Intramolecular Interaction between Hydroxyl Group and π-Electrons. X[1]. *Tertiary Alcohols Related to Phenethyl Alcohol and 3-Buten-1-ol**

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It has been shown in the previous papers[2] that the intramolecular interaction between the hydroxyl group and π-electrons in ω-phenylalkanols and ω-hydroxy-1-alkenes is operative up to phenethyl alcohol and 3-buten-1-ol, respectively. On the other hand, the accumulated data in this laboratory show that there are some alcohols within the above limitation which do not possess the internal interaction, such as 3-cyclohexen-1-ol, and others which have unexpectedly strong O–H stretching absorption (ν_{O-H}) due to the interacting form[3]. The dependence of the occurrence and the

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[1] Part IX: M. Ōki and H. Iwamura, This Bulletin, 33, 427 (1960).

[*] The summary of this work was presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[2] M. Ōki and H. Iwamura, This Bulletin, 32, 567, 1135 (1959).

[3] M. Ōki, H. Iwamura and T. Onoda, Unpublished work.

strength of the interaction on the conformation and the configuration of the molecule may inversely be taken advantage of for elucidation of some problems in the stereochemistry of complex organic compounds including natural products. From the point of the above purpose it will be of value at this stage of investigations to supply further fundamental knowledge relating the strength of the interaction to the conformation of the molecule.

While many authors[4] have recently observed the doublet character of ν_{O-H} of phenethyl alcohol derivatives and 3-buten-1-ol in the infrared absorption, it has been shown by the present authors[2], that their ν_{O-H} absorptions separate into three (Fig. 1), each being exemplified by the following conformational isomers in Fig. 2, in the case of phenethyl alcohol. The higher two bands are derived from the rotational isomerism about C_α–O bond and observed even in saturated alcohols[5]. The highest absorption at about 3636 cm^{-1} (I) has been assigned to the ν_{O-H} of the hydroxyl group with its hydrogen atom between two hydrogen atoms attached to the α-carbon atom, while the second at about 3627 cm^{-1} (II) to the ν_{O-H} with hydroxyl hydrogen between a hydrogen and a carbon atom. The third band at the lowest region of the spectra (III) is of a different kind and has been assigned to ν_{O-H} of the hydroxyl group having intramolecular interaction with π-electrons of the benzene nucleus. In other words, II and III are the rotational isomers about C_α–C_β bond.

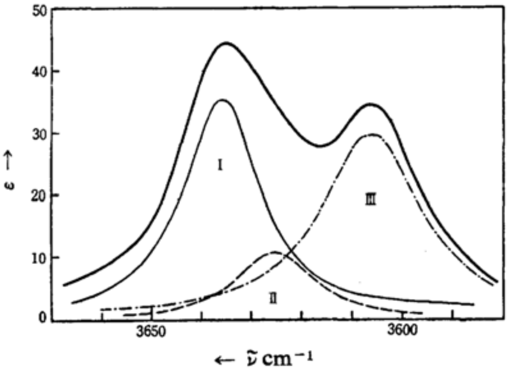

Fig. 1. ν_{O-H} absorption of phenethyl alcohol.

The triplet nature of the infrared absorption mentioned now, however, does not mean the apparent separation of the absorption curve but that the apparent curve can best be represented by an overlap of three symmetric absorption curves of the type of the Lorentz function[6]. Then nine parameters; a_i, b_i and ν_i (i=1, 2 and 3), must be determined in this case and the procedure of the division of the apparent curve is troublesome, whether it is the trial and error method[2] or the least squares method[1]. In the previous paper[1], this difficulty was mentioned and overcome by taking advantage of a tertiary alcohol which shows only doublet ν_{O-H}. The energy of the interaction between an alcoholic hydroxyl group and π-electrons of a benzene nucleus in benzyldimethylcarbinol was thus determined. In the present paper the measurement is extended to the interaction between an alcoholic hydroxyl group and π-electrons of ethylenic double bond in allyldimethylcarbinol. The effect of rotational degrees of freedom on the number of the interacting forms of the molecule and consequently on the apparent ν_{O-H} curve is also discussed.

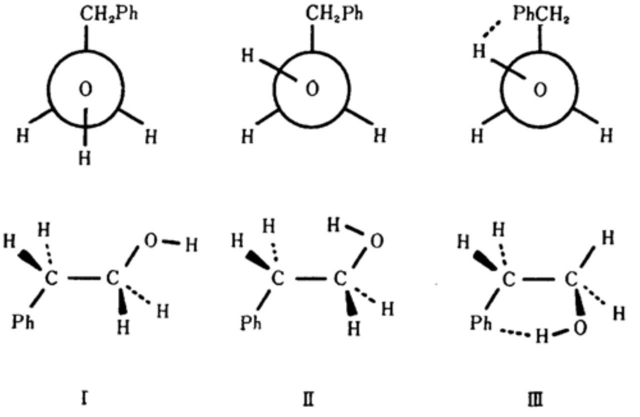

Fig. 2.

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[4] D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957); A. W. Baker and A. T. Shulgin, ibid., **80**, 5358 (1958); I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).

[5] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

[6] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

Experimental

Measurement and Calculation.—Measurement of the ν_{O-H} absorption and the calculation of the band properties and the energy of the interaction were carried out as described previously[1,7], for doublet absorption, Eq. 1 being assumed and six parameters determined by means of the least squares method.

$$D(\nu)=\frac{a_i}{(\nu-\nu_i)^2+b_i^2}+\frac{a_f}{(\nu-\nu_f)^2+b_f^2} \qquad (1)$$

Materials.—Benzyldimethylcarbinol and allyldimethylcarbinol were prepared by action of acetone on benzyl- and allylmagnesium chlorides, respectively, and their physical constants were as follows: benzyldimethylcarbinol b.p. 70°C/3mmHg, n_D^{25} 1.5158. Found: C, 80.10; H, 9.14. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39%. (lit.[8], b. p. 59∼60°C/1.5 mmHg, n_D^{25} 1.5128): allyldimethylcarbinol b. p. 119°, n_D^{25} 1.4250 (lit.[9], b. p. 118∼120°C, n_D^{17} 1.4300).

Dibenzylmethylcarbinol and diallylmethylcarbinol were prepared by action of the corresponding Grignard reagents on ethyl acetate: dibenzylmethylcarbinol b.p. 148°C/3 mmHg, n_D^{23} 1.5686 (lit.[10], b. p. 182°C/15mmHg): diallylmethylcarbinol b. p. 74°C/43 mmHg, n_D^{23} 1.4500 (lit.[11], b. p. 158.4°C). Tribenzylcarbinol and triallylcarbinol were prepared through Grignard reaction between diethyl carbonate and benzyl- and allylmagnesium chlorides, respectively: tribenzylcarbinol m. p. 114∼115°C (lit.[12], m. p. 115°C): triallylcarbinol b. p. 82°C/16mmHg, n_D^{23} 1.4682 (lit.[13], b. p. 191∼192°C, n_D^{21} 1.468).

Results and Discussion

The apparent ν_{O-H} curves of allyldimethylcarbinol at several temperatures are shown in Fig. 3. Each curve can be regarded as an overlap of two Lorentz function curves as is exemplified by the curve at 24°C in Fig. 4, and six parameters determined by applying Eq. 1 to the apparent curves are summarized in Table I. The characteristic tendencies of the dependence of some band properties on temperature such as decrease of the total intensity, increase of the half band-width and shift of the wave numbers to the higher side, are again observed in this case.

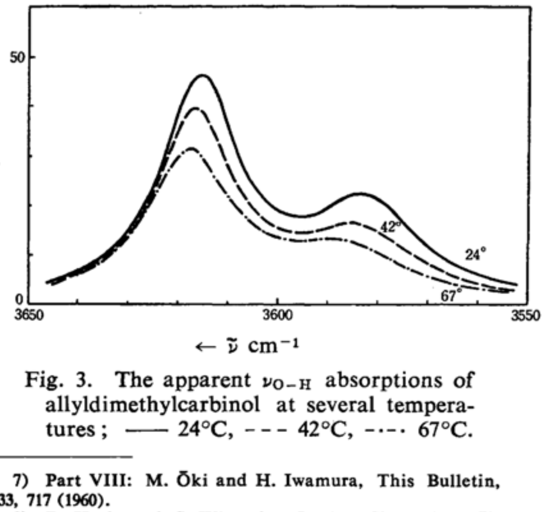

Fig. 3. The apparent ν_{O-H} absorptions of allyldimethylcarbinol at several temperatures; —— 24°C, - - - 42°C, -·-· 67°C.

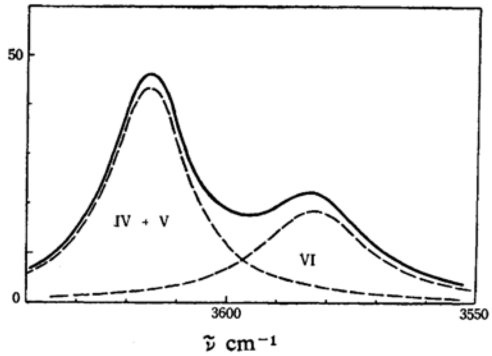

Fig. 4. ν_{O-H} absorption of allyldimethylcarbinol at 24°C.
—— the observed curve
- - - the divided bands

TABLE I. THE EFFECT OF TEMPERATURE ON THE ν_{O-H} ABSOPTION OF ALLYLDIMETHYLCARBINOL

$1/T\times10^3$ °K^{-1}	ν_{O-H}	ν	a	b	$\ln(A_i/A_f)$
3.37	i	3582.7	21.40	13.18	−0.521
	f	3615.9	26.28	9.61	
3.25	i	3583.7	21.31	13.66	−0.529
	f	3616.2	25.70	9.71	
3.17	i	3583.7	19.50	14.87	−0.593
	f	3616.8	23.11	9.74	
3.02	i	3585.2	16.70	15.21	−0.660
	f	3617.3	21.75	10.24	
2.95	i	3587.4	15.41	15.50	−0.699
	f	3618.0	21.58	10.79	

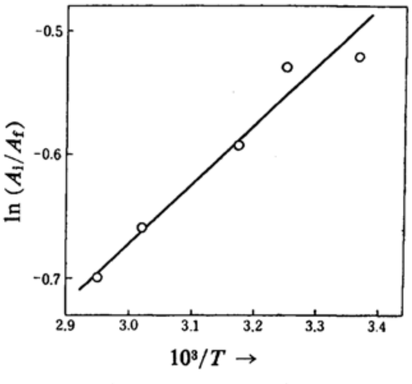

Fig. 5. The temperature dependence of ln (A_i/A_f).

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7) Part VIII: M. Ōki and H. Iwamura, This Bulletin, 33, 717 (1960).
8) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957).
9) S. Coffey, *Rec. trav. chim. Pay-Bas*, **41**, 653 (1922).
10) R. Dolique, *Compt. rend.*, **190**, 881 (1930).
11) B. Sorokin, *Ann.*, **185**, 169 (1877).
12) A. A. Morton and J. R. Stevens, *J. Am. Chem. Soc.*, **53**, 4031 (1931).
13) A. Reformatski, *Ber.*, **41**, 4086 (1908).

TABLE II. THE ENERGIES AND THE ENTROPY TERMS OF THE INTERACTION IN ALLYLDIMETHYL- AND BENZYLDIMETHYLCARBINOLS

Carbinol	$-\Delta H$ (kcal./mol.)	$\Delta S/\boldsymbol{R}-\ln a$	$\Delta\nu_{\max}$ (cm^{-1})
$CH_2=CHCH_2CMe_2OH$	0.90 ± 0.07	$-2.03\pm.012$	33.2
$PhCH_2CMe_2OH$	0.54 ± 0.13	-1.16 ± 0.17	21.4

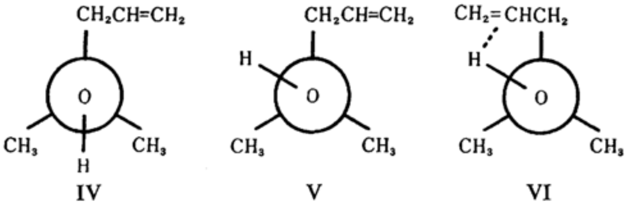

Fig. 6.

Temperature versus $\ln(A_i/A_f)$ relation is shown in Fig. 5. The values obtained therefrom are tabulated in Table II together with those of benzyldimethylcarbinol reported in the preceding paper[1].

The strengths of the interactions are fairly smaller than those ever estimated. That is, Bamford[14] suggested the energy to be 2∼3 kcal./mol. for the interaction between methanol and aromatic nucleus and Schleyer et al.[15] 1.4 kcal./mol. for phenethyl alcohol. However, disappearance of the interacting ν_{O-H} for 3-cyclohexen-1-ol and β-tetralol seems to suggest, that the energy difference between the free and the interacting molecules is less than 1 kcal./mol. While West[16] has recently shown, that olefins are generally stronger proton-acceptors than simple aromatic hydrocarbons in the intermolecular interaction between the hydroxyl group and π-electrons through measurement of the shift of ν_{O-H} from free phenol to phenol in hydrocarbons, it is for the first time that the proposition was realized in the intramolecular interaction through the direct energy measurement.

The doublet nature of the ν_{O-H} of allyldimethylcarbinol as well as benzyldimethylcarbinol shows, that the rotational isomers around C_α–O bond can not be distinguished so far as ν_{O-H} is concerned under the present dispersion of the spectrometer[2]; that is, IV and V in Fig. 6 can not be distinguished and equally give the higher ν_{O-H} at 3616 cm^{-1}. In both forms hydroxyl hydrogen lies between two carbon atoms attached to the α-carbon atom as in *tert*-butyl alcohol[5]. The absorption at 3584 cm^{-1} (VI), on the other hand, can be assigned to the hydroxyl group having internal interaction. In this case, the rotational degree around the C_α–C_β and C_β–C_γ bonds must be fixed favorably for the interaction, i. e., the hydroxyl group and the group carrying π-electrons must be closely situated.

Although it is usual that the energy difference of about one kcal./mol. between two components in an equilibrium mixture makes one at a lower energy level exceedingly predominant, it does not seem to be the case in allyldimethylcarbinol, the ratio A_i/A_f being only 0.59. This could be explained if the absorption intensity per molecule of the interacting ν_{O-H} is much weaker than that of free ν_{O-H} and even small A_i represents a large number of the interacting molecules. However, the assumption is rather contradictory to the knowledge of ordinary hydrogen bonding[17] where the absorption intensity increases on hydrogen bond formation because of increased change of the dipole moment accompanying O–H vibrational motion. The possibility may also be excluded from the fact that, as reported previously[2], the sum of the integrated intensities (A_i+A_f) is almost constant throughout the wide range of substituted phenethyl alcohols. It can preferably be explained by considering the statistical factor contributed from the rotational degree of freedom. Rough computation of the number of the possible conformations for allyldimethylcarbinol was made with the assumption that only the staggered conformations are possible for each bond axis. It may reasonably be assumed that both isomers IV and V have not only the same ν_{O-H} but also almost the same energy in regard to the conformations of the hydroxyl group. As to the C_α–C_β axis, three conformations VII, VIII and the mirror image of the latter in Fig. 7 are assumed to have the same energy as a first approximation. Strictly speaking, however, VII and VIII are different in that the former has

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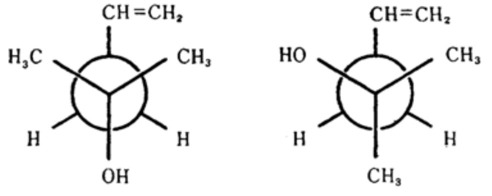
[14] C. H. Bamford, *Discuss. Faraday Soc.*, **16**, 229 (1954).

[15] P. von Schleyer et al., *Tetrahedron Letters*, No. 14, p. 1 (1959).

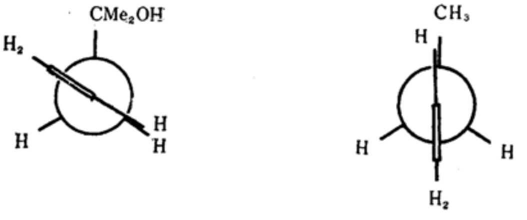
[16] R. West, *J. Am. Chem. Soc.*, **81**, 1614 (1959).

[17] H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).



VII VIII

Fig. 7.



IX X

Fig. 8.

two gauche type interactions in *n*-butane structure, while the latter a gauche interaction in *n*-butane structure and another gauche interaction in *n*-propyl alcohol. Hence the energy difference between VII and VIII becomes $E_g^{bu.}-E_g^{pr.}$, which may be assumed to be zero[18]. Around the C_β–C_γ bond, only the gauche conformations (IX and its mirror image in Fig. 8) may be permitted as in 1-butene, where two gauche forms are more stable than the trans (X) by 1970 cal./mol.[19] Out of eighteen (3×3×2) conformations thus possible, only two can take part in the internal interaction and are stabilized by the energy of the interaction. Therefore the ratio, $w_i/w_f=1/8$, must be introduced as a weight in the following Eq. 2;

$$n_i/n_f=w_i/w_f\cdot e^{-(E_i-E_f)/(RT)} \tag{2}$$

where "n" is the number of the molecules. Substitution of the energy of the interaction obtained above gives $n_i/n_f=0.56$ which is in good agreement with A_i/A_f value of 0.59.

The computation was extended to the data of epicholesterol which shows as high A_i/A_f value as 3.14[20]. The molecule has a fairly rigid structure as in Fig. 9 and the freedom of rotation is left only for C_α–O axis. Out of three possible conformations, only one can take part in the interaction geometrically, the weight becoming 1/2. As the hydroxyl group is now of the secondary alcohol, it is a stronger proton-donor in hydrogen bonding than those of tertiary alcohols[21], while the ethylenic double bond is regarded to be a stronger proton-acceptor than that of allyldimethylcarbinol, because it possesses three alkyl substituents[14]. The strength of the interaction must therefore be greater than that obtained above and is arbitrarily assumed to be 1.0 kcal./mol[22]. Then n_i/n_f becomes 2.7, which satisfactorily explains why epicholesterol, unlike 3-buten-1-ol, shows larger A_i/A_f value than one.

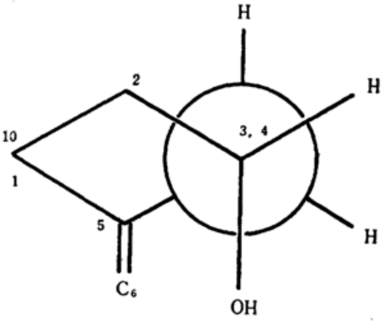


Fig. 9.

Benzyldimethylcarbinol may be treated in the same way. The energy difference between two rotational isomers corresponding to VII and VIII would be marked, the latter being more stable, but is neglected for the sake of convenience as no evaluation is possible. As to the C_β–C_γ bond (Fig. 10), every rotational conformation which must be analogous to that of ethylbenzene[23] favors the interaction, and therefore the rotational degree of freedom about this axis is left out of consideration. Thus w_i/w_f becomes 2/7 in all. This value, together with 1/8 in allyldimethylcarbinol, may be regarded to correspond to the entropy terms of the interaction in Table II and well explains the greater absolute value in the latter than in the former, since ln 2/7 is −1.25 and ln 1/8 is −2.08. The energy difference of 0.54 kcal./mol.

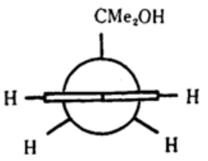


Fig. 10.

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[18] $E_g^{bu.}$ has been regarded to be 800 cal./mol. (K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).), while no datum is available for $E_g^{pr.}$, the energy difference between gauche and trans forms in *n*-propyl alcohol.

[19] J. G. Aston, S. Isserow and G. J. Szasz, *J. Chem. Phys.*, **12**, 336 (1944); **14**, 67 (1946).

[20] M. Ōki and H. Iwamura, This Bulletin, **32**, 307 (1959).

[21] L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 4328 (1954).

[22] Assuming that $\Delta\nu_{max}$ is proportional to the energy of the interaction, $-\Delta H=0.9\times34.1/33.2=0.93$ kcal./mol. is obtained, as $\Delta\nu_{max}$ in epicholesterol amounts to 34.1 cm^{-1}.

[23] F. G. Brickwedde, M. Moskow and R. B. Scott, *J. Chem. Phys.*, **13**, 547 (1945).

TABLE III. ν_{O-H} OF TERTIARY ALCOHOLS RELATED TO 3-BUTEN-1-OL AND PHENETHYL ALCOHOL

Alcohol	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f	n_i/n_f
CH_2=$CHCH_2CMe_2OH$	i	3582.7	21.4	1.50	33.2	0.59	0.56
	f	3615.9	26.3	2.53			
$(CH_2$=$CHCH_2)_2CMeOH$	i	3580.9	25.2	2.58	33.8	1.38	1.29
	f	3614.7	20.2	1.87			
$(CH_2$=$CHCH_2)_3COH$	i	3577.8	25.4	3.87	33.9	3.37	2.25
	f	3611.7	20.4	1.15			
$PhCH_2CMe_2OH$	i	3593.5	16.1	2.02	21.4	0.75	0.71
	f	3614.9	25.1	2.70			
$(PhCH_2)_2CMeOH$	i	3590.8	26.0	4.35	15.2	3.85	1.97
	f	3606.0	26.0	1.13			
$(PhCH_2)_3COH$	i	3580.3	19.3	6.04	—	—	4.92
	f	—	—	—			

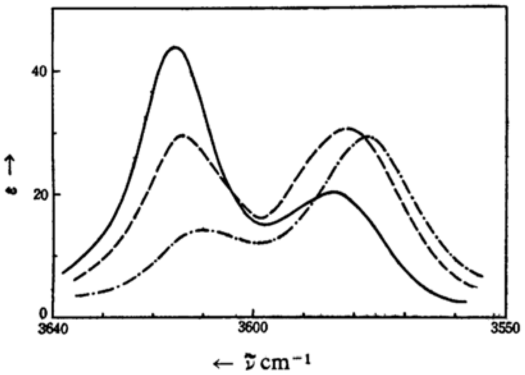

Fig. 11. ν_{O-H} absorptions of allylcarbinols.
—— CH_2=$CHCH_2CMe_2OH$
- - - $(CH_2$=$CHCH_2)_2CMeOH$
-·-·- $(CH_2$=$CHCH_2)_3COH$

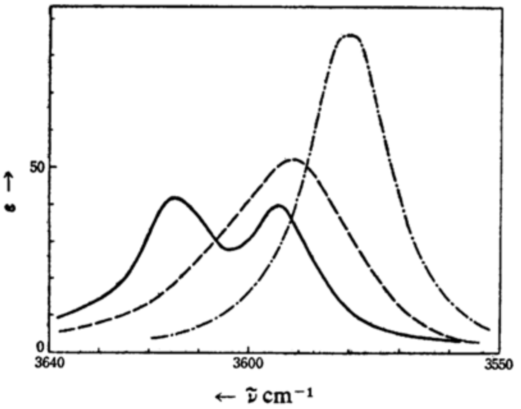

Fig. 12. ν_{O-H} absorptions of benzylcarbinols.
—— $PhCH_2CMe_2OH$ - - - $(PhCH_2)_2CMeOH$
-·-·- $(PhCH_2)_3COH$

obtained for benzyldimethylcarbinol was used as the energy of the interaction and n_i/n_f of 0.71 was obtained as shown in Table III.

In order to see these statistical effects on ν_{O-H} absorption curves, the measurements were extended to some tertiary alcohols related to 3-buten-1-ol and phenethyl alcohol. The apparent ν_{O-H} absorptions are shown in Figs. 11 and 12, respectively, and the numericals are summarized in Table III, the last column being the n_i/n_f values computed as above. The energies of the interaction tabulated in Table II were applied to the same type of compounds, and this procedure may be justified from the constant $\Delta\nu_{max}$ values in the series of allylcarbinols.

In both series the fair agreement between the observed A_i/A_f and the computed A_i/A_f in the lowest homologs does not always hold true in the higher homologs, especially in benzylcarbinol series. The discrepancy can almost exclusively be attributed to the incorrect assumption made in the computation of the weight, that is, to the effect of steric hindrance which disfavors such conformations with the free hydroxyl group as shown in Fig. 13.

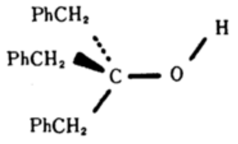

Fig. 13.

It has been shown in this manner, that the ratio of the number of the interacting molecules to the free ones can almost quantitatively be interpreted by considering the statistical or frequency factor of the conformations of the molecules under a given value of the energy of the interaction. In the near future, the computation will be extended to the other organic compounds to explain their ν_{O-H} absorption curves and the conformations of the molecules.

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