[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Absorption Studies. XIII. Stereochemistry of the Hydroxyl Group in Vinyl Alcohols

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In a recent article one of the authors,[1] has discussed the configurations of a series of vinyl alcohols which were prepared by Dr. R. C. Fuson and his co-workers in this Laboratory.[2] A typical example of this class of compounds is β,β-dimesitylvinyl alcohol. These vinyl alcohols appear to be stabilized against enol–keto rearrangement by the steric hindrance of substituent groups such as mesityl. While the reactions of these compounds indicated that they were unquestionably alcohols, it was deemed desirable to make physical test for the presence of hydroxyl by infrared spectroscopy. Mapping of the 3μ region showed the presence of a strong narrow absorption band in the neighborhood of 2.85 μ. This absorption was clearly due to hydroxyl, but the wave length indicates some sort of association or chelation since the value to be expected for free hydroxyl is 2.76 μ. A weak association bond was at first suspected but this possibility was ruled out by the fact that the absorption did not vary with concentration. Furthermore, it was noted that a slight absorption in the expected region 2.76 μ which had at first been attributed to impurities did not disappear no matter how carefully the materials were purified and dried. This behavior recalled the observations of Wulf and his co-workers[3] on the o-chlorophenols and suggested that a coplanar configuration involving the hydroxyl group and a double bond might very well be the explanation for the observed phenomena.

Experimental

Preliminary observations were made on a prism spectrometer but the curves published herewith were all obtained upon the Michigan grating spectrometer,[4] using an echelette grating ruled with 3600 lines to the inch. Two-compartment cells were used so that the transmission of the pure solvent was balanced against that of the solution.

Materials.—The solvent carbon tetrachloride was purified and dried according to the procedure described in previous papers of this series.

The vinyl alcohols studied were prepared by Professor Fuson and his associates and the references thereto are given in ref. (1) of this article.

The benzyl alcohol was Merck reagent grade, b. p. 202–206°. All of the compounds studied were recrystallized and carefully dried. The usual care was taken in the measurement of solvent and weighing of solute. Concentrations are stated as moles per 1000 cubic centimeters of solution.

Results

The experimental observations are presented in the form of curves of log I_0/I where I_0 is the beam intensity through the pure solvent and I the same quantity for the solution, plotted against the wave length in microns. Because of the simple spectrum only the wave lengths of the maxima are indicated. The curve for benzyl alcohol, Fig. 5 at two concentrations, is shown for comparison purposes. It will be noted that the absorption of the unbonded hydroxyl occurs at 2.76 μ while an absorption maximum appears at 2.857 μ at the higher concentration indicating association.

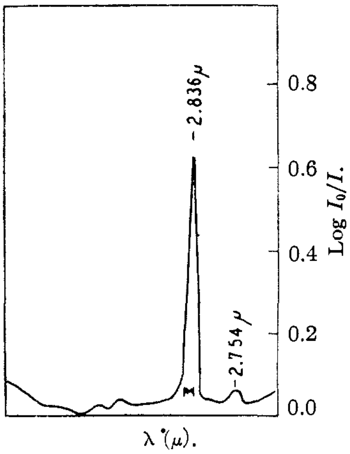

Fig. 1.—β-Mesityl-β-phenylvinyl alcohol.

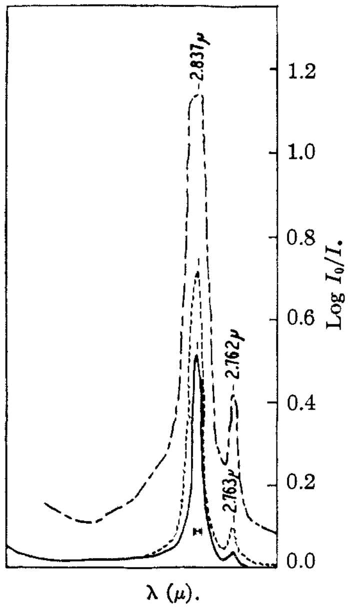

Fig. 2.—β,β-Dimesitylvinyl alcohol at three concentrations.

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[1] W. H. Rodebush and Feldman, THIS JOURNAL, **68**, 896 (1946).

[2] For references, see footnote (1).

[3] O. R. Wulf, U. Liddell and S. B. Hendricks, THIS JOURNAL, **58**, 2287 (1936).

[4] W. W. Sleator, *Astrophys. J.*, **48**, 125 (1918).

The vinyl alcohols, Figs. 1–4, show a very slight absorption peak at or near 2.76 μ and a strong absorption at 2.84–2.86 μ. The relative heights of the two peaks, however, *do* not change, when the concentration is varied and in the case of two of the alcohols (Figs. 3 and 4), when the product of concentration times cell length is held constant, the magnitude of the absorption is independent of concentration. These results eliminate the possibility of association.

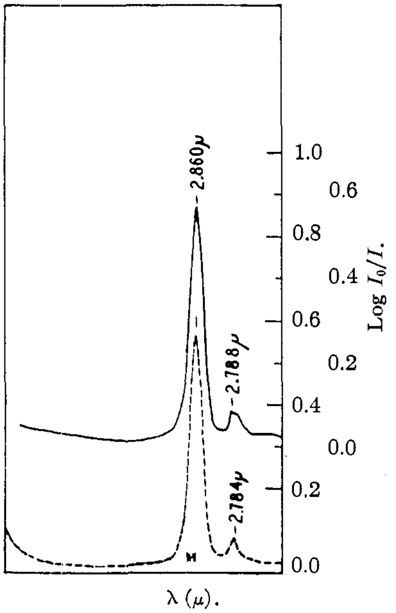

Fig. 3.—α,β-Dimesityl-β-phenylvinyl alcohol at two concentrations. Concentration × cell length constant.

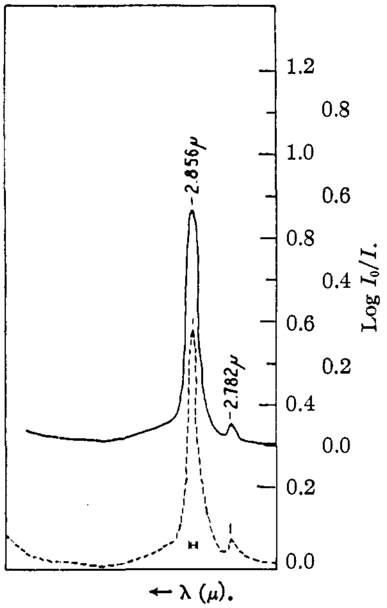

Fig. 4.—Trimesitylvinyl alcohol at two concentrations. Concentration × cell length constant.

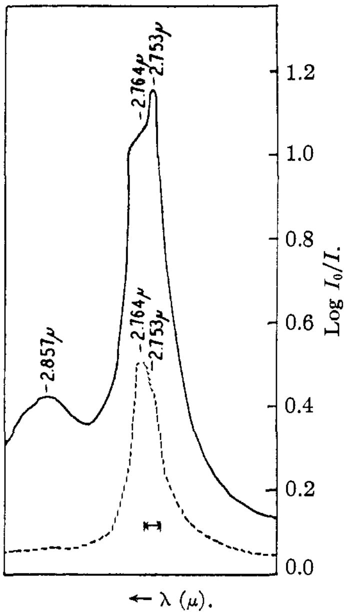

Fig. 5.—Benzyl alcohol in carbon tetrachloride solution. Concentrations 0.006 and 0.03 molal.

The Configuration of Vinyl Alcohols.—For the explanation of the results given we must assume that we are dealing with a situation similar to that found in *o*-chlorophenol, where there are two possible configurations for the hydroxyl group.

The skeleton structure for the vinyl alcohols studied is shown in Fig. 6.[1] The normal bond angles have not been assumed in the figure and it seems probable that a considerable departure from these normal angles may occur because of

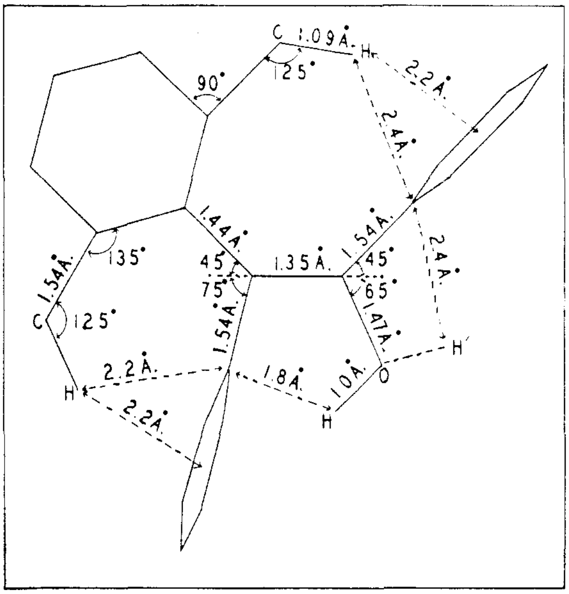

Fig. 6.—Skeleton of vinyl alcohol molecule showing alternating positions for hydroxyl group.

the great crowding of the substituent groups. The conclusions of this paper are not likely to be invalidated by such deviations as may occur. The ultraviolet absorption indicates a great deal of resonance in the molecule and we can be quite certain that one of the structures which contribute to this resonance involves the double bond between carbon and oxygen. This will require that the hydrogen atoms lie in the plane of the oxygen and the carbons of the ethylenic linkage. There are two positions possible therefore for the hydrogen. It is obvious at once that the *trans* position of the hydrogen is the one in which there is a minimum of interference between the hydrogen atom and the rest of the molecule and here we should expect the normal frequency 2.76 μ. The surprising thing is that we find only a small absorption at this frequency, indicating that only a small percentage of hydrogen atoms are in this position at any instant. This means that the *cis* position is the one of lowest energy and this can only be explained by postulating a considerable attraction between the hydrogen atom and some adjacent position of the molecule. A rough estimate of the areas under the curves indicates a ratio of about 50 to 1 in favor of the *cis* position. The difference in energy for the two positions is given, therefore, by $\exp\,(E\ \textit{cis} - E\ \textit{trans})/RT = 50$ and which gives a value for $E\ \textit{cis} - E\ \textit{trans} = 2300$ cal. This quantity of energy might be characteristic of a weak hydrogen bond. In the absence of an atom which would normally act as an electron donor we are forced to explain this attraction as an extraordinary manifestation of the phenomenon known as hyperconjugation.

We shall assume that the substituent group adjacent to the hydrogen in the *cis* position is the mesityl, (sym-2,4,6-trimethylphenyl), group. There is a cumulative weight of evidence that this radical behaves as though there were an accumulation of electronic charge on the carbon atoms in the 1,3,5 positions as a result of hyperconjugation with the methyl groups.

The distance between the hydrogen atom and the (1) carbon is 1.8 Å. = 0.1 which is about the right distance for a hydrogen bond to a carbonium ion.

The assumption that the group adjacent to the hydrogen is mesityl is strongly supported by the necessity of explaining the failure of the vinyl alcohol to rearrange to the corresponding ketone. The mesityl group is known to be attached to the β-carbon atom. If one constructs a model, he sees at once that when the mesityl group is placed perpendicularly to the plane of the C=C—OH nucleus, the methyl groups in the 2 and 6 positions completely shield the β-carbon atom against the approach of the hydrogen atom, which is the necessary initial step in rearrangement.

Summary

If it is assumed that the hydroxyl group and the mesityl group are on the same side of the carbon–carbon double bond in the β-, mesityl-substituted vinyl alcohols, then the coplanar configuration would permit two positions for the hydrogen of the hydroxyl. Two infrared frequencies are observed which are believed to correspond to these two positions.

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