Intramolecular Interaction between Hydroxyl Group and π-Electrons. VII[1]. *Limitation of the Interaction by Chain Length in 2-(ω-Alkenyl)-phenols and 2-(ω-Phenylalkyl)-phenols*

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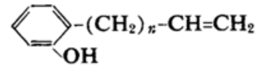
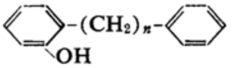
In the previous papers of this series[1,2,3], the authors treated the limitation of the intramolecular interaction between the alcoholic hydroxyl group and π-electrons by the chain length in ω-hydroxy-1-alkenes and ω-phenylalkanols and it has been found that, in the former series, the interaction is observed up to 3-buten-1-ol and in the latter up to 2-phenylethanol[4]. The shift of wave numbers of the O–H stretching vibration (ν_{O-H}) from the free ν_{O-H} to the interacting one, and the absolute intensities of these bands in the infrared absorption were discussed with respect to the configuration, the energy and the entropy of the interaction.

As the phenolic hydroxyl group has a stronger proton donating power in the hydrogen bonding than the alcoholic one, it is naturally expected that the replacement of the alcoholic hydroxyl group in the compounds already studied by the phenolic one will release the limitation of the interaction to compounds with chains longer by one or more carbon atoms and thus some elucidation of the nature of the interaction may be obtained. In this regard, the present authors have extended the study to the two series of 2-(ω-alkenyl)-phenols (I) and 2-(ω-phenylalkyl)-phenols (II), thus completing all the types of the interaction between the alcoholic and phenolic hydroxyl groups and olefinic and benzenoid π-electrons.



I



II

It has been reported that 2-allylphenol, a compound of series I, shows two ν_{O-H} maxima in the 3 μ region of the infrared absorption spectra[5]. The data for 2-hydroxybiphenyl, the lowest member of the second series II, are also available[6]. These two compounds were reexamined together with others, a high precision grating infrared spectrometer[2] being used.

Experimental

Measurement and Calculation.—They were performed similarly as described previously[2]. For the decision of the disappearance of the weaker bands, the measurements were carried out with a quartz cell of 5 cm. optical length without alteration in concentration, which enables to detect a very weak absorption, even if the extinction coefficients were as small as one.

Materials.—The phenols used for the measurement are all known, except 2-(3-butenyl)-phenol, and were prepared in the following ways. The physical constants, after fractional distillation under diminished pressure, well agreed with those in the literature.

2-Vinylphenol (I, $n=0$). — *o*-Coumaric acid was decarboxylated by heating under diminished pressure (ca. 20 mmHg)[7]. B. p. 112°C/17 mmHg, n_D^{27} 1.5775 (lit.[7], b. p. 93~94°C/12 mmHg, $n_D^{35.7}$ 1.577).

2-Allylphenol (I, $n=1$).—Allyl phenyl ether was submitted to Claisen rearrangement[8]. B. p. 109°C/23 mmHg, n_D^{21} 1.5451 (lit[8]., 99°C/12 mmHg, n_D^{20} 1.5453).

2-(3-Butenyl)-phenol (I. $n=2$). — A Grignard reagent was prepared from 31.3 g. (0.2 mol.) of *o*-methoxybenzyl chloride[9], 6 g. (0.25 atom) of magnesium and 150 ml. of ether and the supernatant solution was decanted into a dry flask. To the Grignard solution 24.2 g. (0.2 mol.) of allyl bromide in 50 ml. of ether was added and the mixture was refluxed for two hours to complete the reaction. The mixture was decomposed with aqueous ammonium chloride and the ether layer was dried over potassium carbonate. Fractional distillation gave 19 g. (59% of the theoretical) of 4-(2-methoxyphenyl)-1-butene, b. p. 120~123°C/18 mmHg. To a solution of methylmagnesium iodide prepared from 71 g. (0.5 mol.) of methyl iodide, 12.2 g. (0.5 atom) of magnesium and 200 ml. of ether was added 19 g. of 4-(2-methoxyphenyl)-1-butene. Ether was evaporated and the temperature was gradually raised up to 160° on an oil bath. During this time the mixture became pasty and evolution of ethane was observed. Heating was continued for two hours,

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[1] Part VI: M. Ōki and H. Iwamura, This Bulletin, **32**, 1135 (1959).

[2] Part II: idem, ibid., **32**, 567 (1959).

[3] Part V: idem, ibid., **32**, 955 (1959).

[4] In γ-arylpropanols with such electron donating ring substituents as amino, methoxyl and methyl groups, the interaction was found to be operative, but in γ-phenylpropanol itself it was indecisive.

[5] A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958): R. West, ibid., **81**, 1614 (1959).

[6] O. R. Wulf, ibid., **58**, 2290 (1936); V. von Keussler and G, Rossmy, *Z. Elektrochem.*, **60**, 136 (1956).

[7] K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).

[8] D. S. Tarbell, Org. Reactions, Vol. II, p. 27 (1944), John Wiley & Sons, New York.

[9] M. Simonetta and G. Favini, *J. Chem. Soc.*, **1954**, 1840.

until the evolution of the gas practically ended. The mixture was dissolved in dilute acetic acid and extracted with ether. The ether extracts were extracted with aqueous sodium hydroxide. The aqueous layer was shaken with ether, treated with Norite, and then acidified with dilute hydrochloric acid. Ether extraction followed by fractional distillation gave 12.5 g. of the desired phenol (72% of the theoretical), b.p., 78°C/2.5 mmHg, n_D^{24} 1.5347. *Anal.* Found: C, 80.67; H, 8.31%. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

2-Hydroxybiphenyl (II, n=0). — A commercial product was recrystallized from petroleum ether (b. p. 50~70°C). M. p., 59.0°C (lit[10]., 59°C).

2-Benzylphenol (II, n=1). — Sodium phenolate was C-benzylated with benzyl chloride in toluene according to the method described by L. Claisen and his co-workers[11]. They obtained dimorph, melting at 21°C and 52°C respectively, while the species used in the present work melted at 21C°.

2-Phenethylphenol (II, n=2). — 2-Hydroxystilbene[12] was quantitatively hydrogenated over Raney Ni catalyst. The substance, after recrystallization from benzene, melts at 81°C (lit.,[13] 81°C).

2-(3-Phenylpropyl)-phenol (II, n=3). — To a Grignard reagent prepared from 37 g. (0.2 mol.) of phenethyl bromide, 4.8 g. (0.2 atom) of magnesium and 100 ml. of ether, was added 9.2 g. (0.075 mol.) of salicylaldehyde in 50 ml. of ether, and the mixture was refluxed for two hours under stirring and then was decomposed with dilute acetic acid. The ether layer was separated, washed with aqueous sodium carbonate and dried over potassium carbonate. After evaporating the solvent, the residue was recrystallized from ligroin, giving 13.5 g. of 2-(1-hydroxy-3-phenylpropyl)-phenol (80% of the theoretical), m. p., 60~61°C. *Anal.* Found; C, 78.85, H, 7.05%. Calcd. for $C_{15}H_{16}O_2$: C, 78.92, H, 7.06%. 2-(1-Hydroxy-3-phenylpropyl)-phenol (12.15 g., 0.053 mol.) and 4 g. of a palladium-on-carbon catalyst (5% Pd) in 50 ml. of ethanol were shaken with hydrogen under atmospheric pressure. In one and half hours 1.34 l. of hydrogen was absorbed and the absorption practically stopped. After removing the catalyst and evaporating the solvent, the residue was distilled under diminished pressure, b. p., 148 ~150°C/2.5 mmHg. The distillate set to needles and melted at 21°C. The reported melting point is 21°C[14].

Results and Discussion

The apparent O–H stretching absorption curves of the phenols examined are shown in Figs. 1 and 2, and the data of the two bands in each compounds are recorded in Tables I and II.

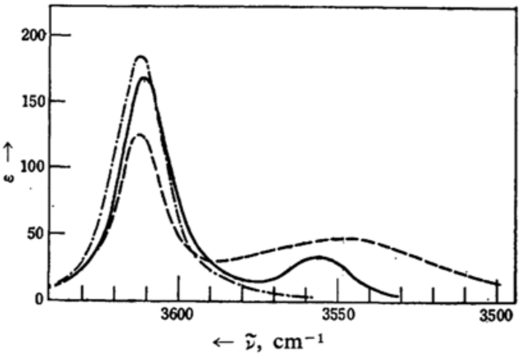

Fig. 1. ν_{O-H} absorptions of 2-(ω-alkenyl)-phenols $o\text{-}HOC_6H_4(CH_2)_nCH{=}CH_2$.
$n=0$ ——, $n=1$ – – –, $n=2$ —·—·—.

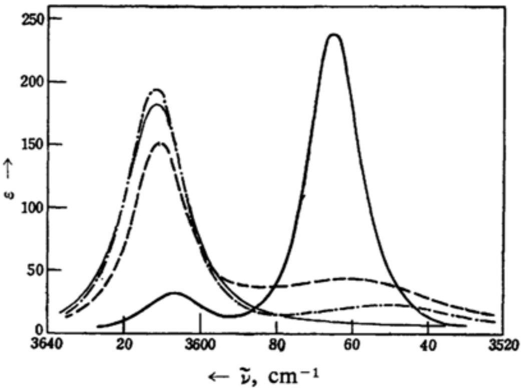

Fig. 2. ν_{O-H} absorptions of 2-(ω-phenylalkyl)-phenols $o\text{-}HOC_6H_4(CH_2)_nC_6H_5$.
$n=0$ ——, $n=1$ – – –, $n=2$ —·—·—,
$n=3$ ——.

It should first be noted that in these phenols the free O–H stretching absorption bands at ca. 3610 cm⁻¹ are always absolutely symmetric in contrast to the unsymetric ones in the free O–H stretching absorption bands in alcohols. This fact gives a support to the idea of the existence of the rotational isomers in alcohols, tentatively developed in a previous paper[15] on the unsymmetry of the free ν_{O-H} bands of almost all alcohols.

In series I, the interaction is effective up to 2-allylphenol (I, $n=1$); the number of the carbon atoms between the hydroxyl group and the nearest carbon atom which carries the π-electron participating in the interaction is three. It is one more than that in 3-buten-1-ol. In series II, the interaction is discernible up to 2-phenethylphenol (II, $n=2$), the number of the intervening carbon atom being two more than that in 2-phenylethanol. It can, therefore, be said that the limitation by the chain length is released by one or two carbon atoms, when an alcoholic hydroxyl group is replaced by a phenolic one, and the results can be

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10) W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 123 (1930).

11) L. Claisen, F. Kremers F. Roth and E. Tietze, ibid., **442**, 210 (1925).

12) H, P. Kaufmann, ibid., **433**, 237 (1923).

13) St. von Kostanecki, A. Rost and W. Szabranski, *Ber.*, **38**, 743 (1905).

14) A. Greewood and M. Nierenstein, *J. Chem. Soc.*, **1920**, 1595.

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

TABLE I. ν_{O-H} ABSORPTIONS OF 2-(ω-ALKENYL)-PHENOLS o-$HOC_6H_4(CH_2)_nCH{=}CH_2$

n	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
0	f.	3611.0	17.8	1.08	53.9	0.26
	i.	3556.8	24.4	0.28		
1	f.	3612.5	16.0	0.67	63.7	1.69
	i.	3548.8	67.4	1.13		
2	f.	3612.4	17.9	1.19	—	—

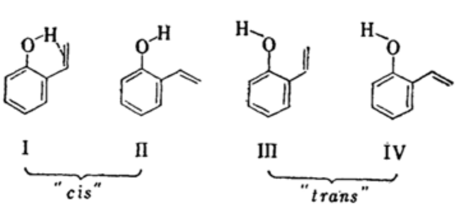
TABLE II. ν_{O-H} ABSORPTIONS OF 2-(ω-PHENYLALKYL)-PHENOLS o-$HOC_6H_4(CH_2)_nC_6H_5$

n	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
0	f.	3607.0	18.2	0.20	42.0	6.4
	i.	3565.0	15.0	1.28		
1	f.	3611.0	17.0	0.87	50.9	0.92
	i.	3560.1	56.2	0.80		
2	f.	3612.0	17.0	1.20	61.5	0.29
	i.	3550.5	47.4	0.35		
3	f.	3611.7	19.5	1.28	—	—

attributed to the higher acidity and the favorable structure of the phenols. In alcohols, intervening carbon atoms are all those of methylenes and there are many internal rotational degrees of freedom, of which carbon skeletons must take an *eclipsed* or at least a *gauche* form for the interaction. This is disadvantageous not only to the energy but also to the entropy of the interaction. In phenols, however, at least O–C=C–C bonds are fixed in a *cis* conformation which is favorable for the interaction. These two factors can not be evaluated quantitatively so far as the present data are concerned.

Although it has been established[16] that the shifts in wave numbers in similar classes of compounds correspond to the lengthening of the X–H bond and to the energy of the interaction, it is not yet known whether this pinciple is applicable to the phenomenon the present authors are dealing with. The energy difference in the free and the interacting forms will be dealt with in the following paper. Although the relationship between the energy and the wave number shift is ambiguous, the following will be still valid in this interaction as is empirically known; 1) The intensities represent the number of the molecules with the hydroxyl group related to the appropriate bands and are dependent not only on the energy but also on the entropy factor. 2) The half band-widths correspond to the rotational degree of freedom.

The most appreciable difference between 2-(ω-alkenyl)-phenols and 2-(ω-phenylalkyl)-phenols is found in the lowest members of the series. 2-Hydroxybiphenyl has 6.4 times as many molecules of the interacting form as those of the free, while 2-vinylphenol has the ratio of only 0.2, the free form being predominant provided that the light absorption per molecule is equal in both free and interacting forms. This phenomenon could be explained in the following way. It is generally accepted that the hydroxyl hydrogen in phenol is situated in the plane of the benzene ring so that 2pπ electrons on the oxygen atom can conjugate with π-electrons in the benzene ring, and this gives rise to the so-called "*cis*" and "*trans*" isomerism in ortho-substituted phenols[6,17]. In the biphenyl molecule, the "*trans*" form gives normal free O–H stretching vibration, while "*cis*" can not help taking the interacting form. Differing from this situation, 2-vinylphenol can be regarded as the composite of the following four conformations (I∼IV) and the hydroxyl group in the



conformation I only can interact with the π-electrons of the vinyl group. Moreover, a full development of conjugation between the benzene ring and the vinyl group will be favored in the conformations II, III and IV which involve less steric interference. Thus the resonance stabilization favors the predominant contribution of II, III and IV in the equilibrium mixture and this is clearly disadvantageous to the interaction. On the other hand, the biphenyl molecule, except in the solid state, has been known not

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[16] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); R. Badger and S. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

[17] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1945, p. 322.

TABLE III. ν_{O-H} ABSORPTION OF 2-HYDROXYSTILBENE

ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A \times 10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
f.	3609.0	17.2	1.10	54.8	0.13
i.	3554.2	21.5	0.14		

to exist in the co-planar structure, but in the crossed structure, the angle between the two benzene rings being regarded as large as ca. 50°[18]. This enables the hydrogen atom of the "*cis*" O–H group to come to the very head of the π-electron clouds. In the interacting conformation of the 2-vinylphenol, the plane of the vinyl group is closely co-planar with that of the benzene ring and the hydrogen atom of the hydroxyl group must approach the π-electron clouds from the side. This difference in the angle of hydrogen approach in the interaction must have a significance to the amount of the interaction, and this kind of mechanism will be dealt with in future issues.

The half band-widths of the interacting ν_{O-H} become greater when a methylene chain is introduced between the hydroxyl group and the group carrying the π-electrons. This is without doubt caused by the participation of many rotational sub-levels to the fundamental transition of the O-H stretching vibration. The interacting forms of these molecules are therefore fairly complicated and have an appreciable degree of freedom.

Inspection of the data obtained with 2-benzylphenol and with 2-allylphenol indicates that these compounds give similar absorption for the interacting form. If this is taken as a significant indication, then it would possibly be the π-electron nearest[19] to the hydroxyl group that accepts the proton. However, it is not proved which π-electron interacts with the hydroxyl group. Hence the above mention is only of a reserved significance.

The measurement was extended to 2-hydroxystilbene, which had been proved to be a *trans*-form from the ultraviolet spectrum[12]. The proton acceptor must be the π-electrons on the central ethylene linkage from the structural requirement. The band properties for O–H stretching vibrations are shown in Table III.

The weaker interaction than that in 2-vinylphenol can be explained on the basis of the electronic effect of the phenyl group attached to the vinyl group, that is, the phenyl group diminishes the electron density on the proton acceptor. This presents a striking contrast to the increased interaction in *o*-propenylphenol, in which the methyl group attached to the vinyl group enriches the π-electron densities at the latter[20].

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[18] O. Bastiansen, *Acta Chem. Scand.*, 3, 408 (1949).

[19] The authors are meaning the π-electron to be another than that born on the phenolic ring.

[20] M. Ōki and H. Iwamura, unpublished. See also Reference 5).