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Intramolecular Interaction between the Hydroxyl Group and the Cyclopropane Ring

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Cyclopropylcarbinol shows two absorption maxima due to the O–H stretching, the lower-frequency band being stronger than the higher. The results are interpreted on the basis of intramolecular interaction between the hydroxyl group and the cyclopropane ring. This kind of interaction is not clearly detected with 2-cyclopropylethanol, but 2,2-dicyclopropylethanol and 2-(1-methylcyclopropyl)ethanol give results which are best interpreted by assuming the presence of the interaction. It is concluded, from the findings on rigid molecules, that O–H···cyclopropane interaction is possible when the hydroxyl group approaches the edge within the plane of the ring. The steric effect of the methyl group is also discussed.

In view of the fact that the pi-electron system behaves as a proton acceptor in interaction with the hydroxyl group,[1] it seemed that it would be interesting to investigate the possible interaction between the three-membered ring and the hydroxyl group. The sigma-electrons forming the so-called "banana bond" are known to be rather mobile, and cyclopropane, oxirane, and aziridine are known to show properties like those of the pi-electron system.

A preliminary report[2] on the interaction of the oxirane ring was published by two of the present

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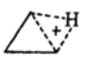
[1] See M. Ōki, H. Iwamura, T. Onoda and M. Iwamura, *Tetrahedron*, **24**, 1905 (1968) and earlier papers.

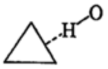
[2] M. Ōki and T. Murayama, This Bulletin, **40**, 1997 (1967).

authors (M. O. and T. M.); this paper will deal with the intramolecular interaction between the hydroxyl group and the cyclopropane ring. The first observation on this phenomenon was reported some 10 years ago,3) and a full paper appeared recently.4) Although the other approaches were made using different model compounds, the conclusion derived by the present authors is in good agreement with that drawn in the aforementioned literature.

The investigation of the intramolecular rather than the intermolecular interaction is convenient for deducing the geometry of the interacting molecule, since the approach of the hydroxyl group can be regulated both in direction and in site. It will be shown that the most preferred conformation of the interacting molecule is such that the hydroxyl group approaches the edge of the cyclopropane ring within the plane of the ring (II). The structure of the protonated cyclopropane rings has previously been discussed with respect to the reaction mechanisms, and it has been suggested to be edge-protonated5) (I). Olah *et al.* also postulated, from the Raman spectrum of protonated tricyclo-[2.2.1.0^{2,6}]heptanes,6) the same structure. The present authors believe that their results support the structure, since the geometry of the interacting molecule corresponds to the first step of the protonation and may be supposed to be close to the protonated structure.



(I)



(II)

TABLE 1. ν_{O-H} DATA OF PRIMARY CYCLOPROPYLALKANOLS

Compound	ν_{max} (cm^{-1})	ε (mol^{-1}·l·cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l·cm^{-2})	A_l/A_h*
Cyclopropylcarbinol	3633.7 3619	27 26	2.3 2.6	1.1
2-Cyclopropylethanol	3637.5 3623	36 19	2.7 1.3	0.48
3-Cyclopropyl-1-propanol	3640.3 3627	58 23	3.6 1.2	0.33
2-(1-Methyl-cyclopropyl)ethanol	3637.7 3625	34 25	2.2 1.6	0.74
2,2-Dicyclopropyl-ethanol	3642 3623.4	21 45	1.5 3.9	2.6

* A_l and A_h denote integrated intensities of the bands at lower and higher frequencies, respectively.

Results and Discussion

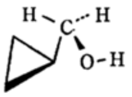
The infrared spectral data of ω-cyclopropylalkanols are collected in Table 1.

The O–H stretching absorption of cyclopropylcarbinol was reported by Schleyer *et al.*3,4); their results are in good agreement with those obtained in the present study. The O–H stretching spectrum of cyclopropylcarbinol shows two maxima, the band at the lower frequency being stronger than that of the higher, in contrast to the case with saturated aliphatic alcohols7) (see Table 2).

TABLE 2. ν_{O-H} DATA OF ALIPHATIC ALCOHOLS

Compound	ν_{max} (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l·cm^{-2})	A_l/A_h	Ref.
CH_3CH_2OH	3637.3 3627	2.8 1.6	0.56	7
$CH_3CH_2CH_2OH$	3639.7 3626	3.4 1.3	0.38	7
$(CH_3)_2CHCH_2OH$	3641.5 3628	3.6 1.8	0.50	7
$(CH_3)_2CHCH_2CH_2OH$	3639.9 3627	3.8 1.6	0.42	

The situation is similar to those of allyl alcohol7) and benzyl alcohol7,8); it is best interpreted by assuming that the hydroxyl group and the cyclopropane ring interact with each other intramolecularly. The intensity of the lower-frequency band is stronger than that of the higher because of the interaction stabilizing the conformation (IV) relative to the free form (III).



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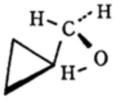

(IV)

2-Cyclopropylethanol (see also Fig. 1) shows two O–H stretching absorptions also, the $\Delta\nu$ (the difference in the wave numbers of the two absorption maxima) being 14.5 cm^{-1} and the (A_l/A_h) ratio of integrated intensities being 0.48. 3-Cyclopropyl-1-propanol likewise shows two maxima, the $\Delta\nu$ and A_l/A_h values being 13.3 cm^{-1} and 0.33 respectively. The saturated alcohols in Table 2 give $\Delta\nu$ values between 10.3 and 13.7 cm^{-1} and A_l/A_h values between 0.38 and 0.56. Thus, 3-cyclopropyl-1-propanol can be considered to have no detectable intramolecular interaction, and the origin of the doublet O–H bands can be attributed to the presence of rotational isomers about the C–O bond. Although the A_l/A_h ratio of 2-cyclopropylethanol is in the range of free primary alcohols, the

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3) P. von R. Schleyer, D. S. Trifan and R. Backskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

4) L. Joris, P. von R. Schleyer and R. Gleiter, *ibid.*, **90**, 327 (1968).

5) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **87**, 4394 (1965).

6) G. A. Olah, A. Commeyras and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

7) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

8) M. Ōki and H. Iwamura, *ibid.*, **32**, 955 (1959).

$\Delta\nu$ is a little larger than the normal value. Thus, 2-cyclopropylethanol is somewhat an intermediate case.

In order to test whether there is the intramolecular interaction in 2-cyclopropylethanol, it may be necessary to change the situation to a more favorable one. This can be done in many ways. One which the authors chose at the outset was adding one more cyclopropyl group at the β-position of ethanol to form 2,2-dicyclopropylethanol. This selection was made because of a previous success in pi-electron systems: triallylcarbinol showed a very strong interaction band due to the favorable entropy factor.9) The data shown in Table 1 and in Fig. 1 indicate an increase in A_l/A_h (2.6 instead of 0.48), although $\Delta\nu$ remains almost intact.

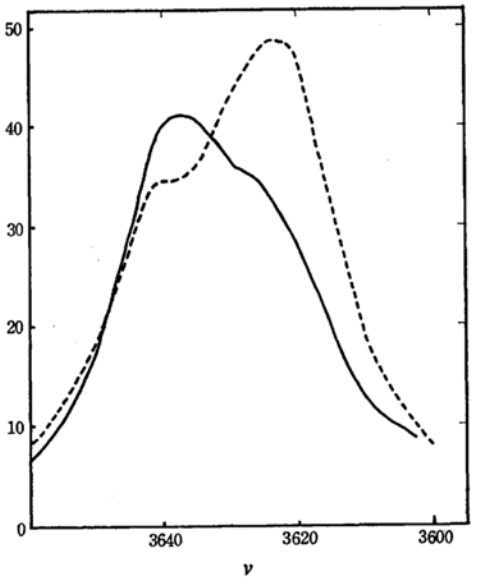
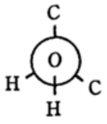


Fig. 1. ν_{O-H} Absorption bands of 2-cyclopropylethanol (——) and 2,2-dicyclopropylethanol (-----).

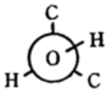
Another proof of the presence of the interaction may be obtained by increasing the electron density of the ring, for the higher electron density should facilitate the interaction. Thus, a methyl group is introduced to the cyclopropane ring. 2-(1-Methylcyclopropyl)ethanol gives a slightly increased A_l/A_h ratio, as is shown in Table 1. Although this fact alone may not be taken as positive evidence, in combination with the above results with 2,2-dicyclopropylethanol it strongly indicates the presence of the intramolecular interaction. It may be concluded that the intramolecular interaction between the hydroxyl group and the cyclopropane ring exists in 2-cyclopropylethanol derivatives, although, because of a small stabilizing energy, it can not be clearly demonstrated unless the situation is favorable for the interaction: it can also be concluded that 3-cyclopropyl-1-propanol has no detectable interaction of this kind.

Fixing the conformation of a molecule favorable for the interaction should also facilitate the interaction. In addition, a molecule with a rigid geometry should give information on the conformation of the interacting molecule. Accordingly, the infrared spectra of tricyclo[3.2.1.0^{2,4}]octan-6-ols10) and related compounds were measured; the results are listed in Tables 3 and 4.

The rotational isomers are possible for secondary alcohols about the C–O axis, as is shown by V and VI. It is known7) that the ν_{O-H} of V appears at about 3626 cm^{-1}, and that of VI, at *ca.* 3617 cm^{-1}.



(V)



(VI)

All the ν_{O-H} absorption bands of tricyclo[3.2.1.0^{2,4}]octan-6-ols possess similar shapes, the lower-frequency side being a little greater than the symmetrical curve. It will be convenient to use the β/α ratio introduced by Aaron and Rader11) in discussing the band shape. Here α and β denote the segments of the half band-width of the high- and low-frequency sides of ν_{max} respectively (Fig. 2).

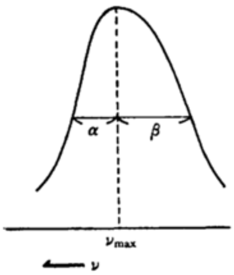


Fig. 2. Explanation of symbols α and β.

If the β/α ratio is greater than unity, the absorption band may be considered to be asymmetric, possibly indicating the presence of a small band at the lower-frequency.

An inspection of Table 3 will show that β/α value is very close to unity when no interaction of the hydroxyl group with the cyclopropane ring is possible because of the geometry of the molecule. The difference in the ratios of exo and endo isomers (VII and VIII) deserves special mention.

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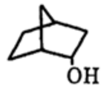
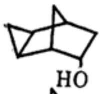
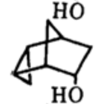
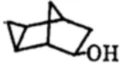
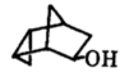
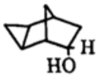
9) M. Ōki and H. Iwamura, This Bulletin, **33**, 1600 (1960).

10) These compounds were generously donated by Professor K. B. Wiberg, Yale University, to whom we wish to express our hearty thanks.

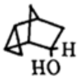
11) H. S. Aaron and C. P. Rader, *J. Am. Chem. Soc.*, **85**, 3046 (1963).

TABLE 3. ν_{O-H} DATA OF TRICYCLO-[3.2.1.0^{2,4}]OCTAN-6-OLS

Compound	ν_{max} (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	β/α
	3625.2	26	0.94
	3627.1	29	1.34
	3627.2	25	1.10
	3624.0	20	1.13
	3624.0	19	1.15



(VII)

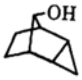


(VIII)

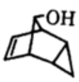
While the β/α value of VIII is very close to unity, that of VII is distinctly higher than anything else in Table 3. This is indicative of the presence of another band on the lower-frequency side.

It will not be unnatural to consider, from the analogous situation of 2-cyclopropylethanol, that there are some portions of molecular species which have an internal O–H···cyclopropane interaction in compound VII, but not in compound VIII. It is now apparent, therefore, that if the O–H group approaches the edge of the cyclopropane ring from the side, the O–H···cyclopropane interaction is possible, while it is impossible if O–H approaches from the upper side to the face of the ring.

The same conclusion was drawn by Schleyer and his co-workers from the fact that tricyclo[3.2.1.0^{2,4}]-octan-8-ol derivatives (IX and X) possess bands corresponding to the interacting molecule.[4]



(IX)

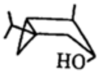


(X)

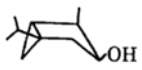
Another evidence, though negative, for the geometry of the interacting molecule can be found in bicyclo[3.1.0]hexan-3-ol derivatives. The conformation of bicyclo[3. 1. 0]hexan-3-ol had been postulated by Winstein and Sonnenberg[12] to be a chair on the basis of the unusually fast solvolysis rate of the tosylate, but their suggestion was later amended to be, rather, a boat form.[13] The NMR data in hand agree with the latter, also. A rationale for this conformation may be the repulsion between axial hydrogens at the 2 and 6 positions, as revealed by the molecular model. Therefore, in thujyl alcohol[14] (XII), the hydroxyl group can not come close to the cyclopropane ring, thus eliminating the possibility of interaction. In neothujyl alcohol (XI) and *cis*-bicyclo[3.1.0]-hexan-3-ol, the interaction would be possible if the geometry were such that the hydroxyl group approached the ring from the upper side. Table 4 indicates this is not the case.

TABLE 4. ν_{O-H} DATA OF BICYCLO[3.1.0]-HEXAN-3-OL DERIVATIVES

Compound	ν_{max} (cm^{-1})	β/α	$A\times10^{-3}$ (mol^{-1}·l·cm^{-2})
cis-Bicyclo[3.1.0]-hexan-3-ol	3625.2	0.99	
Neothujyl alcohol	3624.6	1.0	
Thujyl alcohol	3632.1 3618		2.9 0.74
Cyclopentanol	3626.1	1.1	



(XI)



(XII)

However, these facts cannot be taken as evidence for rejecting the Walsh model of cyclopropane.[15] Although, in this model, the electron density must be high at the center of the ring, this does not necessarily mean that the O–H group can approach the site. The steric repulsion must be severe in order to effect the overlapping of the orbitals concerned, thus outweighing any stabilization by the O–H··· cyclopropane interaction. The present authors

TABLE 5. ν_{O-H} DATA OF SECONDARY CYCLOPROPYLCARBINOLS

Compound	ν_{max} (cm^{-1})	ε (mol^{-1}·l·cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l·cm^{-2})	A_l/A_h
1-Cyclopropylethanol	3631 3616.9	14 57	1.1 3.1	2.8
1-(2,2-Dimethyl-cyclopropyl)ethanol	3616.6	69	3.9	—
1-(*trans*-2-Methyl-cyclopropyl)ethanol	3628 3617.9	13 53	1.3 2.8	2.1
1-(*trans*-2-Methyl-cyclopropyl)-1-propanol	3633 3619.1	9 57	0.6 3.4	5.7

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[12] S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961).

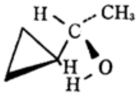
[13] S. Winstein, E. C. Friedrich, R. Baker and Y. I. Lin, *Tetrahedron, Suppl.*, **8**, 621 (1966).

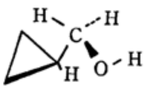
[14] Thujone was kindly donated by Dr. K. Tori of Shionogi & Co. to whom our sincere thanks are due.

[15] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

would like to reserve their conclusion on the electronic structure of the cyclopropane ring until further experimental evidence is obtained.

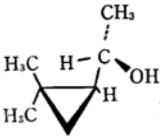
Table 5 presents the ν_{O-H} data of 1-cyclopropylethanol derivatives. It is worthy pointing out that the A_l/A_h ratio is larger with 1-cyclopropylethanol than with cyclopropylcarbinol. These results can be understood when the favorable conformation is considered.

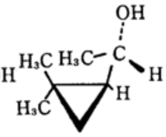

(XIII)

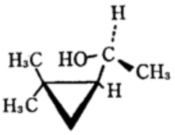

(XIV)

As to the conformation determined by the rotation about the C–O bond, the one (XIV) in which the hydrogen of the O–H group is in between two hydrogens, when illustrated by Newman projection, is favored in primary alcohols, probably because of the steric effect. This conformation is undoubtedly not likely in the O–H···cylopropane interaction. In secondary alcohols, the situation changes and the conformation (XIII), in which O–H can come close to the ring is not unfavorable. This very conformation is necessary for establishing the intramolecular interaction.

The introduction of two methyl groups to the position 2 of the cyclopropane ring causes the free band of 1-cyclopropylethanol to disappear. These results may be explained when steric factor of the methyl group is considered. Due to the steric effect inserted by the methyl group *cis* to the 1-hydroxyethyl, the H-inside conformation (XV) is more stable than the CH_3-inside (XVI) or the O–H-inside (XVII) conformations. Whatever conformation is taken with respect to the C–O axis in XVII, the conformation is not good at establishing the O–H···cyclopropane interaction.


(XV)


(XVI)


(XVII)

These circumstances must reduce the possibility of the existence of the free form. These considerations are supported by the reappearance of the free O–H absorption on the removal of the *cis*-methyl group [1-(*trans*-2-methylcyclopropyl)ethanol], as is shown in Table 5. It is, then, not surprising to find that 1-(*trans*-2-methylcyclopropyl)-1-propanol having methyl and 1-hydroxypropyl groups *trans* to each other, like the corresponding ethanol derivative, shows very small absorption for the free O–H and gives a large A_l/A_h value.

One might argue that the configuration of the alcohol may be different from that shown. However, there are many examples showing the stereochemical outcome of the Simmons-Smith reaction. For example, the reaction of methylene iodide and copper-zinc couple with 2-cyclohexen-1-ol gives bicyclo[4.1.0.]heptan-*cis*-2-ol,[16] whereas 2-cyclohexen-1-ol affords *cis*-2,3-epoxycyclohexan-1-ol on epoxidation.[17] Thus, it may be postulated that epoxidation and Simmons-Smith reaction give the same steric outcome. Then, since it has been established in this laboratory that the oxidation of 4-methyl-3-penten-2-ol with perbenzoic acid affords the threo isomer of the corresponding epoxide,[18] it is natural to consider that the Simmons-Smith reaction of 4-methyl-3-penten-2-ol will give the product of the configuration as shown (the threo isomer).

There is another possibility, that the steric effect of the methyl groups prohibits the approach of the O–H group to the cyclopropane ring in the conformation XVI. However, further study will be necessary before we can discuss this sort of steric effect of the substituents.

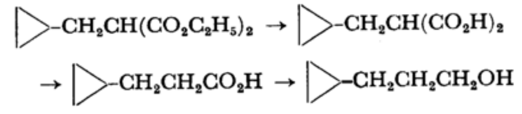
Experimental

Spectral Measurements. A Perkin-Elmer 112G single-beam grating infrared spectrometer was used for measuring the infrared absorption spectra in the 3 μ region, the spectral slit width being 0.8 cm^{-1}.

Wako special-grade carbon tetrachloride was used as the solvent. The concentrations of the alcohols were *ca.* 0.003 mol/*l*, and the length of the quartz optical cell was 2 cm. The obtained absorption band was graphically separated into two symmetrical curves.

Materials. The compounds used in this study were known compounds unless otherwise stated, and their physical constants were checked prior to measurements.

3-Cyclopropyl-1-propanol was synthesized in the following way. Cyclopropylcarbinyl bromide was condensed[19] with diethyl malonate in the presence of sodium ethoxide, and the product was hydrolyzed. The dicarboxylic acid thus obtained lost carbon dioxide on distillation, and the resulting 3-cyclopropylpropionic acid was reduced with lithium aluminum hydride.



3-Cyclopropylpropionic Acid. Diethyl cyclopropylcarbinylmalonate (27 g) was heated with 120 m*l* of 10% aqueous sodium hydroxide until a homogeneous solution was obtained. The solution was acidified with hydrochloric acid, and the dicarboxylic acid was heated

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[16] W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

[17] H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, **1957**, 1958.

[18] M. Ōki and T. Murayama, unpublished work. The epoxide thus prepared was identical with that obtained by G. B. Payne [*J. Org. Chem.*, **27**, 3819 (1962)].

[19] J. A. Arvin and R. Adams, *J. Am. Chem. Soc.*, **50**, 1983 (1928).

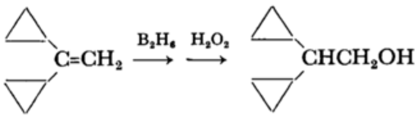
in vacuo, thus affording 3-cyclopropylpropionic acid, bp 104—105°C/17 mmHg, $n_D^{17.5}$ 1.4375, in a 69% yield. This compound had been prepared[20] by the Arndt-Eistert reaction of cyclopropylacetic acid, and the boiling point reported to be 101°C/15 mmHg.

3-Cyclopropyl-1-propanol. 3-Cyclopropylpropionic acid (13 g) in 100 m*l* of ether was added to 6 g of lithium aluminum hydride in 250 m*l* of ether. The distillation of the product gave 7 g (61%) of 3-cyclopropyl-1-propanol, bp 66°C/18 mmHg.

Found: C, 72.18; H, 12.32%. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08%.

NMR (τ): 6.40 (singlet OH), 6.47 (triplet CH_2O), 8.2—9.1 (multiplet CH_2CH_2), 9.2—10.3 (multiplet ring H).

2,2-Dicyclopropylethanol. This was prepared by the hydroboration of 1,1-dicyclopropylethylene, followed by alkaline oxidation. Considering that the hydroboration of vinylcyclopropane, followed by oxidation, has been reported to yield 97 : 3 mixture of 2-cyclopropylethanol and 1-cyclopropylethanol,[21] and considering that 1,1-dicyclopropylethylene has an enhanced steric effect, the purity of the 2,2-dicyclopropylethanol thus prepared was expected to be good. The spectral evidence supported this expectation.

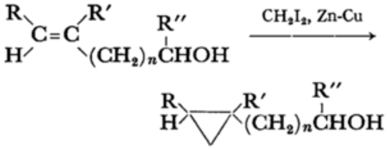


To a solution of 6 g of 1,1-dicyclopropylethylene[22] and 1 g of lithium aluminum hydride in 80 m*l* of dry tetrahydrofuran, was added 4 g of boron trifluoride etherate in 30 m*l* of tetrahydrofuran with cooling in an ice-salt bath. After the solution had been stirred for 3 hr, the excess hydride was decomposed with water. The mixture was treated with 10 m*l* of 3N sodium hydroxide and then with 10 m*l* 33% hydrogen peroxide. The distillation of the product gave 4.2 g (60%) of the crude alcohol. Redistillation afforded pure 2,2-dicyclopropylethanol; bp 106—106.5°C/41 mmHg, $n_D^{26.5}$ 1.4620.

Found: C, 76.04; H, 11.36%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

NMR (τ): 6.55 (doublet CH_2O), 7.22 (singlet OH), 9.30—10.20 (multiplet methine and ring H).

2-(1-Methylcyclopropyl)ethanol and 1-(*trans*-2-methylcyclopropyl)-1-propanol were prepared by the Simmons-Smith reaction of the corresponding olefinic alcohols.



2-(1-Methylcyclopropyl)ethanol. To a suspension of a zinc-copper couple, prepared according to LeGoff[23] from 35 g of glannular zinc in 200 ml of ether, were added 24 m*l* of methylene iodide and 16 g of 3-methyl-3-buten-1-ol in 50 m*l* of ether. After having been refluxed for 2 days, the mixture was treated in the usual manner to afford 3.5 g of the crude product (bp 52—53°C/10 mmHg). A pure sample boiled at 51—52°C/11 mmHg and possessed an n_D^{16} value of 1.4370.

Found: C, 72.18; H, 12.15%. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.06%.

NMR (τ): 6.20—6.60 (multiplet CH_2O and OH), 8.59 (triplet β-CH_2), 9.00 (singlet CH_3), 9.70—9.90 (multiplet ring H).

1-(*trans*-2-Methylcyclopropyl)-1-propanol. This was similarly prepared from 4-hexen-3-ol in 49% yield. Bp 45—47°C/8 mmHg, $n_D^{18.5}$ 1.4362.

Found: C, 73.38; H, 12.40%. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36%.

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[20] J. H. Turnbull and E. S. Wallis, *J. Org. Chem.*, **21**, 663 (1956).

[21] S. Nishida, I. Moritani, K. Ito and K. Sakai, *ibid.*, **32**, 939 (1967).

[22] I. A. D'yakonov and I. M. Stroiman, *Zh. Obshch. Khim.*, **33**, 4019 (1963); *Chem. Abstr.*, **60**, 9159 g (1964).

[23] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).