content was transferred under nitrogen to a distillation flask. The product was not soluble in benzene. The benzene and other low-boiling material were removed by distillation without rectification by lowering the pressure gradually to 10 mm at 40°. Most of the benzene was separated by distillation through a 36-in. column. The residue was distilled through a 20-in. spiral wire column to give 28 g, bp 121° at atmospheric pressure to 110° at 200 mm. Gas chromatography showed that it contained about 70% of one material and several other products in small amounts. A fraction boiling between 122 and 124°, which was about 85% pure according to gas chromatography, was analyzed, n^{30}D 1.4572, d^{20}_{20} 0.814 (lit.[13] bp 118°, n^{27}D 1.4557).

Anal. Calcd for C_9H_{12}: C, 88.82; H, 11.18; mol wt, 108. Found: C, 88.55; H, 11.39; mol wt (largest parent peak by mass spectroscopy), 108.

The product was purified further by gas chromatography. Its infrared absorption spectrum showed bands at 6.06, 6.10, 10.12, 11.0, and 11.35 μ indicating the presence of both a vinyl and a vinylidene group. All of the positions of the absorption peaks were identical with the positions reported for **5**.[14]

(13) W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, **27**, 1988 (1962).
(14) R. P. Hall, M.S. Thesis, Ohio University, Athens, Ohio, 1961, p 10.

Reduction of 1-Methylene-2-vinylcyclopentane.—1-Methylene-2-vinylcyclopentane (2 ml), which was about 85% pure, was hydrogenated over platinum oxide in a Parr hydrogenator at 40 psi and room temperature. After 1 hr the pressure had decreased to 37.5 psi. Gas chromatography showed the presence of two major peaks: 35% of peak I and 54% of peak II. A comparison with the two 1-ethyl-2-methylcyclopentanes obtained by hydrolysis of the TIBA–cyclooctadiene reaction product showed that peak I and peak II had the same retention times as **3** and **2**, respectively. Further support was obtained from the infrared and mass spectra of the products which had been purified by gas chromatography.

Hydrogenation of **5** over prereduced platinum oxide in acetic acid has been reported to give 66% of **2** and 34% of **3**.[13]

Registry No.—TIBA, 100-99-2; **1**, 111-78-4.

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Hydrogenolysis of Cyclopropanes

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Several cyclopropane derivatives bearing unsaturated functional groups directly on the three-membered ring, including ketones, acids, and esters, were prepared and subjected to hydrogenolysis at room temperature and atmospheric pressure over a palladium-on-carbon catalyst. Exclusive C_1–C_2 bond cleavage was observed for all cyclopropyl methyl ketones studied. Predominant C_1–C_2 bond cleavage (>70%) was observed for the cyclopropanecarboxylic acids and cyclopropanecarboxylic acid esters. For cyclopropanes bearing phenyl groups as the only unsaturated substituent, exclusive cleavage adjacent to the phenyl-substituted carbon atom was observed. This preference for C_1–C_2 bond cleavage may be due to polarization effects of the unsaturated substituents and/or binding of the unsaturated functional groups to the catalyst surface.

Although the cyclopropyl system is one that has been extensively studied, relatively few investigations have been carried out involving the ability of cyclopropanes to undergo hydrogenolysis.[2] In the previous studies only a small percentage of the work has dealt with the hydrogenolysis of cyclopropane rings adjacent to unsaturated groups. In addition, comparisons of the effect of structure on reactivity are often difficult to make because different catalysts as well as various reaction temperatures and pressures have been used. Cyclopropyl methyl ketone has been hydrogenated using copper–chromium, Raney nickel, zinc, zinc–copper, and copper catalysts. Various products result depending upon the catalyst employed.[2a] Several alkenylcyclopropanes have been hydrogenated,[2] but the only systematic study of the effect of structure upon the nature of the hydrogenation products has dealt with the differences observed in the behavior of 2-cyclopropyl-1- and -2-alkenes.[3] The only report of the effect of phenyl substituents was concerned with the relative reactivities of phenylcyclopropane and the various diphenylcyclopropanes.[4]

In an attempt to elucidate the effect of adjacent unsaturated groups on the direction of ring opening of the three-membered ring, several such cyclopropanes were prepared and hydrogenated at room temperature and atmospheric pressure in the presence of palladium on carbon. In all the cases studied hydrogenolysis of the cyclopropane ring could result in various products determined by the direction of bond cleavage. The results of these hydrogenolyses and their implications are discussed.

Results and Discussion

The results of the present study into the mode of ring opening of unsaturated cyclopropane derivatives upon hydrogenation at room temperature and atmospheric pressure over 10% palladium-on-carbon catalyst are presented in Table I.

Upon hydrogenation all the cyclopropanes bearing an adjacent carbonyl group preferentially undergo ring opening at the C_1–C_2[5] bond of the three-membered ring. In the case of the cyclopropyl methyl ketones hydrogenolysis occurs exclusively at the C_1–C_2 bond of the cyclopropane ring, while with the esters and acids a minimum of 70% of the ring-opened products results from rupture of the C_1–C_2 bond of the three-membered ring. The results of the hydrogenolyses of the cyclopropylcarbinols (**19**–**21**), acetates (**22**–**24**), *trans*-1,2-diphenylcyclopropane (**25**), and 1,1-dimethyl-2-phenylcyclopropane (**26**) indicate that, in those compounds in which a benzene ring is the only unsaturated moiety in conjugation with the three-membered ring, exclusive

(1) This work is taken in part from the M.S. Thesis of A. L. S.
(2) For reviews see (a) M. Yu. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962); (b) J. Newham, *Chem. Rev.*, **63**, 123 (1963).
(3) V. A. Slabey and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 3887 (1952).
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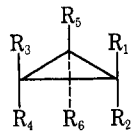
(5) See Table I for numbering system.

TABLE I

DIRECTION OF RING OPENING UPON HYDROGENOLYSIS OF CYCLOPROPANES



Compd	R_1	R_2	R_3	R_4	R_5	R_6	Bond cleaved, %[a,b] C_1–C_2	C_1–C_3	C_2–C_3
1	$COCH_3$	H	H	H	H	H	50	50	
2	$COCH_3$	H	H	C_4H_8[c]	H	...[c]	50	50	
3	$COCH_3$	H	H	C_6H_5	H	H	100		
4	$COCH_3$	H	CH_3	C_6H_5	H	H	100		
5	$COCH_3$	C_6H_5	H	CH_3	H	CH_3	50	50	
6	$COCH_3$	C_6H_5	CH_3	H	H	CH_3	50	50	
7	$COCH_3$	CH_3	C_6H_5	C_6H_5	H	H	100		
8	$COCH_3$	CH_3	H	C_6H_5	H	H	100[d]		
9	$COCH_3$	H	C_6H_5	C_6H_5	H	H	100[e]		
10	$CO_2C_2H_5$	H	H	C_6H_5	H	H	100		
11	CO_2CH_3	CH_3	C_6H_5	C_6H_5	H	H	89	11	
12	CO_2CH_3	CH_3	H	C_6H_5	H	H	85[d]	15[d]	
13	CO_2CH_3	H	C_6H_5	C_6H_5	H	H	80[e]		20[e]
14	CO_2H	H	H	C_6H_5	H	H	100		
15	CO_2H	H	C_6H_5	C_6H_5	H	H	100		
16	CO_2H	CH_3	C_6H_5	C_6H_5	H	H	100		
17	CO_2H	H	C_6H_5	H	H	H	100[d]		
18	CO_2H	CH_3	H	C_6H_5	H	H	70[d]	30[d]	
19	CH_2OH	CH_3	C_6H_5	C_6H_5	H	H	100		
20	CH_2OH	CH_3	H	C_6H_5	H	H			100[d]
21	CH_3CHOH	H	C_6H_5	C_6H_5	H	H			100[e]
22	$OCOCH_3$	C_6H_5	C_6H_5	H	H	H	100[f]		
23	$OCOCH_3$	CH_3	CH_3	CH_3	H	H		No reaction	
24	$OCOCH_3$	CH_3	H	C_6H_5	H	H			100[d,f]
25	C_6H_5	H	H	C_6H_5	H	H	100[e]		
26	CH_3	CH_3	C_6H_5	H	H	H			100[d]

[a] C_1 is the carbon atom bearing R_1 and R_2, C_2 is the carbon atom bearing R_3 and R_4, and C_3 is the carbon atom bearing R_5 and R_6. [b] All percentages are ±5% as analysis was by nmr. [c] A tetramethylene grouping bridges R_4 and R_6. [d] Dr. W. Wiedemann, unpublished results. [e] Dr. B. Plummer, unpublished results. [f] The acetoxy group was also cleaved.

cleavage of a carbon–carbon bond adjacent to the aromatic ring takes place.

The hydrogenolysis of alkylcyclopropanes typically occurs with cleavage of the bond between those two carbon atoms of the three-membered ring which carry the largest number of hydrogen atoms.[2] Inspection of Table I reveals that the behavior of cyclopropane derivatives containing an adjacent carbonyl function under conditions of hydrogenolysis is quite different from that exhibited by alkylcyclopropanes under similar reaction conditions as evidenced by the predominance of C_1–C_2 bond cleavage observed in this study.

Palladium was chosen for the catalyst because of reports that many other hydrogenation catalysts cause isomerization of alkylcyclopropanes to open-chain alkenes which are then hydrogenated, whereas palladium leads only to direct hydrogenolysis of the three-membered ring.[2] Palladium is also a specific catalyst for the hydrogenolysis of conjugated cyclopropane compounds. For example, phenylcyclopropane is hydrogenolyzed 90 times more rapidly in the presence of palladium than in the presence of platinum. In the former case the only product is *n*-propylbenzene, whereas in the latter case *n*-propylbenzene and possibly cyclopropylcyclohexane are also formed.[6]

The mechanisms of hydrogenolysis of cyclopropanes are not well understood.[2] There are, however, some studies in the literature which lend some understanding to the present results. The rates of hydrogenolysis of phenylcyclopropanes on palladium at 20° have been found to be *trans*-1,2-diphenylcyclopropane > phenylcyclopropane > *cis*-1,2-diphenylcyclopropane > 1,1-diphenylcyclopropane.[4] It was reported that under these conditions 1,1-diphenylcyclopropane fails to react. The Raman spectra of these compounds show a corresponding decrease in the conjugation of the substrate as the rate of hydrogenolysis decreases.[7] This was taken as evidence that polarization or conjugative effects and not steric hindrance are the important factors in determining the direction and rate of cleavage of phenyl-substituted cyclopropanes.

When unsaturated substituents are present on a cyclopropane ring, the point(s) of adsorption on the catalyst surface is not as well defined as with alkyl-substituted cyclopropanes.[2b] The possibility that phenylcyclopropane is initially adsorbed at the aromatic ring and that hydrogenolysis occurs by way of a migration of the adsorbed site to the cyclopropyl ring does not seem likely based on deuterium exchange studies.[2b] It has been suggested that the hydrogenation of alkenes in conjugation with a phenyl substituent proceeds *via* a species in which the olefinic bond is adsorbed on the catalyst surface while the aromatic ring is simultane-

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(7) V. T. Aleksanyan and Kh. Sterin, *Dokl. Akad. Nauk SSSR*, **131**, 1373 (1960); *Chem. Abstr.*, **57**, 7929 (1962).

ously π complexed to the metal.[8] Such a phenyl effect could conceivably be operative in the case of phenylcyclopropanes. Although 1,4-conjugate addition has been proposed for some of the hydrogenolyses of cyclopropyl methyl ketone,[2a] no supportive evidence has been provided. It has also been suggested that 1,4-conjugate addition may be involved in the hydrogenolysis of alkenylcyclopropanes.[2a] However, in a study of the hydrogenolysis of isopropenylcyclopropane over palladium it was shown that the product that would result from 1,4-conjugate addition could be formed by the isomerization by palladium of the product that would result from 1,2 addition of hydrogen to the cyclopropyl ring.[9]

The most probable explanations for the formation of the major hydrogenolysis products observed in this study resulting from the rupture of the bond between C_1 and C_2 thus appear to be based upon (1) the action of polarization effects acting through conjugative or inductive forces tending to weaken the C_1–C_2 bond of the cyclopropane ring and leading to chemisorption with simultaneous ring cleavage, and (2) an interaction of the unsaturated functional groups on C_1 and C_2 with the catalyst surface in such a manner as to properly orient the cyclopropyl ring for cleavage of the C_1–C_2 bond. These two effects may operate separately or in conjunction with one another. Steric effects do not appear to be of any consequence as is most noticeably shown by the fact that 2,2-diphenyl-1-methylcyclopropyl methyl ketone (**7**) readily undergoes hydrogenolysis at the sterically shielded C_1–C_2 bond.

The formation of the minor products observed in the hydrogenolysis of some of the acids and esters does not show a definite pattern at this time. As there are many factors that could affect the formation of these products, no attempt will be made to interpret these results until further work is performed to determine if a definite pattern does exist.

The observation that 1-methyl-*trans*-2-phenylcyclopropyl acetate (**24**) undergoes cleavage of the acetoxy group as well as hydrogenolysis of the three-membered ring while 1,2,2-trimethylcyclopropyl acetate (**23**) fails to react suggests that the acetoxy function is lost in the former case from a species in which the cyclopropane ring is bound to the catalyst.

Experimental Section

General.—Melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected. Boiling points are uncorrected. The ir spectra were recorded with a Beckman IR-10. Nmr spectra were determined with a Varian A-60 spectrometer using TMS as an internal standard. Glpc analyses were performed on either an Aerograph Model 200 or an F & M Model 700. Preparative scale glpc was performed on an Aerograph Autoprep Model A-700. All elemental analyses were performed by A. Bernhardt, Mülheim, Germany.

The hydrogenolyses of substituted cyclopropanes were carried out in an atmospheric pressure hydrogenation apparatus of essentially the same design as that described by Wiberg,[10] the principal difference being that water rather than mercury was used in the 500-ml buret. The hydrogenations were carried out using 10% palladium on carbon as the catalyst in 95% ethanol unless otherwise noted. In a typical experiment 1 g of the cyclopropane compound was dissolved in 25 ml of solvent and, along with 150 mg of catalyst, was charged to a hydrogenation flask equipped with a magnetic stirring bar. The system was alternately evacuated and filled with hydrogen five times and then the magnetic stirrer was started. When the uptake of hydrogen ceased, the catalyst was removed by filtration, and after the removal of solvent by distillation at atmospheric pressure, the crude reaction product was analyzed by nmr and ir spectroscopy. The product distribution is based entirely on nmr analysis and is therefore accurate to ±5%. The overall yield of ring-opened products was 90% or greater unless otherwise stated. In general, the ketones took up the theoretical amount of hydrogen in a few hours, whereas the acids and esters required several days for complete hydrogenolysis of the cyclopropane ring.

Diphenyldiazomethane was prepared by the method of Smith and Howard,[11] employing a modification described by Miller.[12]

Cyclopropyl methyl ketone (**1**) was commercially available and was used without purification. Hydrogenolysis of **1** produced 2-pentanone as the only product: ir (CCl_4) 1715 cm^{-1}; nmr (CCl_4) δ 0.98 (t, 3), 1.48 (m, 2), 2.07 (s, 3), 2.35 (t, 2). A mixture melting point of the 2,4-dinitrophenylhydrazone prepared from the product with an authentic sample showed no melting point depression. The ir spectra of the two derivatives were identical.

***exo*-7-Norcaryl methyl ketone** (**2**)[13] gave only cyclohexylacetone upon hydrogenolysis: ir (CCl_4) 1715 cm^{-1}; nmr (CCl_4) δ 1.37 (m, 11), 2.02 (s, 3), 2.20 (d, 2). A 2,4-dinitrophenylhydrazone derivative of the reaction product was prepared, mp 117–118° (lit.[14] mp 115–117°).

***trans*-2-Phenylcyclopropyl methyl ketone** (**3**)[15] gave only 5-phenyl-2-pentanone upon hydrogenolysis: ir (CCl_4) 1720 cm^{-1}; nmr (CCl_4) δ 1.92 (s, 3), 2.15 (m, 6), 7.13 (s, 5). The spectroscopic identification of the product was supported by preparation of two derivatives: 2,4-dinitrophenylhydrazone, mp 77.5–79° (lit.[16] mp 78°); semicarbazone, mp 130–133.5° (lit.[17] mp 135–136°).

***cis*-2-Methyl-*trans*-2-phenylcyclopropyl methyl ketone** (**4**) was prepared in 14% yield from *cis*-2-methyl-*trans*-2-phenylcyclopropanecarboxylic acid and methyllithium using the method described by Tegner,[18] bp 52–57° (0.4–0.5 mm). A 2,4-dinitrophenylhydrazone derivative was prepared yielding orange crystals (ethanol), mp 161.5–163.5°.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12; N, 15.81. Found: C, 60.83; H, 5.26; N, 15.64.

Hydrogenolysis of **4** produced only 5-phenyl-2-hexanone: ir (CCl_4) 1722 cm^{-1}; nmr (CCl_4) δ 1.21 (d, 3), 1.88 (s, 3), 2.28 (m, 5), 7.15 (s, 5). A semicarbazone of the product was prepared, mp 146–148° (lit.[19] mp 147°).

***trans,trans*-2,3-Dimethyl-1-phenylcyclopropyl methyl ketone** (**5**)[20] gave only 4-methyl-3-phenyl-2-hexanone upon hydrogenolysis: ir (CCl_4) 1720 cm^{-1}; nmr (CCl_4) δ 0.93 (m, 9), 1.97 (s, 3), 3.38 (d, 1), 7.20 (s, 5).

***cis,trans*-2,3-Dimethyl-1-phenylcyclopropyl Methyl Ketone** (**6**).[20]—The hydrogenation product was shown to be the same as that resulting from the isomeric ketone, **5**, based on ir, nmr, and glpc (5-ft 15% Apiezon L on 60–80 Chromosorb W at 185°) comparisons.

2,2-Diphenyl-1-methylcyclopropyl methyl ketone (**7**)[21] gave 5,5-diphenyl-3-methyl-2-pentanone as the only hydrogenolysis product: ir (CCl_4) 1710 cm^{-1}; nmr (CCl_4) δ 0.93 (d, 3), 1.75 (s, 3), 2.32 (m, 3), 3.83 (m, 1), 7.05 (s, 10).

1-Methyl-*trans*-2-phenylcyclopropyl methyl ketone (**8**)[22] gave

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(21) F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4838 (1962).

(22) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966).

only 3-methyl-5-phenyl-2-pentanone upon hydrogenolysis: nmr (CCl_4) δ 1.04 (d, 3), 2.00 (s, 3), 2.06 (m, 5), 7.12 (s, 5).

2,2-Diphenylcyclopropyl methyl ketone (9)[21] gave only 5,5-diphenyl-2-pentanone: ir (CCl_4) 1720 cm^{-1}; nmr (CCl_4) δ 1.95 (s, 3), 2.20 (m, 4), 3.78 (t, 1), 7.10 (s, 10).

Ethyl *trans*-2-phenylcyclopropanecarboxylate (10)[15] gave only ethyl 4-phenylbutanoate upon hydrogenolysis: ir (CCl_4) 1745 cm^{-1}; nmr (CCl_4) δ 1.20 (t, 3), 2.03 (m, 4), 2.60 (t, 2), 4.05 (quartet, 2), 7.15 (s, 5).

Methyl 2,2-diphenyl-1-methylcyclopropanecarboxylate (11)[23] gave a mixture of products upon hydrogenolysis. The reaction mixture exhibited ir (CCl_4) 1738 cm^{-1}; nmr (CCl_4) δ 1.27 (m), 2.28 (m), 3.20 (s), 3.33 (s), 3.45 (s), 3.88 (m), 7.23 (m). Interpretation of these data along with the observed nmr integrated peak areas led to the conclusion that the reaction mixture consisted of 26% unreacted starting material, 66% methyl 4,4-diphenyl-2-methylbutanoate, and 8% methyl 3,3-diphenyl-2-methylbutanoate.

Methyl 1-methyl-*trans*-2-phenylcyclopropanecarboxylate (12) was prepared from the corresponding acid, **18**, by treatment with diazomethane. The crude product was subjected directly to hydrogenolysis and gave an 85:15 mixture of methyl 2-methyl-4-phenylbutanoate–methyl 2-methyl-3-phenylbutanoate as shown by ir and nmr spectroscopy and glpc analysis.

Methyl 2,2-diphenylcyclopropanecarboxylate (13)[23] gave a mixture of 80% methyl 4,4-diphenylbutanoate and 20% methyl 3,3-diphenyl-2-methylbutanoate upon hydrogenolysis: nmr (CCl_4) δ 1.08 (d), 2.20 (m), 3.34 (s), 3.48 (s), 3.86 (m), 7.10 (s).

Ethyl *cis*- and *trans*-2-Methyl-2-phenylcyclopropanecarboxylates.—These isomeric esters were prepared by a method analogous to that used by Burger and Yost[24] to prepare ethyl 2-phenylcyclopropanecarboxylate. In this case α-methylstyrene and ethyl diazoacetate were the reagents used. The mixture of isomers was obtained in 44% yield, bp 70–78° (0.75 mm). The ratio of ethyl *trans*-2-methyl-*cis*-2-phenylcyclopropanecarboxylate to ethyl *cis*-2-methyl-*trans*-2-phenylcyclopropanecarboxylate was found to be 1:3 by glpc analysis (5-ft Apiezon L on 60–80 Chromosorb W at 160°). Separation of the isomers was effected by initial enhancement of the isomer ratio by use of a Nester–Faust annular Teflon spinning-band distillation column followed by preparative scale glpc (20-ft SE-30 on 30–60 Chromosorb P).

Anal. Calcd for $C_{13}H_{16}O_2$ (ethyl *cis*-2-methyl-*trans*-2-phenylcyclopropanecarboxylate): C, 76.44; H, 7.90. Found: C, 76.41; H, 7.74.

Anal. Calcd for $C_{13}H_{16}O_2$ (ethyl *trans*-2-methyl-*cis*-2-phenylcyclopropanecarboxylate): C, 76.44; H, 7.90. Found: C, 76.24; H, 7.70.

Structure assignments for the geometrical isomers were made using the chemical shift of the methylene protons in the carboethoxy group as a criterion.[25] Thus the structure of ethyl *cis*-2-methyl-*trans*-2-phenylcyclopropanecarboxylate was assigned to the compound with nmr (CCl_4) δ 1.22 (t, 3), 1.40 (m, 2), 1.50 (s, 3), 1.90 (doublet of doublets, 1), 4.13 (quartet, 2), 7.20 (s, 5), and the structure of ethyl *trans*-2-methyl-*cis*-2-phenylcyclopropanecarboxylate to the compound with nmr (CCl_4) δ 0.85 (m, 4), 1.37 (s, 3), 1.72 (m, 2), 3.74 (quartet, 2), 7.17 (s, 5).

***trans*-2-Phenylcyclopropanecarboxylic acid** (14)[15] gave only 4-phenylbutanoic acid upon hydrogenolysis: ir (CCl_4) 2940, 1720 cm^{-1}; nmr (CCl_4) δ 2.12 (m, 4), 2.67 (t, 2), 7.17 (s, 5), 12.09 (s, 1).

2,2-Diphenylcyclopropanecarboxylic acid (15)[23] gave only 4,4-diphenylbutanoic acid upon hydrogenolysis in ethyl acetate: ir ($CHCl_3$) 3020, 1710 cm^{-1}; nmr ($CDCl_3$) δ 2.33 (m, 4), 3.77 (m, 1), 7.17 (s, 10), 11.30 (s, 1).

1-Methyl-2,2-diphenylcyclopropanecarboxylic acid (16)[22] was hydrogenated using a 2:3 mixture of ethanol–ethyl acetate as the solvent to give 4,4-diphenyl-2-methylbutanoic acid as the only product: ir (CCl_4) 2950, 1705 cm^{-1}; nmr (CCl_4) δ 1.15 (d, 3), 2.17 (m, 3), 3.83 (t, 1), 6.90 (s, 10), 11.73 (s, 1).

***cis*-2-Phenylcyclopropanecarboxylic acid** (17)[15] gave only 4-phenylbutanoic acid upon hydrogenolysis: nmr (CCl_4) δ 2.10 (m, 4), 2.67 (t, 2), 7.17 (s, 5), 12.41 (s, 1).

1-Methyl-*trans*-2-phenylcyclopropanecarboxylic acid (18)[22] gave a mixture of 70% 2-methyl-4-phenylbutanoic acid and 30% 2-methyl-3-phenylbutanoic acid: nmr (CCl_4) δ 1.19 (m), 1.77 (m), 2.53 (m), 3.48 (m), 7.08 (s), 10.50 (s).

***cis*-2-Methyl-*trans*-2-phenylcyclopropanecarboxylic acid** was prepared by saponification of the corresponding ethyl ester in ethanol in 66% yield, mp 46–48° (lit.[26] mp 52.5–53°) from petroleum ether (bp 35–60°).

2,2-Diphenyl-1-methylcyclopropylcarbinol (19)[27] gave only 4,4-diphenyl-2-methyl-1-butanol upon hydrogenolysis: ir (CCl_4) 3600, 3345 cm^{-1}; nmr (CCl_4) δ 0.83 (d, 3), 1.81 (m, 3), 2.70 (s, 1), 3.22 (d, 2), 3.88 (m, 1), 7.10 (s, 10).

1-Methyl-*trans*-2-phenylcyclopropylcarbinol (20) was prepared by reduction of the corresponding acid, **18**, with lithium aluminum hydride.[28] 2,2-Dimethyl-3-phenylpropanol was the only product obtained upon hydrogenation: nmr (CCl_4) δ 0.84 (s, 6), 2.49 (s, 2), 2.56 (s, 1), 3.17 (s, 2), 7.15 (s, 5).

2,2-Diphenylcyclopropylmethylcarbinol (21) was prepared by sodium borohydride reduction of the corresponding ketone, **9**, and was hydrogenated without purification to give 1,2-dimethyl-3,3-diphenyl-1-propanol as the only product: ir (CCl_4) 3380 cm^{-1}; nmr (CCl_4) δ 0.88 (m, 6), 2.37 (m, 1), 2.47 (s, 1), 3.65 (m, 2), 7.15 (m, 10).

***cis*-1,2-Diphenylcyclopropyl acetate** (22) was prepared as previously described by Freeman.[29] The isomers were separated[30] by distillation through a Nester–Faust 24-in. spinning-band distillation column. The fraction with bp 100–110° (0.06 mm) was found to be greater than 95% *cis*-1,2-diphenylcyclopropyl acetate by glpc analysis. Crystallization of this material from hexane yielded pure **22**, mp 74.5–75.0°.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 81.05; H, 6.61.

The hydrogenation of this acetate in a 2:3 mixture of ethanol–ethyl acetate required 2 mol of hydrogen per mol of cyclopropyl compound. The ir and nmr spectra of the product was identical with those of an authentic sample of 1,3-diphenylpropane.

1,2,2-Trimethylcyclopropyl acetate (23)[20,29] failed to undergo hydrogenolysis in either ethyl acetate or acetic acid.

1-Methyl-*trans*-2-phenylcyclopropyl acetate (24)[29] gave only 2-methyl-1-phenylpropane upon hydrogenolysis: nmr (CCl_4) δ 0.89 (d, 6), 1.71 (m, 1), 2.41 (d, 2), 7.09 (s, 5).

***trans*-1,2-Diphenylcyclopropane** (25)[31] gave only 1,3-diphenylpropane upon hydrogenolysis: nmr (CCl_4) δ 1.93 (m, 2), 2.58 (t, 4), 7.15 (s, 10).

1,1-Dimethyl-2-phenylcyclopropane (26)[28] was prepared from the corresponding carbinol, **20**, and yielded only 2,2-dimethyl-1-phenylpropane upon hydrogenation: nmr (CCl_4) δ 0.91 (s, 9), 2.40 (s, 2), 7.09 (s, 5).

Registry No.—**1**, 765-43-5; **2**, 10330-36-6; **3**, 14063-86-6; **4**, 15967-24-5; **5**, 27067-36-3; **6**, 27067-37-4; **7**, 27067-38-5; **8**, 27067-39-6; **9**, 27067-40-9; **10**, 946-39-4; **11**, 6975-21-9; **12**, 27067-43-2; **13**, 19179-60-3; **14**, 939-90-2; **15**, 7150-12-1; **16**, 27067-47-6; **17**, 939-89-9; **18**, 13005-22-6; **19**, 27067-50-1; **20**, 27067-51-2; **21**, 27067-52-3; **22**, 27067-53-4; **23**, 16526-20-8; **24**, 16526-24-2; **25**, 1138-47-2; **26**, 7653-94-3; ethyl *cis*-2-methyl-*trans*-2-phenylcyclopropanecarboxylate, 27070-05-9; ethyl *trans*-2-methyl-*cis*-2-phenylcyclopropanecarboxylate, 27070-06-0.

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