[CONTRIBUTION FROM THE DOW CHEMICAL CO.]

Physical and Chemical Effects of Substituent Groups on Multiple Bonds. I. Methyl Substituted Olefins

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The chemical and physical effects of the substitution of a methyl group onto an aliphatic double bond are described. The employment of 2-allylphenol as the parent olefin permits the use of the hydrogen bonding phenolic hydroxyl group to be used as an independent probe. In this manner the variation of basicity and the geometric availability of the double bond has been correlated through a series of methyl homologs.

Empirical correlations of infrared spectra have established the fact that some chemical groups always give rise to frequencies in certain spectral regions. These frequencies have been termed "group" or "characteristic" frequencies, many of which have been collected and published in catalog form. They have been extremely helpful in the elucidation of molecular structure, in the identification of unknown samples, and even in assay approximations for total group content. In large part, the rapid growth and extensive use of the infrared technique is due to the existence of such frequencies and the speed and ease with which they can be detected.

The occurrence of characteristic frequencies is due to the fact that each originating group is, to a first approximation, effectively isolated from the rest of the molecule either by extraordinarily large internal force constants or by the small mass of some of the group atoms. Consequently, changes in the molecular structure adjacent to the group do not, within this approximation, influence the group vibrations. Upon closer examination, however, one finds that the precise values do depend upon the structure of the entire molecule. Rather than being detrimental, this dependence on structure markedly increases the usefulness of the characteristic frequencies since not only can the general type of group be determined but frequently the specific nature of the adjacent molecular structure as well.

The variation of the group vibrations can be ascribed to both physical and chemical effects. The physical effects result either from a change in the mechanical coupling of vibrations (including those due to Fermi resonance) or from the mass effect of substituent groups. The latter effect usually lowers the group frequency as the masses of the adjacent substituent atoms are increased. Chemical effects, on the other hand, can either raise or lower the frequency of the vibrating group by means of polar changes propagated along the chain or by field interactions such as dipole–dipole associations. In general, the two effects differ in that physical effects do not change the force constants of the bonds in question, but chemical effects do. Therefore, in studying spectra and the variations of group frequencies, the importance and extent of each must be considered.

This paper investigates, by the hydrogen bonding techniques of an earlier paper,[1] the magnitude of chemical effects on the ethylenic ($C{=}C$) functional groups in substituted *o*-allylphenols. As shown previously, and discussed more fully below, a weak hydrogen bond occurs in these compounds between the O–H group and the ethylenic π-electrons. The strength of the bond varies as different groups are substituted directly on the carbon atoms of the double bond thus showing that the electronic nature of the π-electrons is different for each compound. Since the O–H group is well insulated from the portion of the molecule being changed, it can be considered as an independent probe external to the functional group, and therefore unaffected by the physical changes which affect the group frequency. Consequently, differences observed in the strength of hydrogen bonding are due only to chemical effects and not to any of the above described physical effects. Moreover, the energy of bonding can be measured both by the relative intensity of the associated O–H bond and by the $\Delta\nu_{OH}$ shift in compounds where steric interactions are absent. In particular, this paper discusses the methyl-substituted allyl phenols, and shows that the chemical effects of a methyl group are appreciably different from those of a hydrogen. This is contrary to some recent assumptions[2] concerning the effects of methyl substitution on the acetylenic $C{\equiv}C$ functional group, in which all of the changes were ascribed to physical mass effects. We believe that the basicity of the acetylenic π-electrons is changed in a manner analogous to that for the ethylenic π-electrons and that our data can be extrapolated to include this second class of compounds. As in the ethylenic series, each additional methyl group probably causes a further increase in the basicity of the π-electrons and, therefore, the strength of the $C{=}C$ or $C{\equiv}C$ bond. This is indicated both by a general trend toward higher stretching frequencies and, in the allyl series, by an increase in the strength of the hydrogen bond. Therefore, we conclude that chemical effects of this type, particularly in the acetylenic compounds, are very important and in some compounds may be much larger than physical effects.

Experimental

The spectra were obtained with a Beckman DK-2 spectrophotometer in the fundamental O–H stretching region at 3600 cm.$^{-1}$ and with a Beckman IR-7 prism grating spectrophotometer in the fundamental O–D stretching region at 2600 cm.$^{-1}$. The samples were run at approximately 0.005 *M* concentration in CCl_4, considerably below the concentration required for intermolecular association. The spectra were calibrated[3] by recording the vapor spectra of water and ammonia directly over the O–H bands. The

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[1] A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958).

[2] R. C. Lord and F. A. Miller, *Appl. Spect.*, **10**, 115 (1956).

[3] A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr., *J. Opt. Soc. Amer.*, **43**, 941 (1953).

TABLE I

	Substituents 2	3	4	5	6	Half-width	ν_{OH} Free	ν_{OH} Bonded	$\Delta\nu_{OH}$	Relative absorbance bonded/free
1	Hydrogen	H	H	H	H		3612.5			
2	$-CH_2CH{=}CH_2$	H	H	H	H	100	3613.6	3549.2	64.4	0.37
3	$-CH_2CH{=}CHCH_3$	H	H	H	H	119	3614.1	3521.5	92.6	.40
4	$-CH(CH_3)CH{=}CH_2$	H	H	H	H	79	3613.5	3523.9	89.6	.46
5	$-CH_2C(CH_3){=}CH_2$	H	H	H	H	48	3610.9	3540.2	70.7	4.5
6	$-CH_2CH{=}C(CH_3)_2$	H	H	H	H		3614.2	3486.7	127.5	
7	$-C(CH_3)_2CH{=}CH_2$	H	H	H	H	76	3614.6	3494.2	120.4	
8	$-CH_2CH{=}CHCl$	H	H	H	H		3612.3	None		
9	$-CH_2CH{=}CH_2$	H	H	H	CH_3		3619.4	3550.4	69.0	
10	$-CH_2CH{=}CH_2$	CH_3	H	CH_3	H		3615.0	3553.5	61.5	0.17
11	$-CH_2CH{=}CH_2$	H	H	CH_3	CH_3	83	3620.2	3550.5	69.7	.61
12	$-CH_2CH{=}CH_2$	CH_3	H	CH_3	CH_3		3623.4	3559.5	63.9	.45
13	$-CH_2CH{=}CH_2$	H	H	H	$CH_2CH{=}CH_2$	96	3614.9	3549.2	65.7	1.11

frequencies are believed to be accurate to within ±1 cm.$^{-1}$, except for a possible ±2 cm.$^{-1}$ for some of the very broad associated O–H bands. The frequencies are more accurate than the values previously published[1] since the original spectra were not independently calibrated and the $\Delta\nu_{OH}$ shifts were referred to the free O–H band in unsubstituted phenol rather than to the free O-H band in each spectrum. The latter point is particularly important because methyl groups on the ring increase the free O–H frequency by as much as 13 cm.$^{-1}$.

The allylphenols employed were, except as noted below, either prepared as described in the literature, or obtained from commercial sources and purified by distillation or chromatography as required.

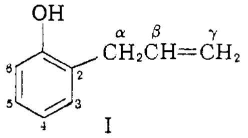
The 2-(γ,γ-dimethylallyl)-phenol obtained commercially was found to be a mixture of the *o*- and *p*-isomers which could not be satisfactorily separated by distillation. Preparation of this material by the interaction of sodium phenolate and 1-bromo-3-methylbutene-2 in benzene[4] yielded the desired *o*-isomer exclusively.

2-(α,α-Dimethylallyl)-phenol can be satisfactorily prepared by the Claisen rearrangement of γ,γ-dimethylallyl phenyl ether, which proceeds normally in the presence of anhydrous Na_2CO_3 (10% by weight).[5] Attempted thermal rearrangement without Na_2CO_3, or in the presence of neutral salts, yielded unsubstituted phenol as the only recognizable acidic product.

2-(β-Methallyl)-phenol was converted to the O–D compound by direct exchange between D_2O and a dilute solution of the phenol in CCl_4. An exchange of 80% was effected by a single pass. The solution was dried with P_2O_5 and run as described above.

Results

In replacing the hydrogens on the α-, β- or γ-carbons of the allyl group with methyl groups,



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steric interaction limiting the number of statistical positions available to the allyl group is introduced for the α-, β- and *cis*-γ-compounds, but not for the *trans*-γ-compound. Therefore, only in this last compound is the hydrogen bonding directly comparable to that in the parent 2-allylphenol. However, from the spectra of the α- and β-methyl compounds and of the dimethyl compounds discussed below, the nature of the steric interactions and the bonding in the two rotational isomers of each compound can be investigated. Two rotational isomers occur because of the possibility of bonding to each side of the π-bond. Table I lists the frequencies of the free and associated O–H bands of the 2-allylphenols together with the relative half-width of some of the associated bands measured with respect to that in 2-allylphenol. Also listed are the relative maximum peak absorbances (ratio of bonded to free) and the $\Delta\nu_{OH}$ shifts.

A visual comparison of the hydrogen bonding in the α-, β- and *trans*-γ-compounds with that in 2-allylphenol is given by the spectra in Fig. 1.

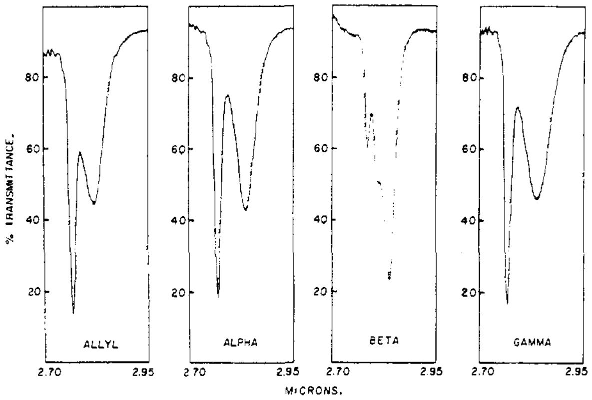

Fig. 1.—The O–H spectra of, from left to right, 2-allylphenol, 2-(α-methylallyl)-phenol, 2-(β-methylallyl)-phenol and 2-(γ-methylallyl)-phenol. The frequencies and associated band half-widths are given in Table I.

As shown in Table I, the frequencies of the unassociated O–H bands in 2-allylphenol and 2-*trans*-γ-methylallylphenol are identical within experimental accuracy. Therefore, the chemical nature and hydrogen bonding powers of the O–H groups are very probably equal. However, the value of $\Delta\gamma_{OH}$ has increased from 64.4 cm.$^{-1}$ in the former compound to 92.6 cm.$^{-1}$ in the latter and the relative peak absorbance of the bonded O–H has increased from 0.37 to 0.40. If one ignores any slight change in absorptivity,[6] then the increase in band half-width and the observed increase in absorbance indicate that the relative proportion of the bonded OH also has increased. Consequently, inasmuch as the structure change produces no effect on the O–H group, and there is no steric complication, the increase in bonding is due only to an increase in the basicity of the π-electrons. Therefore, the conclusion follows that

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[4] C. D. Hurd and W. A. Hoffman, *J. Org. Chem.*, **5**, 212 (1940).

[5] L. Claisen, *J. prakt. Chem.*, [2] **105**, 65 (1922).

the methyl group, compared to hydrogen, is effectively electron releasing, thereby increasing the availability of the π-electrons for hydrogen bonding. This conclusion has, furthermore, been well substantiated by many independent studies[6–8] of Hammett σ-values for substituted aromatic systems and by studies[9] of the relative electronegativities of hydrogen and carbon.

An increase in the C═C bond energy upon methyl substitution has been noted as a general trend in the simple ethylenic compounds[10] and unquestionably applies to the present methyl-substituted compounds. It has been shown above that similar substitution changes increase the basicity of the π-electrons. Further, it is well known that electronegative groups, such as chlorine, reduce the C═C force constant. We have shown in an earlier paper[1] that electronegative groups substituted directly on a carbon atom of a double bond decrease the basicity of the π-electrons, so much so that in 2-*trans*-γ-chloroallylphenol intramolecular hydrogen bonding cannot be detected. It seems clear, therefore, that *a direct correlation has been established between basicity of the π-electrons and the strength of the C═C bond.*

These changes can be discussed more conveniently in terms of hybridization changes[11] in the bonds of the ethylenic carbon on which the different groups are being substituted. The replacement of an ethylenic hydrogen by a methyl group increases the amount of *s*-character in the hybridized orbital because of the lower electronegativity of the methyl group. This increases the amount of *p*-character in the orbitals involved in the other two σ-bonds, a change which would ordinarily decrease the force constants of these bonds. For the π-bond, however, a comparable change in the π-orbital increases the force constant by allowing a greater overlap with the π-orbital on the adjacent ethylenic carbon. This is due to the fact that the π-orbitals are not directed toward one another but are bent from each other at considerable angles; therefore, any extension of either orbital tends to increase the overlap. This also increases the availability of the π-electrons to hydrogen bonding as discussed above from a different standpoint.

Oppositely, replacement of the hydrogen by a group which has a greater electronegativity, such as chlorine, increases the amount of *p*-character in the bond and the amount of *s*-character in the other two σ-bonds. This also "pulls in" the π-orbital on this carbon and thus decreases the overlap in the π-bond. The bond strength thereby is decreased although this is tempered by the back resonance ability of the group or atom substituted onto the ethylenic carbon.

In comparison with the γ-isomer in which the methyl group is substituted directly on the C═C functional group, an α-methyl substituent should produce a smaller effect upon the C═C force constant because of the insulation of the intermediate methylene group. Nevertheless, the effect upon the hydrogen bond is surprisingly large since the $\Delta\nu_{OH}$ shift is 89.6 cm.$^{-1}$ and the absorbance ratio has increased from the value 0.37 in 2-allylphenol to 0.46. An examination of molecular models shows that a considerable portion of this change is undoubtedly due to the constructive interaction between the methyl group and both the O–H and the ring hydrogen adjacent to the allyl group. This forces the C═C group slightly closer to the O–H group for the rotational isomer in which both the vinyl group and the α-methyl group are toward the O–H. At the same time, this markedly decreases the freedom of rotation of the allyl group. As a consequence, the $\Delta\nu_{OH}$ is increased by 39% and the band half-width is decreased by 21% from the values in 2-allylphenol.

2-β-Methylallylphenol exhibits an increasing basicity of the π-electrons equivalent to that in the *trans*-γ-compound. There is also a repulsive steric interaction between the substituent methyl group and both the O–H group and the aromatic ring. The interaction with the O–H group restricts the rotation of the allyl group and, contrary to that in the α-methyl compound, tends to limit the extent of hydrogen bonding with the C═C π-electrons. The interaction with the ring destabilizes one of the rotational isomers and greatly reduces the population in this statistical state. Since the $\Delta\nu_{OH}$ shift is much less than in the *trans*-γ-compound, it is probably this isomer which in the parent allylphenol can form the strongest hydrogen bond. Even so, the $\Delta\nu_{OH}$ shift is 70.7 cm.$^{-1}$ while the ratio of bonded to free O–H as increased to the remarkable value of 4.5. As a result of the strong reduction in rotational freedom, the half-width of the associated band is 52% less than in 2-allylphenol.

A third band, which occurs in this spectrum as a shoulder on the high frequency side of the stronger associated O–H band, has a ν_{OH} frequency of approximately 3571 cm.$^{-1}$. This band might be due to either an associated O–H frequency belonging to a rotational isomer or to an overtone or combination band from lower-lying fundamentals. In order to determine the origin of this band, a sample of O-deuterio-2-(β-methylallyl)-phenol was prepared and its spectrum obtained on Beckman IR-7 prism grating instrument. The O–D stretching bands, given in Fig. 2, are nearly identical in both shape and relative absorbances to those of the O–H compound (Fig. 1). The shoulder is still present in the same relative amount, thus indicating that the band is due to a bonded O–H. The $\Delta\nu_{OD}$ shift between the two major peaks is only 47.7 cm.$^{-1}$ as compared to the $\Delta\nu_{OH}$ shift of 70.7 cm.$^{-1}$.

Dimethyl Homologs.—The basicity of the π-electrons in 2-(γ,γ-dimethylallyl)-phenol is expected to be larger than that of any of the monomethylated compounds because there are two methyl groups on the double bond carbon. However, the *cis*-methyl group probably introduces some steric interaction with the O–H group modifying the strength of the hydrogen bond. The observed $\Delta\nu_{OH}$ shift has increased to 127 cm.$^{-1}$ (Fig. 3), which is approxi-

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(6) L. P. Hammett, This Journal, **59**, 96 (1937).

(7) R. W. Taft, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 556.

(8) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(9) W. L. G. Gent, *Quart. Revs.*, **2**, 383 (1948).

(10) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 2463 (1958).

(11) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947); *Trans. Faraday Soc.*, **53**, 403 (1957).

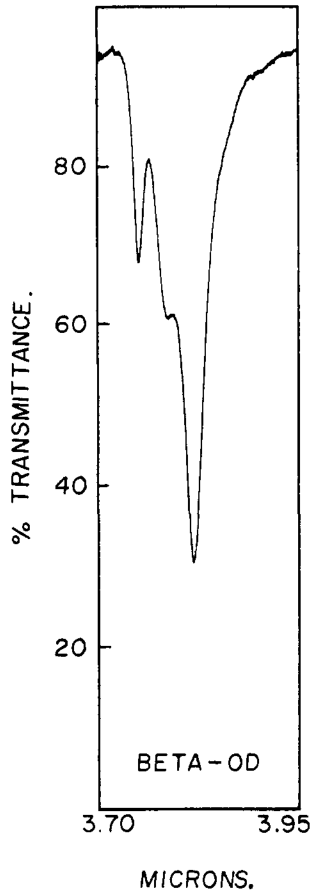

Fig. 2.—The O–D spectrum of 2-(β-methylallyl)-phenol obtained on the Beckman IR-7 prism-grating spectrophotometer. The band shape is identical to that of the O–H compound, thus indicating that the small shoulder is due to a rotational isomer. The effective resolution is about 0.8 cm.$^{-1}$.

mately twice that for a single methyl group. The increment of $\Delta\nu_{OH}$ shift due to one methyl ($\Delta\nu_{OH\,trans\text{-}\gamma\text{-methylallyl}}$ minus $\Delta\nu_{OH\text{ allyl}}$) is 26.6 cm.$^{-1}$ and that due to two methyls ($\Delta\gamma_{OH\ \gamma,\gamma\text{-dimethylallyl}}$ minus $\Delta\nu_{OH\text{ allyl}}$) is 58.1 cm.$^{-1}$.

The 2-(α,α-dimethylallyl)-phenol, similar to the γ,γ-compound, has a $\Delta\nu_{OH}$ shift slightly greater than twice that for the monomethyl compound. From this, we conclude that there is no striking evidence pointing toward a *gem*-dimethyl effect upon basicity of the ethylenic π-electrons. Any effect, if such occurs, is masked by the complicated steric interactions.

Band Half-widths.—As might be expected, the greater energy of bonding in 2-(*trans*-γ-methylallyl)-phenol produces an increase in the half-width of the associated O–H band. This increase is about 20% and very probably is due to anharmonicity of the potential energy function as described, in part, by two recent publications.[12,13] Due to this anharmonicity, the force constant of the O–H bond has the form

$$K' = K - ax$$

where K is the harmonic approximation and x is the internuclear separation. Therefore, statistical perturbation effects will markedly increase the half-width as the energy of bonding increases. This is well illustrated by the half-widths of the associated O–H bands of the α-, β- and *trans*-γ-methylallylphenols. For example, the $\Delta\nu_{OH}$ shifts for the α- and γ-isomers are nearly equal (89.6 cm.$^{-1}$ *vs.* 92.6 cm.$^{-1}$) but the band half-width is 51% larger in the γ-isomer. The steric interaction in the former, strongly restricts the number of rotational configurations which can be taken up by the allyl group and this factor alone appears to be influencing the difference in the band half-width. Furthermore, despite the fact that the $\Delta\nu_{OH}$ shift of the β-isomer is not as large as those in the α- and γ-isomers, the bonded/free absorbance ratio is very much larger and the band half-width of the associated O–H band is even smaller than in the α-compound. It is only in the *trans*-γ-compound, exhibiting no change in steric interaction from that in the parent allylphenol, that the band half-width increases.

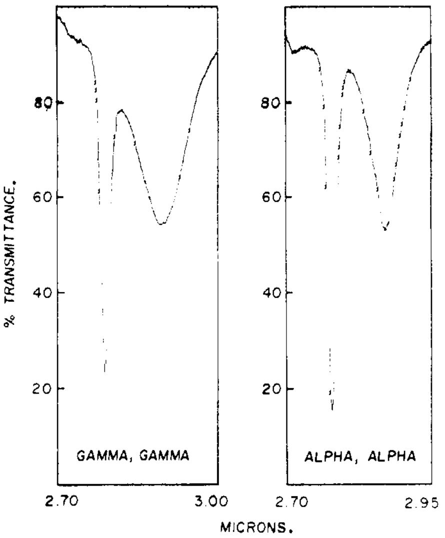

Fig. 3.—The O–H spectra of 2-(γ,γ-dimethylallyl)-phenol and 2-(α,α-dimethylallyl)-phenol. The narrowness of the associated band in the latter compound attests to the importance of steric effects in band widths.

Steric and Polar Effect of Ring Substituents.—As mentioned above, the electron-donating properties of methyl groups have been well substantiated by studies correlating Hammett σ-values with both chemical reactivities and some infrared[14,15] frequencies. One of these studies[14] showed that the phenolic O–H stretching frequency increases as the electron-releasing ability of the ring substituent increases. Therefore, the unassociated O–H frequency is expected to rise as the number of ring alkyl groups increases. However, the increase is surprisingly large (up to 36 cm.$^{-1}$) when both positions *ortho* to the O–H group are substituted. This is far greater than can be accounted for by polar or resonance effects alone, particularly since a single alkyl group generally causes a change of only 2–3 cm.$^{-1}$. Moreover, in a dialkyl substituted phenol

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(12) S. Bratoz and D. Hadzi, *J. Chem. Phys.*, **27**, 991 (1957).

(13) H. L. Frisch and G. L. Vidale, *ibid.*, **25**, 982 (1956).

(14) A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

(15) R. D. Kross and V. A. Fassel, THIS JOURNAL, **78**, 4225 (1956).

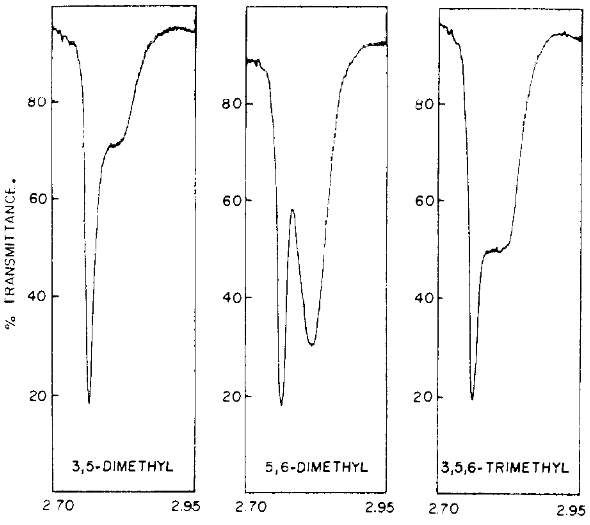

Fig. 4.—The O–H spectra, from left to right, of 2-allyl-3,5-dimethylphenol, 2-allyl-5,6-dimethylphenol and 2-allyl-3,5,6-trimethylphenol.

other than *ortho–ortho*, one finds the expected increase of 2–5 cm.$^{-1}$.

In a forthcoming publication, this *ortho–ortho*-dialkyl effect will be discussed and the suggestion made that it is due to a repulsive steric interaction between the hydrogen of the O–H group and the hydrogens of the alkyl group. Due to the large resonance interaction between the oxygen and the aromatic ring, the steric interaction is not enough to rotate the O–H group out of plane, but instead there is a decrease in the O–H internuclear distance and an increase in the O–H stretching frequency. Consequently, the remarkably high values of ν_{OH} do not reflect the true acidity of such phenols and possibly not their hydrogen bonding powers if these could be determined free from steric complications. (This is to be discussed in detail in a later paper.) This naturally poses the question regarding the way $\Delta\nu_{OH}$ values should be computed for allylphenols. If they are based on the free O–H in each spectrum, then the $\Delta\nu_{OH}$ possibly would be larger for 6-substituted compounds than would be a measure of the energy of the intramolecular hydrogen bond.

The above discussion is amply demonstrated by the data in Table I and the spectra in Fig. 4, which show that ν_{OH} values change from 3612.3 cm.$^{-1}$ in phenol to 3613.6 in 2-allylphenol to 3624.4 cm.$^{-1}$ in 2-allyl-3,5,6-trimethylphenol. In the last compound the buttressing effects of the 3- and 5-methyl groups increase the steric effect of the 2-allyl and 6-methyl groups by 50% or more. This is shown by a comparison with 2-allyl-6-methylphenol which has a ν_{OH} value of 3619.4 cm.$^{-1}$.

The $\Delta\nu_{OH}$ shift of 2-allyl-5,6-dimethylphenol, computed in the usual way, has increased from the value of 64.4 cm.$^{-1}$ in 2-allylphenol to 69.7 cm.$^{-1}$. However, the ν_{OH} value of the associated band is 2 cm.$^{-1}$ higher than that in 2-allylphenol, thus throwing doubt on the validity of $\Delta\nu_{OH}$ values as an index of bonding energy where steric effects are important.

In a previous publication,[1] a 3-methyl group on the ring adjacent to the allyl group was shown to decrease the proportion of the associated O–H because the allyl group is forced slightly out of plane and away from the O–H group. On the other hand, a 6-methyl group, in addition to increasing the $\Delta\nu_{OH}$ shift, as described above, greatly increases the proportion of associated O–H. This may be due mainly to a proton–proton interaction between the methyl and O–H groups, increasing the relative proportion of the in-plane O–H pointing toward the allyl group.

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[Contribution from the Department of Chemistry, Oklahoma State University]

Secondary Hydrogen Isotope Effects in the Hydrolysis of Methyl *p*-Methyl-*t*-benzoate

By Ernest M. Hodnett, Ray D. Taylor, Jose-Vicente Tormo and Robert E. Lewis

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Methyl *p*-methyl-*t*-benzoate has been hydrolyzed in basic aqueous alcoholic solution and in 99–100% sulfuric acid. The tritium-labeled compound reacts slower than the ordinary compound in the basic solution but at the same rate as the ordinary compound in 99–100% sulfuric acid. These differences are explained on the basis of (1) greater electron release of the tritium atom through the inductive effect and (2) smaller electron release by the tritium atom through the electromeric effect.

Molecules having different isotopes of hydrogen may react at different rates even though a bond to the isotopic atom is not broken or formed in the reaction. These secondary isotope effects are as large as 5% for each deuterium atom in such reactions as the acetolysis of deuterated methyl-*p*-tolylcarbinyl chlorides.[2] In general the effect of the heavier isotope is to slow the reaction,[2,3] but in two reported cases the molecule labeled

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(1) Taken from theses presented by Ray D. Taylor and Jose-Vicente Tormo to the Graduate School of Oklahoma State University in partial fulfillment of the requirements for Master of Science degrees. This investigation was supported in part by the Research Corporation and in part by the U. S. Atomic Energy Commission and the Research Foundation of Oklahoma State University through Contract No. AT(11-1)-71, Project No. 5, and was conducted in the Radioisotopes and Radiations Laboratory.

(2) E. S. Lewis and G. M. Coppinger, This Journal, **76**, 4495 (1954).

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