Anal. Calcd. for $C_{17}H_{13}O_5N_2Br$: C, 50.4; H, 3.21; N, 6.91; Br, 19.75. Found: C, 50.3; H, 3.25; N, 6.79; Br, 20.1.

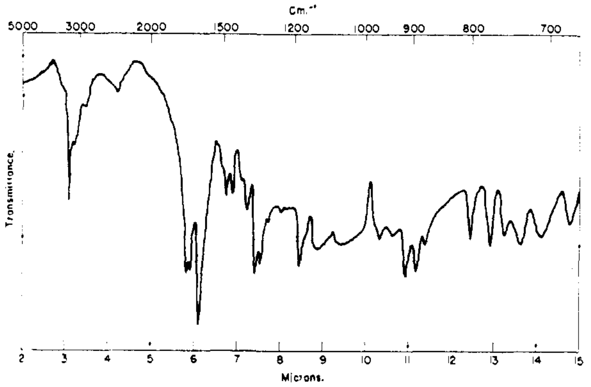

Fig. 1.—Lactam of N-(β-aminoethyl)-chelidamic acid.

Acknowledgment.—The author is grateful to Professor J. H. Shroyer, his major advisor at Bradley University, and to Drs. C. D. Evans and J. C. Cowan, his immediate supervisors at the Northern Regional Research Laboratory, for their interest in this work. Thanks are also due to Dr. E. H. Melvin for the ultraviolet and infrared data and to Mr. C. H. Van Etten for the microanalyses.

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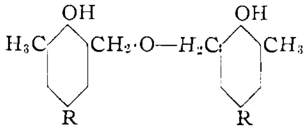
Hydrogen Bonding in Phenolic Resin Intermediates

BY G. R. SPRENGLING[1]

RECEIVED JULY 24, 1953

The properties of phenolic resins might be expected to be peculiarly influenced by hydrogen bonding, for these resins contain many hydroxyl groups particularly subject to such bonds. Indeed hydrogen bonds often have been postulated[2] as an explanation for the peculiarities in behavior of certain phenolic intermediates. So far, however, we lack sure knowledge of the position, nature, effect, and even of the existence of such bonds. This paper is intended to present certain facts concerning hydrogen bonding in the field of novolac-type, phenolic resins.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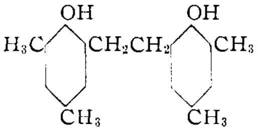
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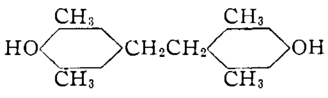
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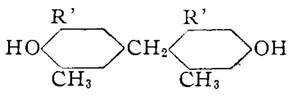
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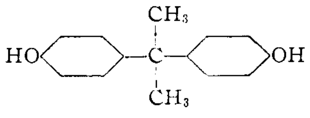
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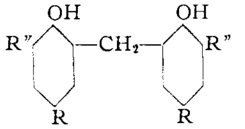
VI

R = $-CH_3$ or $-C(CH_3)_3$, R′ = $-CH_3$ or $-CH_2OH$, R″ = $-H$ or $-CH_3$

In the course of some titrations of carboxylic acids in presence of low molecular weight phenolic resins it was noted that the presence of some acid weaker than the carboxylic interfered with the end-points of the latter. The parent phenol itself proved not to be responsible for this effect. Therefore a study of the acidity of other intermediates possibly present in the mixture was made.

A titration system suitable for this study was found in anhydrous ethylenediamine,[3] using an ethylenediamine solution of sodium (*p*-aminoethoxide) as titrant and recording the potential between two Sb electrodes, one in the titrant and one in the titration vessel. In this system carboxylic acids and all phenols, including so-called "pseudo-phenols," can be titrated easily. Examination of a series of compounds containing two phenolic nuclei linked in various ways by this means showed that the acidity of various *o*-dibenzyl ethers (I), diphenylethanes (II and III) and *p*-diphenylmethanes (IV and V) does not deviate very much from that of a simple phenol (Fig. 1). Also, as was to be expected, the two hydroxyls present in these compounds do not differ appreciably in acidity. The titration curve of various *o*-diphenylmethanes (VI), however, showed a very sharp break after addition of sufficient alkali to neutralize only one of the two hydroxyls, and little or no indication of the other.

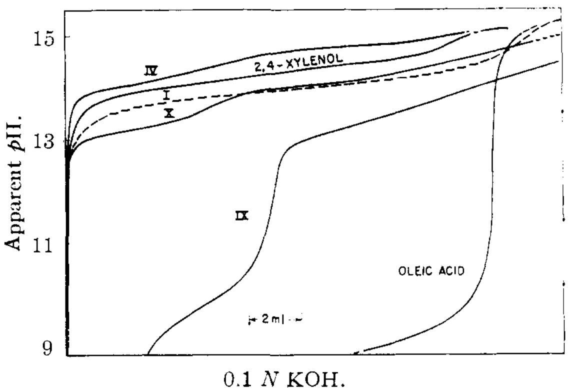

Fig. 1.—Titrations in isopropyl alcohol-benzene 1:1.

This seemingly somewhat unusual result was corroborated by titration in benzene-isopropyl alcohol system[4] against glass-calomel electrodes. Results in this latter system are more reproducible

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(1) Scientific paper 1636, Westinghouse Research Laboratories.

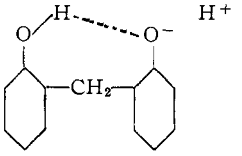
(2) H. L. Bender, A. G. Farnham and J. W. Guyer, U. S. Patent 2,464,207 (1949); K. Hultzsch, *Angew. Chem.*, **61**, 93 (1949); H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196 (1948).

(3) M. L. Moss, J. H. Elliott and R. T. Hall, *Anal. Chem.*, **20**, 784 (1948).

(4) L. Lykken, P. Porter, H. D. Ruliffson and F. D. Tuemmler, *ibid.*, **16**, 219 (1944).

and easier to interpret than those obtained in ethylenediamine. Again the *o*-diphenylmethanes showed a great difference between the acidities of their two phenolic hydroxyls. Moreover, judging by the height and steepness of the end-point break, as well as by the apparent *p*H at the half-neutralization point, the first hydroxyl in the *o*-diphenylmethanes is hyperacid, lying about halfway between phenol and oleic acid in acidity (Fig. 2).

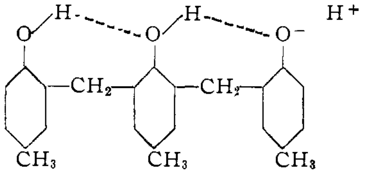
Only two modes of interaction that might explain this phenomenon are readily apparent, resonance and hydrogen bonding. In all of the compounds discussed resonance between the two rings is blocked by the linking group. Moreover, resonance should affect the *p*-diphenylmethanes equally as well as the *o*-diphenylmethanes. The difference in acidity of the two hydroxyls in the *o*-diphenylmethanes must therefore be due to the presence of an intramolecular hydrogen bond from one hydroxyl to the other, which increases the tendency of the second hydroxyl to lose its proton. Examination of the space model of such a molecule



shows that the strain-free ring necessary for formation of such a hydrogen bond is possible. Infrared spectra of compounds in this class of *o*-diphenylmethanes have shown an absorption interpreted as due to an intramolecular hydrogen bond.[5]

To verify the presence of a hydrogen bond as indicated, further substances were titrated. As would be predicted, a tribody with methylene bridges in ortho position showed only one hyperacid hydroxyl of the three present. This appears to be yet a little more acid than the first hydroxyl of the dibody (Fig. 2c), which is to be expected, since the

VII



proton from ring 2 is able to form a better bond to ring 1, being itself released somewhat by the bond from ring 3. The hydroxyls on rings 2 and 3 appear to differ somewhat in acidity, but not enough to allow a differential titration. The hyperacid hydroxyl can thus be assumed to be on ring 1 or 3, on the end of the chain. If hydrogen bonds formed to the hydroxyl on ring 2 from the hydroxyls on both rings 3 and 1, making the hydroxyl on ring 2 hyperacid, then the hydroxyls on the other two rings could be expected to be of low but equal acidity. Further, the hydroxyl on ring 2 may be expected to have the lowest initial acidity, a property of 2,6-alkyl substituted phenols.

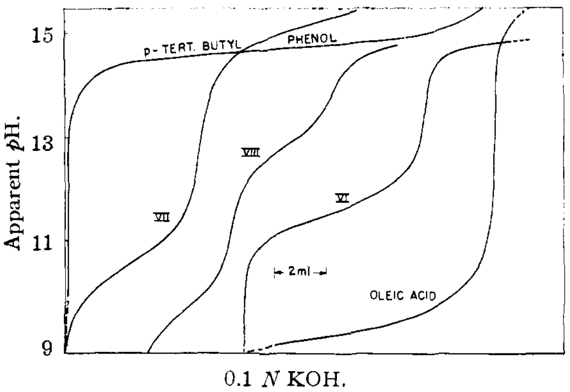
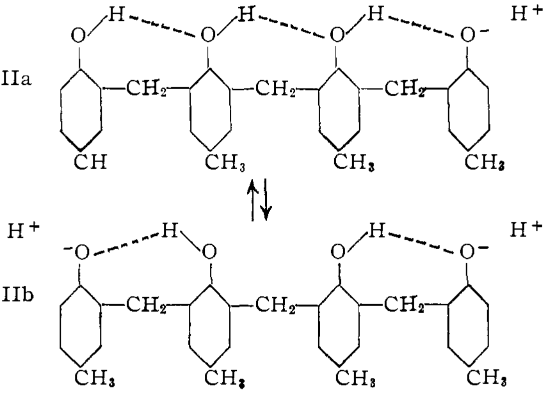


Fig. 2.—Titrations in isopropyl alcohol–benzene 1:1.

VIIIa

VIIIb



Carrying the chain one step further the straight chain tetrabody shows one hyperacid hydroxyl of the four present (Fig. 2). This can only be explained by formation of all the hydrogen bonds toward one end, as in VIIIa. The titration curve also shows a second hydroxyl somewhat more acid than phenol. We may assume that the chain is becoming too long to be held rigidly in the position needed for hydrogen bond formation by the weak forces available. Therefore there will be an equilibrium between form *VIIIa* and the more flexible *VIIIb*. This causes two hydroxyls of the four present to be hyperacid, but because of the equilibrium with form VIIIa, one of them is much more acid than the other.

In corroboration of the theory advanced above, a branched tetrabody (IX) shows one hyperacid hydroxyl of the four present, the other three being of weak and nearly equal acidity, and an ortho–para linked tribody (X) shows no hyperacidity at all (Fig. 1), since its structure precludes formation of intramolecular hydrogen bonds.

Certain conclusions may be drawn on the basis of the above information concerning the behavior and properties of novolacs at temperatures not too far above room temperature. For example, we may expect phenolic resins linked essentially by methylene bridges in ortho-position to the phenolic hydroxyls to differ from all other phenolic resins in some properties. Wherever such an ortho–ortho link occurs the resin chain must be relatively rigid, since the tendency to form a hydrogen bond ring

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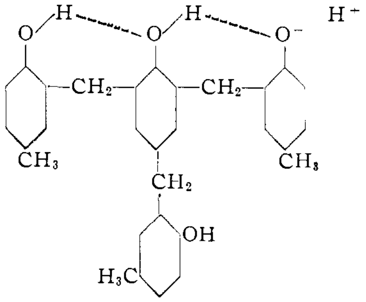
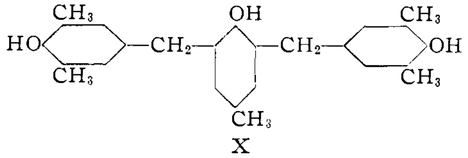
(5) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1260 (1947); N. D. Coggeshall, THIS JOURNAL, **72**, 2836 (1950). Coggeshall's ultraviolet spectroscopic results on the ionization of "bis-phenol alkanes existing in *cis*- and *trans* isomeric forms" support our interpretation as well as they do his own.


IX


X

will hold the adjacent phenolic nuclei in a fixed position relative to each other. This will be true of segments in the chain molecules of every novolac resin, since such resins are linked only by methylene bridges as far as is known, and a goodly proportion of these bridges in any such resin must be of the ortho–ortho type. Further, the formation of intramolecular hydrogen bonds precludes in corresponding degree the formation of such bonds between adjacent resin molecules, thus impairing the intermolecular cohesion. It may be noted here that novolac resins are generally brittle solids.

A prediction may also be made concerning the further reaction of such novolac chain molecules with formaldehyde, and through this with further phenol nuclei. Resonance in phenols activates their ortho- and para-positions to cationic attack,[6] as by formaldehyde. In a phenolic nucleus with hyperacid hydroxyl this effect will be intensified—thus, in the end nucleus of an ortho-linked methylene bridge chain. This nucleus should therefore be more reactive than the rest of the molecule. This is true, of course, of ortho-linked segments within a chain also. Therefore, on further reaction with formaldehyde and phenol an ortho-linked novolac chain or segment of a chain will tend always to grow at its end, instead of branching. Since growth continues chiefly as ortho-linked segments added to the ortho-linked portion of a chain molecule, the branches will be in the para position. Being comparatively unreactive, the branches will tend to be short.

Experimental

Bis-(2-hydroxy-3,5-dimethylbenzyl) ether (I, R = $-CH_3$) was synthesized by the method of Hultzsch,[7] m.p. 99.7–100.3° (cor.) (reported m.p. 100°).

Bis-(2-hydroxy-3-methyl-5-*t*-butylbenzyl) ether (I, R = $-C(CH_3)_3$) was prepared according to Hultzsch,[8] m.p. 131.8–132.3° (cor.) (reported m.p. 131.5°).

α,β-Bis-(2-hydroxy-3,5-dimethylphenyl)-ethane (II) was synthesized by the method of Fries and Brandes,[9] m.p. 168.2–168.7° (cor.) (reported m.p. 168°).

α,β-Bis-(4-hydroxy-3,5-dimethylphenyl)-ethane (III) was recovered from the products formed by heating 4-hydroxymethyl-2,6-dimethylphenol with oleic acid. The product crystallizes from the oleic acid recovered from the reaction (by distillation in vacuum). Recrystallized repeatedly, from methanol–water, m.p. 169.0–169.4° (cor.) (reported m.p. 166.7°).[9]

Bis-(4-hydroxy-3,5-dimethylphenyl)-methane (IV, R' = $-CH_3$) was obtained as a by-product of 4-hydroxymethyl-2,6-dimethylphenol by the method of Adler.[10] The product was recrystallized from methanol–water and ethyl acetate, m.p. 175.2–176.5° (cor.) (reported m.p. 175°).

Bis-(4-hydroxy-3-hydroxymethyl-5-methylphenyl)-methane (IV, R' = $-CH_2OH$) was obtained by the method of Hanus[11] and recrystallized from toluene and ethanol–water, m.p. 154.6–155.1° (cor.) (reference m.p. 155°).

2,2-Bis-(4-hydroxyphenyl)-propane (V) was a commercial product of the Dow Chemical Company.

Bis-(2-hydroxy-3,5-dimethylphenyl)-methane (VI, R = R" = $-CH_3$) was obtained by the method of Fries and Kann,[12] and recrystallized from ethanol–water and benzene–hexane, m.p. 147.8° (cor.) (reference m.p. 146°).

Bis-(2-hydroxy-3-methyl-5-*t*-butylphenyl)-methane (VI, R = $-CH_3$, R" = $-C(CH_3)_3$) was synthesized by the method of Hultzsch,[8] and recrystallized from hexane, m.p. 141.7–142.2° (cor.) (reference m.p. 140°).

Bis-(2-hydroxy-5-methylphenyl)-methane (VI, R = $-CH_3$, R" = $-H$) was made by the method of Koebner,[13] and recrystallized from benzene–hexane and ethanol–water. The substance is dimorphic. The product of recrystallization is the lower-melting form, m.p. 94.5–95.0°, unstable above its melting point. The higher-melting, stable form was obtained by distilling the substance at 0.3 mm. pressure, m.p. 125.4–126.3° (cor.) (reference m.p. 126°).

2,6-Bis-(2-hydroxy-5-methylbenzyl)-4-methylphenol (VII) was obtained by the method of Koebner.[13] The substance is accompanied by considerable dimer (VI) which causes little depression of the melting point. To remove this it was recrystallized from xylene, then from glacial acetic acid, and finally from xylene again, m.p. 212–214.6° (cor.) (reference m.p. 215°).

3,3'-Bis-(2-hydroxy-5-methylbenzyl)-2,2'-dihydroxy-5,5'-dimethyldiphenylmethane (VIII) was synthesized by the method of Hunter, *et al.*,[14] and recrystallized from ethylene chloride and benzene–hexane, m.p. 176–179° (cor.) (reference m.p. 177–179°).

2,4,6-Tris-(2-hydroxy-5-methylbenzyl)-phenol (IX) was synthesized from 2,4,5-tris-(acetoxymethyl)-phenyl acetate and *p*-cresol by the method of Carpenter and Hunter,[15] recrystallized from benzene–xylene, m.p. 184.5–185.0° (cor.) (reported m.p. 184–187°).

2,6-Bis-(4-hydroxy-3,5-dimethylbenzyl)-4-methylphenol (X) was synthesized by heating a solution of 3.17 g. of 2,6-bis-(hydroxymethyl)-4-methylphenol[16] in 24 g. of 2,6-xylenol catalyzed with 2 ml. of concd. hydrochloric acid on the steam-bath for 3 hours, and removing excess xylenol from the crystalline product by filtering with suction at 60°. The product was recrystallized from methanol–water and benzene–xylene, then vacuum sublimed at 0.05 mm. pressure, and recrystallized again from methanol containing 4–5% water, m.p. 187.3–188.1° (cor.).

The titrations in ethylenediamine were done according to Moss,[3] using antimony electrodes as directed therein. Voltages were measured using the millivolt scale and titration input jacks of a Macbeth *p*H meter. About 200–400 mv. of bucking potential was added in the electrode circuit by take-off with a variable potentiometer across a 1.5 v. dry cell to put the voltmeter on scale initially. The resistance across the electrodes in the titration cell was found to be about 100.000 ohms initially, decreasing as the titration progressed. Ethylenediamine as solvent (Eastman Kodak, No. 1915) was dried over sodium and barium oxide, then distilled from sodium in a stream of dry nitrogen. Titra-

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(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 142, 189.

(7) K. Hultzsch, *Ber.*, **74**, 902 (1941).

(8) K. Hultzsch, *J. prakt. Chem.*, **159**, 169, 171 (1941).

(9) K. Fries and E. Brandes, *Ann.*, **542**, 48 (1939).

(10) E. Adler, H. V. Euler and J. O. Cedwall, *Arkiv. Kemi, Mineral. Geol.*, **15A**, [7] 12 (1941).

(11) F. Hanus, *J. prakt. Chem.*, **155**, 330 (1940).

(12) K. Fries and K. Kann, *Ann.*, **353**, 352 (1907).

(13) M. Koebner, *Angew. Chem.*, **46**, 251 (1933).

(14) R. F. Hunter, R. A. Morton and A. T. Carpenter, *J. Chem Soc.*, 441 (1950).

(15) A. T. Carpenter and R. F. Hunter, *J. Appl. Chem.*, **1** 21, (1951).

(16) F. Ullmann and K. Brittner, *Ber.*, **42**, 2640 (1909).

tions in this medium always showed a sharp end-point break of from 30–60 mv. for pseudo-phenols and phenols to 150–190 mv. for "hyperacid" dihydroxydiphenylmethanes and carboxylic acids. Some judgment of the relative acidities of different compounds could also be made on the basis of the bucking potential needed to obtain the same millivolt reading at half-neutralization. In general, however, the antimony electrodes did not give potentials reproducible from one day to the next, being apparently too much influenced by the surface condition of the metal, etc. Also, despite sharp and unmistakable end-points, the initial portion of a titration curve was generally irregular. Titration curves for this medium are therefore not given here.

Titrations in benzene–isopropyl alcohol were carried out as described by Lykken[4] and as set forth in A.S.T.M. methods D 663-46T. Isopropyl alcohol (Eimer and Amend, No. A-416) and benzene (Mallinckrodt, thiophene-free) were used as received. A Beckman No. 4990 glass electrode was found suitable for these titrations, though the electrode tends to a lower and lower peak *p*H for any given substance over the course of several months and must finally be replaced. To get the entire course of all titrations within the scale of the Macbeth *p*H meter, the instrument was adjusted to read *p*H 2.0 in a *p*H 4.0 buffer. All readings of "apparent *p*H" read on the scale during titration were then adjusted accordingly by adding two *p*H units. The highest reading possible thus becomes "apparent" *p*H 16. The curves obtained by this method, as shown in Figs. 1 and 2, are typical of a class unless stated to be specifically of one compound. Thus the curve given as that of a dihydroxydibenzyl ether is actually one obtained using bis-(2-hydroxy-3-methyl-5-*t*-butylbenzyl) ether, but the titration curves of all the compounds of this class investigated resemble each other so closely that it was deemed useless to give the curves of more than one.

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EAST PITTSBURGH, PENNA.

The Absorption Spectra of the 2-Furyl and 2-Thienyl Analogs of Chalcone[1]

BY H. HARRY SZMANT AND HENRY J. PLANINSEK

RECEIVED OCTOBER 16, 1953

In a previous publication[2] dealing with the absorption spectra of α,β-unsaturated ketones A—CH=CH—CO—B it was noted that the replacement of the phenyl by the 2-furyl group in position A gave a consistent bathochromic effect of 33–34 mμ regardless of whether the B group consisted of a phenyl or a 2-thienyl group and, furthermore, that the replacement of the phenyl by the 2-thienyl group in position B gave a smaller but rather constant bathochromic effect regardless of whether the A group was the phenyl or the 2-furyl group. In a later publication[3] it was possible to express the effects of substituents on the absorption spectra of chalcones in terms of several generalizations relating the degree of batho- and hypsochromic effects to the electronic nature and the location of the substituents. Since the replacement of the phenyl groups in the chalcone molecule by resonating heterocyclic nuclei can be regarded as a way of forming substituted chalcones, and in view of the above mentioned regularities, it became desirable to examine the whole series of eight chalcone analogs in which one or both phenyl groups are replaced by the 2-thienyl and/or the 2-furyl group.

The spectral results obtained in this study are listed in Table I. (1) The replacement of the phenyl by either the 2-furyl or the 2-thienyl group causes an approximately threefold greater bathochromic effect when the replacement occurs in position A. (2) There is a small but consistent difference between the effects caused by the 2-furyl and the 2-thienyl groups. The 2-thienyl group causes a slightly greater bathochromic effect when the replacement occurs in position A while the opposite is true when the replacement occurs in position B.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF
A—CH=CH—CO—B

			Absorption maxima			
No.	A	B	λ, mμ	ε × 10^{-4}	λ′, mμ	ε′ × 10^{-4}
1	Phenyl	Phenyl	312[a]	2.67[a]	230[a]	0.89[a]
2	2-Thienyl	Phenyl	345	1.92	275	1.01
3	2-Furyl	Phenyl	344[b]	2.68[b]	260[b]	0.85[b]
4	Phenyl	2-Thienyl	320[b]	1.93[b]	..	..
5	Phenyl	2-Furyl	324	1.07	228	0.85
6	2-Thienyl	2-Thienyl	354	3.70	285	.85
7	2-Furyl	2-Thienyl	353[b]	2.43[b]	243[b]	.56[b]
8	2-Furyl	2-Furyl	354	6.08	256	.43
9	2-Thienyl	2-Furyl	355	4.82	(298)	(.99)

[a] Reported in ref. 3. [b] Reported in ref. 2.

The first of the above conclusions is in excellent agreement with generalization no. 1 which was deduced from the examination of the spectra of a great number of substituted chalcones.[3] This implies that the two heterocyclic nuclei have a greater electron-donating character than the phenyl group, and this conclusion agrees with the observations of Braude and co-workers[4] dealing with the spectra of vinyl derivatives of the three ring systems. Also the decrease in rates of the acid-catalyzed semicarbazone formation when benzaldehyde is compared to 2-furancarboxaldehyde and 2-thienaldehyde[5] can be attributed to the greater electron-releasing effects of the heterocyclic nuclei which effect would thus stabilize the protonated aldehyde intermediate toward the attack of the semicarbazide molecule.

The slightly greater electron-releasing effect of the 2-thienyl group as compared to the 2-furyl group (deduced from their relative bathochromic effects in position A) is confirmed by the results of Braude.[4] The results of the same group of investigators[6] dealing with the rates of the acid-catalyzed rearrangements of substituted 1-crotyl alcohols, however, seem to indicate a greater electron release in the case of the 2-furyl group and these investigators attribute the difference to the greater "electromeric polarizability" of the 2-furyl group as compared to that of the 2-thienyl group.

The slightly greater bathochromic effect noted when the 2-furyl group replaces the 2-thienyl group in the position B implies that under these circumstances the first group is more electron-attracting.[7] The fact that the 2-furyl group can be more electron-attracting than either the phenyl or the 2-thienyl group is brought out by the comparison of

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[1] From the M.Sc. thesis of Henry J. Planinsek, Duquesne University, Aug., 1951.

[2] H. H. Szmant and A. J. Basso, THIS JOURNAL, **73**, 4521 (1951).

[3] H. H. Szmant and A. J. Basso, *ibid.*, **74**, 4397 (1952).

[4] E. A. Braude, *et al.*, *J. Chem. Soc.*, 4155 (1952).

[5] K. C. Schreiber and F. J. Vancheri, Meeting-in-Miniature, Pittsburgh, Pa., June 11, 1953.

[6] E. A. Braude and J. S. Fawcett, *J. Chem. Soc.*, 4158 (1952).

[7] The bathochromic effect of electron-attracting groups at B in the case of substituted chalcones was summarized as generalization no. 3 in ref. 3.