Anal. Calcd. for $C_{25}H_{34}O_8$: C, 64.99: H, 7.42. Found: C, 65.27: H, 7.38.

Compound II (R = H) was isolated by addition of water to the acetic acid filtrate from above: 0.2 g., m.p. 224–225°, lit.[2] m.p. 226–227°, ν_{max}^{KBr} (cm.$^{-1}$) 1730 and 1758. The dimethyl ester II (R = CH_3) was prepared by addition of ethereal diazomethane and was found to be identical with II (R = CH_3) obtained by permanganate oxidation of maleopimaric acid followed by esterification as previously described[5] in melting point (m.p. 180°, alone and on admixture) and by infrared and n.m.r. spectra.

Compound III was isolated from the aqueous acetic acid filtrate as previously described[2] and, after crystallization from hot acetone, gave m.p. 289–290° (100 mg.); ν_{max}^{KBr} (cm.$^{-1}$) 2950, 1777, and 1720; n.m.r. ($CDCl_3$) δ 0.72 (doublet, J = 7 c.p.s.), 0.85, 1.07 (doublet, J = 7 c.p.s.), 1.20, 3.20, (14 H), and 3.71 (OCH_3), no olefinic hydrogen atoms were evident; negative tetranitromethane test.

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.83; H, 7.97. Found: C, 69.77; H, 7.91.

Concentration of the filtrate after removal of X, II, and III gave a residue which, by melting point and infrared spectrum, appeared to be almost entirely starting material.

Preparation of the Tetramethyl Ester of X.—An ethereal solution of diazomethane (excess) was added to 250 mg. of X dissolved in 30 ml. of methanol and, after standing overnight, the solution was filtered. Evaporation of the filtrate gave the tetramethyl ester (72%) which melted at 128–132° after recrystallization from water–methanol, ν_{max}^{KBr} (cm.$^{-1}$) 1754–1724 (broad) and 1250–1176. The n.m.r. spectrum of the tetramethyl ester, on integration, showed 30 ± 3% of the total hydrogen present as methoxyl hydrogen (theoretical value 28.5%) by the appearance of three peaks at δ 3.57, 3.63, and 3.69. The saponification equivalent found was 510 (calculated for $C_{28}H_{42}O_9$: 523) assuming four carboxyl groups; if three carboxyl groups are present the saponification equivalent found would have been in the vicinity of 382.

Preparation of III by Direct Epoxidation of I.—A solution containing 3 ml. of trifluoroacetic anhydride and 1 ml. of 90% hydrogen peroxide in 10 ml. of methylene chloride was added dropwise over an interval of 20 min. to a stirred suspension of 4 g. of disodium hydrogen phosphate in 30 ml. of methylene chloride containing 2.5 g. of methyl maleopimarate.[7] The solution was refluxed for 45 min., stirred at room temperature an additional 48 hr., washed with 10% sodium sulfite solution, then filtered; the filtrate was further washed with 10% sodium bicarbonate solution and finally with water. After drying over anhydrous magnesium sulfate, the organic layer was concentrated with a rotary evaporator to give 2.1 g. of crude product which, after recrystallization from acetone, gave 1.5 g. of III identical in melting point (m.p. 289–290°; alone and on admixture) and in infrared and n.m.r. spectra with III obtained by the ozonolysis of I as described above.

Preparation of IV.—Trimethyl fumaropimarate (V,[6] 1.08 g.) was epoxidized with trifluoroperacetic acid as described above to give 0.45 g. of IV: m.p. 179–181° after recrystallization from ether; ν_{max}^{KBr} (cm.$^{-1}$) 1738 and 2950; n.m.r. ($CDCl_3$) δ 0.71, 1.00 (doublet, J = 6 c.p.s.), 1.03, 1.32 (doublet, J = 6 c.p.s.), 3.18 (14 H), 3.66, 3.70, and 3.80.

Anal. Calcd. for $C_{27}H_{40}O_7$: C, 68.12; H, 8.47. Found: C, 68.37; H, 8.43.

Compound III (0.33 g.) was refluxed in a solution of 10 ml. of methanol and 10 ml. of 25% aqueous sodium hydroxide for 34 hr. (shorter reflux times resulted in complete recovery of III). The solution was diluted with water and acidified with dilute hydrochloric acid, and the precipitate was taken up in ether. The ether extract, after drying, was evaporated to give 0.26 g. of product: m.p. 185–198°; ν_{max}^{KBr} 2570–3500 (broad). This material (0.19 g.) was dissolved in 30 ml. of ether and to this solution ethereal diazomethane was added. Evaporation of the ether solution yielded 0.065 g. of unreacted III, m.p. 287–291°, and the remainder as a gummy mass which could not be crystallized. Thin layer chromatography on 25-μ-thick silica gel coated glass plates using 3:7 methyl acetate–n-hexane as the mobile phase and detection by iodine vapors showed that this gummy material was predominantly the same as IV (R_f 0.45), the other components presumably being the C-15 epimer of IV and unreacted III.

Reaction of VI with Trifluoroperacetic Acid. Preparation of VII.—Trimethyl ester VI (2.58 g.) was treated with trifluoroacetic anhydride and hydrogen peroxide as described above. After the usual work-up 2.6 g. of white glassy product was obtained which, after three recrystallizations from methanol, gave 1.5 g. of VII: m.p. 146–148°; ν_{max}^{KBr} (cm.$^{-1}$) 3400, 1762, and 1709; n.m.r. (CCl_4) δ 1.00, 1.02 (doublet, J = 6 c.p.s.), 1.13, 1.20 (doublet, J = 6 c.p.s.), 3.64, 3.71, 3.84 (14 H, after addition of D_2O).

Anal. Calcd. for $C_{26}H_{38}O_7$: C, 67.59; H, 8.29. Found: C, 67.42; H, 8.38.

VI was unchanged after refluxing in methanolic sodium hydroxide for 8 hr. followed by acidification and re-esterification with diazomethane.

Relative Shielding of *cis* and *trans* Methyls of Some Substituted Methylcyclopropanes[1]

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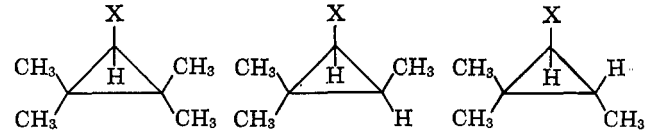
The n.m.r. spectra of **1**–**9** are the subject of this Note. In particular the relative chemical shifts of methyls *cis* and *trans* to the X functions are discussed.



1, X = CO_2CH_3 **2**, X = CO_2CH_3 **3**, X = CO_2CH_3
4, X = CH_2OH **5**, X = CH_2OH **6**, X = CH_2OH
7, X = $C(CH_3)_2OH$ **8**, X = $C(CH_3)_2OH$ **9**, X = $C(CH_3)_2OH$

The three esters **1**, **2**, and **3** were obtained *via* copper-catalyzed addition of diazoacetic ester to 2,3-dimethyl-2-butene[2] and 2-methyl-2-butene.[3] Isomers **2** and **3**, arising from addition to 2-methyl-2-butene, could unfortunately not be separated by the vapor phase chromatography equipment available at the time. However, mixtures enriched in **2** (70%) and **3** (90%) were obtained by partial saponification, the stereochemical assignments of *cis* and *trans* being made on the basis of relative saponification rates.[4] Primary alcohol **4** and mixtures enriched in **5** and **6** were derived from **1** and the mixtures enriched in **2** and **3** by reduction with lithium aluminum hydride. Tertiary alcohol **7** and mixtures enriched in **8** and **9** were formed from the same starting materials by treatment with methyllithium. Spectra of the mixtures of tertiary alcohols were consistent with **8** (80%) and **9** (80%) predominating in the mixtures derived from **2** (70%) and **3** (90%), respectively. The stereochemistry of the major isomer in each mixture was clearly revealed by the two coupling constants of 9.5 and 6.0 c.p.s. observed for the cyclopropyl hydrogen at τ *ca.* 9.9, the *cis* isomer being

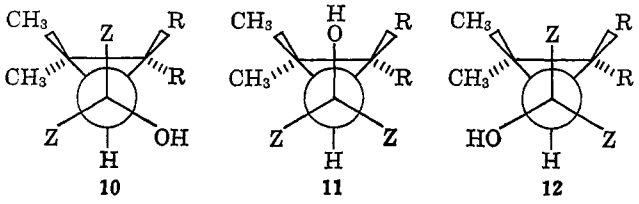
(1) This investigation was supported in part by Petroleum Research Fund Grant 1116-A4. Acknowledgment is also made of National Science Foundation Grant G 19108 which contributed to the purchase of the n.m.r. spectrometer used in this research.

(2) A. P. Meschcheryakov and I. E. Dolgii, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 931 (1960).

(3) P. S. Skell and R. M. Etter [*Chem. Ind.* (London), 624 (1958)] performed this addition in a competitive rate study but gave no experimental details and did not refer to the individual isomers **2** and **3**.

(4) See P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961); W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).

associated with the larger value.[5] Spectra of the mixtures of primary alcohols were consistent with **5** and **6** predominating in the mixtures derived from **2** (70%) and **3** (90%), respectively. Although it was not possible to analyze the mixtures of **5** and **6** accurately because of overlapping signals, it was nevertheless possible to assign stereochemistry to the major isomer in each mixture on the basis of the patterns associated with the hydroxymethyl hydrogens. The absorption of the major isomer derived from **2** (70%) closely resembles that of **4**; an A_2X pattern, J = 7 c.p.s., at τ *ca.* 6.5 is seen for the grouping >CHCH$_2$O–. By contrast, the major isomer derived from **3** (90%) shows a distinct ABX pattern, J_{AB} = 11 c.p.s., J_{AX} = *ca.* 8 c.p.s., J_{BX} = *ca.* 6 c.p.s. These results are readily interpreted by considering the relative stabilities of the most stable conformations of the hydroxymethyl group **10** and **12** (Z = H). In **4** (tetramethyl) $E_{10} = E_{12}$ (A_2X); in **5** (*cis* trimethyl) $E_{10} \approx E_{12}$ (A_2X); and in **6** (*trans* trimethyl) $E_{10} < E_{12}$ (ABX).



10 **11** **12**

Having established the stereochemical composition of our mixtures, we can consider the relative shifts of methyls *cis* and *trans* to the carbomethoxy, hydroxymethyl, and hydroxypropyl groups. Values recorded for the *cis* and *trans* trimethyl compounds are those calculated for the individual isomers by allowing for the presence of contaminating isomer in the mixtures used. All shifts refer to tetramethylsilane as internal reference. Data for the esters and tertiary alcohols are recorded in Table I.

TABLE I

CHEMICAL SHIFTS OF METHYLS

Solvent	Compd.	τ[a] C(CH$_3$)$_2$OH	*cis*	*trans*	Δ (*trans* – *cis*), p.p.m.
CCl_4	1		8.78	8.82	0.04
C_6H_6	1		8.68	9.03	0.35
C_6H_6	2		8.75 (8.75)	9.10	0.35 (0.35)
C_6H_6	3		8.74	9.10 (9.15)	0.36 (0.41)
CCl_4	7	8.74	8.79	8.94	0.15
CCl_4	8	8.72	8.80 (8.82)	8.97	0.17 (0.15)
CCl_4	9	8.77	8.80	(8.97) 9.01	(0.17) 0.21
C_6H_6	7	8.82	8.68	8.92	0.24
C_6H_6	8	8.81	8.69 (8.71)	8.96	0.27 (0.25)
C_6H_6	9	8.80, 8.86	8.69	(8.98) 9.02	(0.29) 0.33

[a] Parenthesized shifts are associated with AB_3 patterns.

It is convenient to discuss first the spectra of tertiary alcohols **7**–**9**. In carbon tetrachloride solution **7** (tetramethyl) shows three equally intense singlets at τ 8.74, 8.79, and 8.94. The problem of assigning the methyl lines to *cis*, *trans*, and hydroxypropyl methyls was solved by examination of the spectra of **8** and **9**. In **8** (*cis* trimethyl) the hydroxypropyl methyls clearly correspond to the intense singlet at τ 8.72. At high field (τ 8.97) is a single methyl line from the *trans* methyl and at low field are the two *cis* methyls, one a singlet at τ 8.80 and the other part of an AB_3 pattern centered at τ 8.82. Similarly in the spectrum of **9** (*trans* trimethyl) at low field are the hydroxypropyl methyls (τ 8.77) and the single *cis* methyl (τ 8.80), and at high field are the two *trans* methyls (τ 9.01 for the singlet, intensified by superposition of the strongest line of the AB_3 spectrum of the split *trans* methyl centered at τ 8.97). Thus *cis* methyls are deshielded relative to *trans* by 0.15 to 0.21 p.p.m.

This large shift difference can be explained on a conformational basis. In the tertiary alcohols, hydroxyl being smaller than methyl, the most stable conformation of the hydroxypropyl group is **11** (Z = CH_3). In this preferred conformation the hydroxyl oxygen is only about 2 Å. away from the nearer hydrogens of the *cis* methyls and is therefore likely to have a marked influence on the chemical shift of these hydrogens through bond anisotropy,[6] direct field,[7] and, possibly, dispersion[8] effects. The geometry of **11** is such that it is likely that all of these effects contribute to the observed deshielding of *cis* methyls. Deshielding of a similar magnitude has been observed for methyl groups similarly situated with respect to hydroxyl groups (1,3-diaxial) in several steroid molecules.[9]

Solvent shifts (relative to tetramethylsilane) were observed in changing to benzene solution. Although three equally intense singlets are present at τ 8.68, 8.82, and 8.92 in the spectrum of **7**, much the same shifts as those in carbon tetrachloride, they are not attributable in the same order to the same methyls, as ascertained by inspection of the spectra of **8** and **9** in benzene. The lowest field shifts (τ 8.68–8.71) now correspond to the *cis* methyls and the intermediate field shifts (τ 8.81–8.86) to the hydroxypropyl methyls, the high field shifts of the *trans* methyls (τ 8.92–9.02) being unchanged. Thus change of solvent leads to a further deshielding of *cis* methyls relative to *trans* (Δ = 0.24–0.33 p.p.m.) along with relative shielding of hydroxypropyl methyls. This change is consistent with hydrogen bonding of a benzene molecule to the hydroxyl proton,[10] the benzene molecule preferring to hydrogen bond so that the bulk of the ring is furthest from the negative end of the oxygen dipole, *i.e.*, it lies over the hydroxypropyl methyls, thus shielding them and simultaneously deshielding the *cis* methyls (see **13**). The magnitude of the upfield shift of the hydroxypropyl methyls in **7** and **8** (0.08 and 0.09 p.p.m.) correlates well with the shift of the methyl line we observe for *t*-butyl alcohol (0.05 p.p.m.).

One further problem to explain concerns the hydroxypropyl methyls of **9**. Although they are intrinsically magnetically nonequivalent, their shifts are almost identical in carbon tetrachloride and a single line is seen. In benzene, however, two distinct lines at τ 8.80

(5) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963); J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962).

(6) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, p. 112.

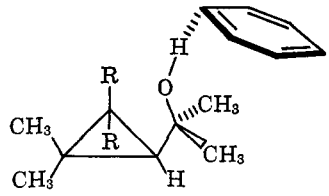
(7) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(8) T. Schaefer, W. F. Reynolds, and T. Yonamoto, *ibid.*, **41**, 2969 (1963); A. Bothner-By, *J. Mol. Spectry.*, **5**, 52 (1960).

(9) See T. Okamoto and Y. Kawazoe, *Chem. Pharm. Bull.* (Tokyo), **11**, 643 (1963). Additional references and data may be found in N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 1964, Chapter 2.

(10) See G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 3, p. 202, and references therein.

and 8.86 are visible. The absence of one of the *cis* methyls in **9** relieves some of the steric congestion present in **7** and **8** and changes the conformation of the hydroxypropyl group in two ways. Slight rotation about the carbon–carbon bond joining the group to the ring relieves some of the interaction with the remaining *cis* methyl group. This interaction is further decreased by rotation about the carbon–oxygen bond, the hydroxyl proton becoming asymmetric with respect to the two hydroxypropyl methyls (see **14**).[11] In benzene,



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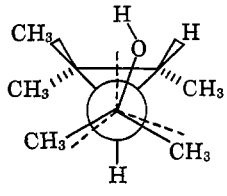

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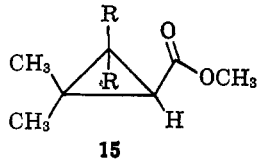
therefore, the intrinsic but small nonequivalence of the two methyls is magnified by hydrogen bonding to the asymmetrically disposed hydroxyl group.

The spectra of primary alcohols **4**–**6** were not very rewarding. In **4** two distinct methyl lines are present but the separation is small (0.10 p.p.m.) in both carbon tetrachloride and benzene. The spectrum of **5** shows two shifts ($\Delta \approx 0.09$ p.p.m.), the higher field being stronger, indicating that *cis* methyls are slightly shielded relative to *trans*. This small difference can be attributed to the magnetic anisotropy term arising from the hydroxymethyl–ring carbon–carbon bond of preferred conformations **10** and **12** (Z = H).[12] The smaller shift difference ($\Delta \approx 0.04$ p.p.m.) observed in the spectrum of **6** can be similarly explained as the change from **5** to **6** involves transfer of a methyl *syn*[13] to a *cis* methyl to *syn* to a *trans* methyl. This change relatively deshields the *cis* methyl of **6** and leads to collapse of the methyl lines.[14]

The spectrum of ester **1** in carbon tetrachloride shows that *cis* and *trans* methyls are almost indistinguishable (τ 8.78 and 8.82). In fact the shift difference was too small to allow interpretation of the spectra of **2** and **3** in carbon tetrachloride solution[15] and we have no evidence for correlating the shifts of **1** with *cis* and *trans* methyls. The assignment of Table I is arbitrary. In benzene solution, however, a large shift difference was observed for the methyls of **7**, lines appearing at τ 8.68 and 9.03, and stereochemical correlations were readily made by examining the spectra of **2** and **3** in benzene solution. Both show two unequally intense methyl lines from coincidental superposition of the strongest line of the expected AB_3 pattern on one of the two methyl singlets. In the *cis* isomer the stronger line occurs at low field while the high-field line is intensified in the *trans* isomer. Thus, unambiguously in benzene solution, methyls *cis* to the ester are deshielded relative to *trans*.[16] This relationship can be attributed to differential solvation of *cis* and *trans* methyls by the magnetically anisotropic benzene molecules. Benzene molecules approaching *cis* methyls are repelled by the electrons on the periphery of the ester. On the other hand benzene molecules approaching *trans* methyls are attracted by the positive end of the ester dipole: the net effect is relative deshielding of *cis* methyls. The magnitude of the shift difference in benzene is, in fact, similar to that observed for equatorial (deshielded) and axial (shielded) methyls adjacent to a ketone function.[17]



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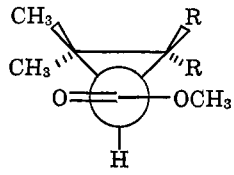

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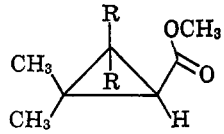

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As in the primary and tertiary alcohol series the conformation of the ester group should be considered. However, geometries and relative energies of conformational minima of **1** are not as easily defined. They can be discussed in terms of **15**, **16**, and **17**, not necessarily energy minima but representative of conformations in which an oxygen atom does and does not lie over the cyclopropane ring. Conformations analogous to **15** and **17**, showing maximum conjugation of the carbonyl group with the cyclopropane ring, have been demonstrated to be energy minima for cyclopropanecarboxaldehyde.[18] However, the *cis* methyls of **15** and **17** probably destabilize the conformations relative to **16**. We are tempted to reverse the arguments and draw conclusions about the conformation of the ester group from the n.m.r. data. If we *anticipate* a relatively large deshielding effect from conformations **15** and **17**, where an oxygen atom is very close to the *cis* methyls, the observed absence of a large shift difference in carbon tetrachloride then suggests that conformations like **16** are more populated than **15** or **17** in this solvent.

Experimental

Physical Data.—Melting points were taken in capillary tubes in a Thomas–Hoover melting point apparatus and are uncorrected. Vapor phase chromatographic data were obtained with a 5 ft. × 0.25 in. column of 5% Carbowax 20M on Teflon 6 using an Aerograph Model A-90-P2. The n.m.r. spectra of *ca.* 10% solutions were recorded using a Varian A-60 spectrometer with tetramethylsilane as an internal reference. Relative areas of peaks were obtained by weighing.

(11) The *direction* of rotation of the proton with respect to the *cis* methyl is arbitrarily shown in **14**.

(12) The angle between the C–C bond and a line joining the midpoint of the bond to the neighboring methyl hydrogens can vary from *ca.* 75 to 110°.

(13) An obvious convention to retain the significance of *cis* and *trans* with respect to the X function.

(14) An alternative explanation for the relative deshielding involves some population of conformation **11** which is relatively less unfavorable in the absence of one of the *cis* methyls.

(15) The published spectra of methyl *cis*- and *trans*-1,2-dimethylcyclopropanecarboxylate are similarly difficult to interpret. See Van Auken and Rinehart.[4]

(16) These results could lead to a simple method of assigning configurations to many 1-methylalkenes which are trisubstituted. For problems involved in assigning configurations to trisubstituted olefins, see J. W. Cornforth, R. H. Cornforth, and K.K. Mathew, *J. Chem. Soc.*, 112 (1959); R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

(17) N. S. Bhacca and D. H. Williams, *Tetrahedron Letters*, **No. 42**, 3127 (1964). A more extensive discussion is found in Chapter 7 of Bhacca and Williams.[9]

(18) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, **No. 13**, 705 (1964).

Methyl 2,2,3,3-Tetramethylcyclopropanecarboxylate (1).—2,2,3,3-Tetramethylcyclopropanecarboxylic acid,[2] m.p. 117–118°, was esterified with a distilled solution of ethereal diazomethane. Work-up, followed by distillation at 25 mm., yielded analytically pure ester, $n^{25}D$ 1.4382, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.43 (3H, singlet), 8.78 (6H, singlet), 8.82 (6H, singlet), and 8.90 (1H, singlet).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.23; H, 10.26. Found: 69.43; H, 10.33.

2,2,3,3-Tetramethyl-1-hydroxymethylcyclopropane (4).—A solution of 4.0 g. (25.6 mmoles) of **1** in 25 ml. of ether was added to a stirred, cooled solution of 3.8 g. (100 mmoles) of lithium aluminum hydride in 100 ml. of ether. The solution was refluxed for 30 min. and then cooled. A solution of 27 g. of ammonium chloride in 100 ml. of water was added cautiously with stirring and cooling, and the resulting mixture was stirred for 18 hr. Separation of the ether layer and extraction of the aqueous layer with ether, followed by further work-up yielded 3.5 g. of a slightly yellow residue. Distillation at 20 mm. yielded 2.48 g. (76%) of analytically pure alcohol, $n^{25}D$ 1.4483, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.46 (2H, doublet, J = 7.5 c.p.s.), 8.25 (1H, broad), 8.91 (6H, singlet), 9.00 (6H, singlet), and 9.53 (1H, triplet, J = 7.5 c.p.s.).

Anal. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 75.05; H, 12.45.

Alcohol **4** was further characterized by preparation of the *p*-nitrobenzoate, m.p. 104.5–106° from alcohol; n.m.r. chemical shifts (CCl_4) at τ *ca.* 1.8 (4H), 5.63 (2H, doublet, J = 8 c.p.s.), 8.84 (6H, singlet), 8.90 (6H, singlet), and 9.27 (1H, triplet, J = 8 c.p.s.).

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.98; H, 6.86. Found: C, 64.87; H, 6.82.

α,α,2,2,3,3-Hexamethyl-1-hydroxymethylcyclopropane (7).—The reported preparation[19] involves the addition of methyl Grignard to ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate. We found it convenient to prepare **7** from the reaction of excess ethereal methyllithium on 2,2,3,3-tetramethylcyclopropanecarboxylic acid, the mixture being allowed to stand at room temperature for 2 days. Work-up, followed by distillation at 30 mm., yielded analytically pure **7**, in 70% yield, $n^{25}D$ 1.4368, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 8.73 (6H, singlet), 8.78 (6H, singlet), 8.94 (6H, singlet), 9.32 (1H, singlet), and 9.90 (1H, singlet).

Methyl 2,2,3-Trimethylcyclopropanecarboxylate (Mixtures Enriched in *cis* and *trans* Isomers).—A solution of 25 g. (0.357 mole) of 2-methyl-2-butene[20] and 31.4 g. of ethyl diazoacetate[21] (92% by volumetric assay or 0.253 mole) was added *via* a dilution head, over a period of 12 hr., to a stirred and vigorously refluxing mixture of 25 g. (0.357 mole) of 2-methyl-2-butene, 20 g. of diethyl maleate, and 3 g. of powdered copper. (The reaction flask was heated with an oil bath maintained at 125 to 135°.) After nitrogen evolution had ceased (0.265 mole as measured by a wet-test meter, Precision Scientific Co.), the mixture was cooled and filtered. Distillation yielded initially 24 g. of recovered 2-methyl-2-butene and then 19 g. (32% based on unrecovered olefin) of product, b.p. 105–115° (65 mm.).

The ethyl ester was saponified and the resulting acid was esterified with distilled ethereal diazomethane, 11.2 g. of ethyl ester yielding 8.06 g. (78%) of methyl ester, b.p. 63–64° (24 mm.), showing a single peak by vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.42 (1.7H, singlet), 6.44 (1.3H, singlet), and 8.83–8.94 (11.0H) corresponding to a 43:57 mixture of *cis* and *trans* isomers. Partial saponification of this *ca.* 1:1 mixture (56 mmoles) of methyl esters by refluxing overnight in a solution of 1.57 g. (24 mmoles) of 85% potassium hydroxide in 75 ml. of methanol–water (2:1 v./v.) yielded, after work-up and distillation, 4.21 g. of recovered ester; n.m.r. chemical shifts at τ 6.42 and 6.44 corresponding to a 37:63 mixture of *cis* and *trans* isomers. Work-up of the acid formed in the saponification, followed by esterification with diazomethane and subsequent distillation, yielded 2.05 g. of ester; n.m.r. chemical shifts (CCl_4) at τ 6.42 and 6.44 corresponding to a 10:90 mixture of *cis* and *trans* isomers.

Partial saponification of another batch of methyl ester, under slightly different conditions, led to the recovery of *cis*-enriched ester. Thus, saponification of 8.24 g. (58 mmoles) of a *ca.* 1:1 mixture of isomers with a solution of 1.65 g. (25 mmoles) of 85% potassium hydroxide in 52 ml. of methanol–water (3.3:1 v./v.) by warming on a steam bath for 12 hr. yielded, after work-up and distillation, 3.38 g. of recovered ester; n.m.r. chemical shifts (CCl_4) at τ 6.42 and 6.44 corresponding to a 70:30 mixture of *cis* and *trans* isomers. (Recovered acid yielded a 37:63 mixture of *cis* and *trans* isomers.) Another partial saponification of the 3.38 g. (24 mmoles) of recovered ester with a solution of 0.66 g. (10 mmoles) of 85% potassium hydroxide in 19 ml. of methanol–water (3.75:1 v./v.) by warming for several days yielded 1.33 g. of recovered ester which was not further enriched in *cis* isomer (*cis–trans* 70:30).

2,2,3-Trimethyl-1-hydroxymethylcyclopropane (Mixtures Enriched in *cis* and *trans* Isomers).—Following the procedure given for the preparation of **2**, 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (70% *cis*) was reduced with lithium aluminum hydride. After work-up, distillation at 25 mm. yielded 249 mg. (62%) of a mixture of *cis* and *trans* primary alcohols **5** and **6**; n.m.r. chemical shifts (CCl_4) at τ *ca.* 6.5 (2.0H, predominantly as an A_2X pattern), 7.4 (1H, broad singlet), and 8.94–9.63 (11.0H).

Similarly, 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (90% *trans*) was reduced, yielding 283 mg. (71%) of a mixture of **5** and **6**; n.m.r. chemical shifts at τ *ca.* 6.5 (2.0H, predominantly as an ABX pattern), 7.1 (1H, broad singlet), and 8.93–9.85 (11.0H).

α,α,2,2,3-Pentamethyl-1-hydroxymethylcyclopropane (Mixtures Enriched in *cis* and *trans* Isomers).—To 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (70% *cis*) in 30 ml. of ether was added a solution of methyllithium (*ca.* 20 mmoles) in 50 ml. of ether. The solution was refluxed for 4 hr. and then allowed to stand at room temperature for 12 hr. Work-up (no acid treatment!), followed by distillation at 25 mm., gave 265 mg. (53%) of a mixture of *cis* and *trans* tertiary alcohols **8** and **9** which showed only one peak (unresolved) on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ *ca.* 9.9 (0.8H, predominantly half of an AB pattern, J = 9.5 c.p.s.) and 8.72–9.66 (17.0H).

Similarly, 160 mg. (1.1 mmole) of a mixture of **2** and **3** (90% *trans*) was converted to 90 mg. (56%) of a mixture of **8** and **9** which showed only one peak (unresolved) on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ *ca.* 9.7 (1.2H, predominantly half of an AB pattern, J = 6.0 c.p.s.) and 8.7–9.6 (17.0H).

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The Boron Trifluoride Catalyzed Reaction of Acetophenone with Acetic Anhydride

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That the acid-catalyzed reaction of acetophenone with acetic anhydride yields a methyldiphenylpyrylium salt has been known for 50 years.[2–8] Dypnone has been used as the ketonic reactant in place of acetophenone.[5,7] The use of boron trifluoride in this regard has not been reported.

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