-5; **3** *p*-phenylphenacyl ester, 16205-66-6; **4,** 16205-67-7; **4** acid, 14590-54-6; **5,** 10488-03-6; **5** acid, 3471-10-1; **6,** 16205-71-3; **12,** 16205-72-4; (−)-menthyl cinnamate, 16205-99-5; **10,** 16205-73-5.

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[15] Melting and boiling points were uncorrected. Optical rotation was measured on an automatic spectropolarimeter, Yanagimoto Model ORD-3. The ir spectra were recorded with a Hitachi infrared spectrophotometer, EPI-S2.