of gas was evolved. Stirring was continued for an additional 1.5 hours and the reaction mixture permitted to stand overnight. The mixture was carefully decomposed by the dropwise addition of 10 ml. of water followed by 6 ml. of 20% sodium hydroxide. The total hydrogen evolved during decomposition of excess hydride and complexes was 6150 ml. (0.274 mole). The mixture was filtered and the salts washed twice with small portions of solvent. The solutions were combined, dried over anhydrous sodium sulfate, and most of the ether removed. Fractional distillation of the remainder gave 4.1 g. of *n*-hexylamine (27% yield) and 5.4 g. of 2-butyl-1,3-octanediamine (36% yield); mixed m.p. of the latter's diacetyl derivative (132–133°) with an authentic sample, no depression. *Anal.* Calcd. for $C_{16}H_{32}O_2N_2$: C, 67.56; H, 11.34; N, 9.84. Found: C, 67.50; H, 11.20; N, 9.37. The total recovery of identified products was 63%.

In run 11 (Table I) the reaction mixture was stirred for two hours and decomposed by the careful addition of water. Besides 3.0 g. of *n*-butyronitrile (29% yield) there was obtained 3.6 g. of material A (b.p. 78–90° (1.5 mm.), $n^{24}D$ 1.4516). On warming with dilute hydrochloric acid, A yielded *n*-butyraldehyde (m.p. of 2,4-dinitrophenylhydrazone, 121–122°; mixed m.p. with authentic sample, no depression) and material B (b.p. 64–68° (0.5 mm.), $n^{26}D$ 1.4459). The infrared spectrum of B indicated the presence of both nitrile and amine functions. Reduction of B with hydride, followed by benzoylation, gave crystals of m.p. 164–165°, identical with N,N'-dibenzoyl-2-ethyl-1,3-hexanediamine (Table I, ref. *h*). Although not positively identified, it would appear that B was the unknown α-ethyl-β-aminocapronitrile and that A was the anil of *n*-butyraldehyde and α-ethyl-β-aminocapronitrile.

Carbonation of the Products from DA Reduction of Phenylacetonitrile.—The reduction of 0.15 mole of phenylacetonitrile in ether (1.1 MRHN) was accompanied by the evolution of 0.0817 mole of gas. Dry carbon dioxide gas was bubbled into the stirred reaction mixture for eight hours. After the usual hydrolysis and isolation procedure there was obtained 2.1 g. of phenethylamine (12% yield, b.p. 104° (34 mm.), $n^{25}D$ 1.5299) and 8.9 g. of residue. Exhaustive studies of both the residue and of the ether-insoluble inorganic solid from hydrolysis failed to uncover any α-phenyl-β-aminopropionic acid.[17]

Oxidation of the Products from DA Reduction of Phenylacetonitrile.—Reduction of phenylacetonitrile (0.15 mole) was carried out in the usual way at 0.8 MRHN, with evolution of 0.092 mole of hydrogen. After standing overnight, dry (carbon dioxide-free) air was bubbled through the stirred mixture for 5.5 hours at an approximate rate of 70 cc./minute. The color progressed from yellow-green to dark green to red. Hydrolysis afforded 0.038 mole of gas and a deep red reaction mixture. The products of the reaction were 6.4 g. of phenethylamine (34.9% yield) and 1.2 g. of α-phenyl-β-aminoethanol (6.6% yield).[18]

Reduction of β-Iminonitriles to 1,3-Diamines.—α-(*n*-Butyl)-β-iminocaprylonitrile was prepared from *n*-capronitrile by the Thorpe reaction (b.p. 144–150° (1.5 mm.), $n^{23}D$ 1.4954, d^{23}_4 0.8948, yield 45.2%).[24] Attempted reduction of the β-iminonitrile with hydride in ether (DA, 3 MRHN), and in refluxing tetrahydrofuran (DA, 4 MRHN), failed to give the desired 1,3-diamine. In each case some reaction had occurred, but 60–70% of unchanged β-iminonitrile was recovered.[25] Catalytic reduction[26] over platinum oxide in acetic anhydride (40 lb. hydrogen), however, yielded N,N'-diacetyl-2-butyl-1,3-octanediamine, m.p. 132–133°, identical with the product obtained in the hydride reduction of *n*-capronitrile (Table I, run 12).

α,γ-Diphenyl-β-iminobutyronitrile was prepared from phenylacetonitrile in 44.5% yield (b.p. 204–208° (1 mm.), lit. 203–205° (1 mm.).[24] Catalytic reduction, as described above, gave N,N'-diacetyl-2,4-diphenyl-1,3-butanediamine in low yield (m.p. 232–233°), identical with the material obtained in hydride reduction of phenylacetonitrile (Table I, run 7). *Anal.* Calcd. for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.63. Found: C, 73.76; H, 7.49; N, 8.41.

(24) Adkins and Whitman, Table I, ref. *g*.

(25) No instances of the successful reduction of ketimines to secondary amines by hydride appear to have been reported.

(26) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 228.

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Unsaturated Phenols. III.[1a,b] Alkali Isomerization

BY ALFRED R. BADER

RECEIVED OCTOBER 29, 1955

The alkali isomerizations of the six β,γ-unsaturated phenols I–VI have been compared with that of *o*-allylphenol. All six are isomerized with greater difficulty than is *o*-allylphenol and, surprisingly, the *ortho* isomers are isomerized faster than the corresponding *para* isomers. The possible mechanisms of isomerization are considered.

The ease[2] of isomerization of allyl- to propenylphenol and of related systems, such as eugenol to isoeugenol, raises the question of whether that ease of isomerization is due largely to the products' conjugation with the benzene ring or to their hyperconjugation with the terminal methyl group. To answer this, the isomerizations of six β,γ-unsaturated phenols, I–VI, accessible through the acid-catalyzed reactions of dienes with phenol[3–5] have been studied.

o-Allylphenol is isomerized to *o*-propenylphenol by the action of methanolic potassium hydroxide at 110° in six to ten hours.[6] Under those conditions *none* of the phenols I–VI is isomerized to any measurable extent. After 100 hours, both cyclopentenylphenols, II and V, and *p*-3-methylcrotylphenol (VI) were recovered, essentially unchanged, while there was found to be *ca.* 80 and 60% isomerization in the *o*-substituted phenols I and III, respectively, and 30% isomerization in the *p*-crotylphenol (IV). Only when I–VI were heated with potassium hydroxide without solvents at 200° could the six conjugated phenols be isolated in good yields.

When the difficulty of isomerizing all γ-substituted β,γ-unsaturated phenols was realized, but before the surprisingly faster isomerization of *ortho* alkenylphenols in a given *ortho–para* pair was noted, an attempt was made to highlight the difference in reactivity of allylphenol and γ-substi-

(1) (a) For Paper II, see THIS JOURNAL, **77**, 4155 (1955); (b) presented in part before the XIV International Congress of Pure and Applied Chemistry, Zürich, July, 1955.

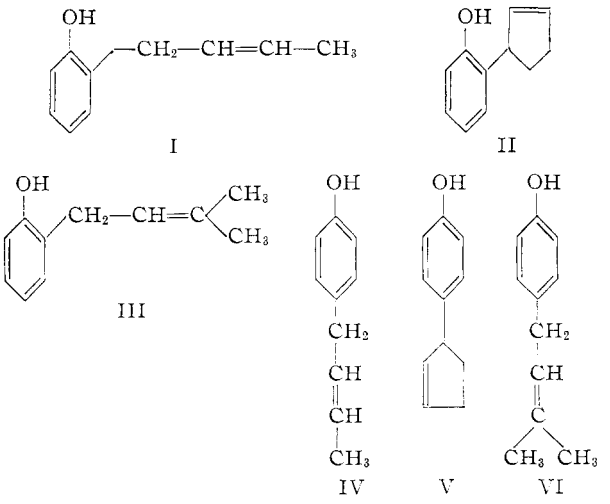
(2) D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1944, p. 19.

(3) W. Proell, *J. Org. Chem.*, **16**, 178 (1951).

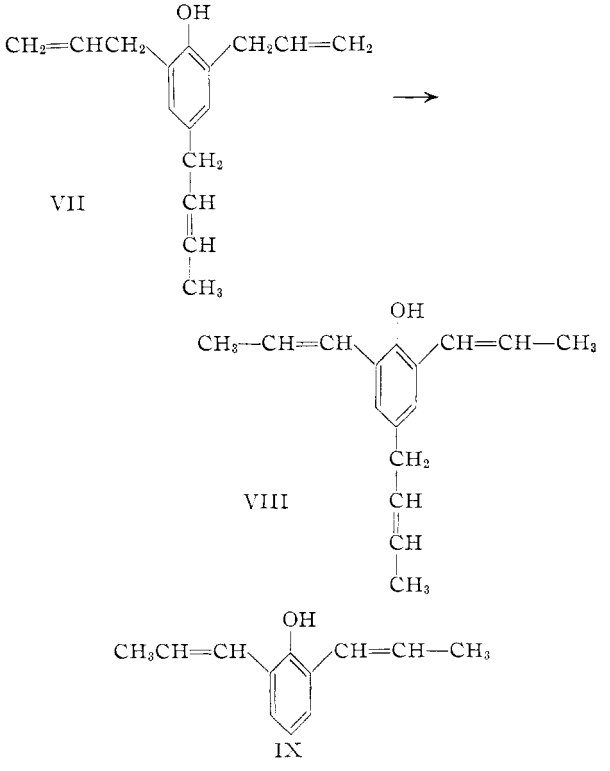
(4) A. R. Bader, THIS JOURNAL, **75**, 5967 (1953).

(5) H. Pines and J. A. Vesely, U. S. Patents 2,553,470 and 2,578,206 (May and December, 1951).

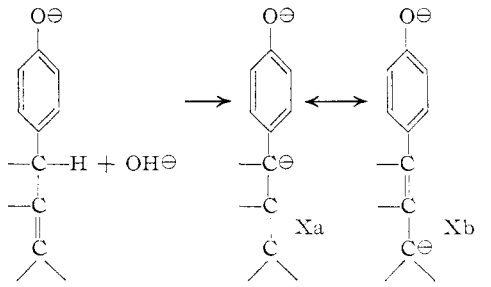
(6) See p. 27 of ref. 2.



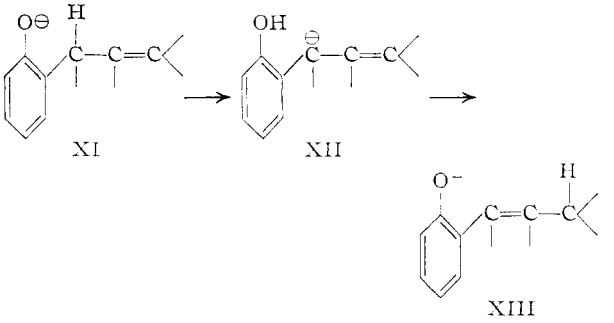
tuted β,γ-unsaturated phenols by isomerizing VII exclusively to VIII. The 2,6-diallyl-4-crotylphenol (VII) was synthesized *via* successive O-alkylations and Claisen rearrangements from IV, and the mild conditions sufficient to isomerize *o*-allylphenol to *o*-propenylphenol yielded only VIII, as shown by its ultraviolet spectrum which was very similar to that of IX.



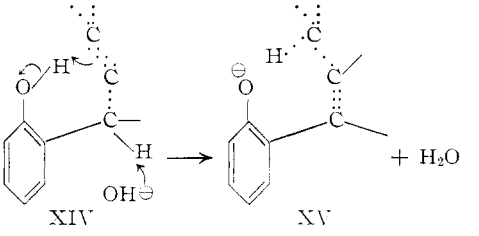
If the isomerizations of all β,γ-alkenylphenols proceed by removal of a proton from the phenolate ion, perhaps with simultaneous γ-addition of a proton, it seemed reasonable to suppose that both steric and electrostatic effects would, in any *ortho–para* pair, make the reaction *ortho* to the phenolate oxygen, even if concerted, the slower of the two. Thus, the faster isomerization of *ortho* alkenylphenols suggested that a different mechanism might be



operative with *ortho* isomers, and several were considered. One was a unimolecular reaction of the ion, XI, possibly with concerted γ-carbon proton attachment



and perhaps involving a solvent bridge to explain the unreactivity of *o*-cyclopentenylphenol; the simple intramolecular mechanism would have a small steric factor. Alternately, a cyclic mechanism XIV → XV, with or without solvent bridge, was considered. This involves the abstraction of a

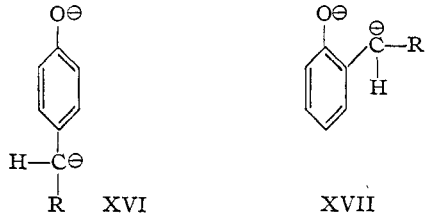


proton from the α-carbon atom of the un-ionized phenol with concerted proton transfer from the phenolic hydroxyl to the γ-carbon atom.

In the mechanism involving simply abstraction of a proton by hydroxide from the α-carbon atom of the phenolate ion, the rate must be dependent on alkali concentration. In the other mechanisms considered for *ortho* isomers, the rate would be roughly independent of the concentration of alkali in excess of that required to form the phenolate. Actually, the rate of isomerization of *para and ortho* alkenylphenols is very dependent on the concentration of alkali; there is no isomerization of I or IV with equivalent amounts of methanolic potassium hydroxide at 110° for 40 hours, and even in the reaction at 200° excess potassium hydroxide is required to effect the isomerization.[7]

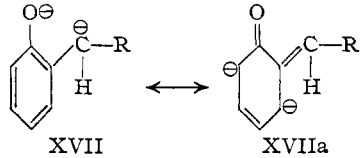
(7) This is similar to the isomerization of eugenol to isoeugenol (S. K. Gokhale, J. S. Sudborough and H. E. Watson, *J. Indian Inst. Sci.*, **6**, 241 (1923)) which at 220° also requires at least two equivalents of potassium hydroxide and in which sodium hydroxide is ineffective. Mr. M. F. Carroll has kindly told me that in the industrial isomerization of eugenol a well-defined, crystalline dipotassium isoeugenol can be isolated. This may, however, be just a solid compound of the phenolate with potassium hydroxide.

The dependence of the rate of isomerization on the alkali concentration appeared to rule out the special mechanisms considered for *ortho* isomers, and it became necessary to reconsider the initial assumption that steric and electrostatic effects would make the abstraction of a proton ortho to the phenolate oxygen the slower. Sterically, this is certainly so.



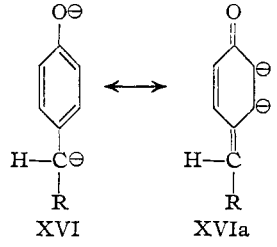
XVI XVII

As to electrostatic effect, the initial assumption was based on the closer proximity of negative charges in XVII than XVI. It may be, however, that under the reaction conditions, there is a higher electron density at the *para*, rather than the *ortho* position of the phenolate, making abstraction of a proton next to it more difficult. Also XVII must be stabilized by resonance with XVIIa, having both



XVII XVIIa

charges in the ring and *para* to each other. The *para* isomer XVI is stabilized less because the corresponding structure XVIa has adjacent negative charges. Thus, the stabilization of XVII by XVIIa may make the isomerizations of the *ortho* isomers the faster.

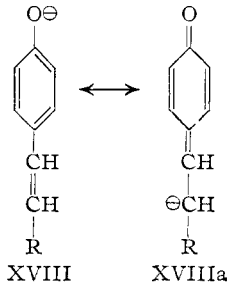


XVI XVIa

As allyl- and propenylphenol are about equally hyperconjugated (a benzyl group being roughly the equivalent of methyl), conjugation alone determines the equilibrium. The same applies to the isomerization of the cyclopentenylphenols. The crotylphenols are doubly and the 3-methylcrotylphenols triply hyperconjugated, while the corresponding conjugated phenols are singly hyperconjugated; here hyperconjugation opposes isomerization. Even the 3-methylcrotylphenols are isomerized, showing that conjugation is the more important driving force.

As the rates of isomerization are rates of ionization, one might try to correlate them with the acidities of the unconjugated olefins. The acidities of allyl-, crotyl- and 3-methylcrotyl-aromatics decrease in that order because one of the structures (*e.g.*, Xb) contributing to the anion becomes progressively a primary, secondary and tertiary anionic structure and hence less stable. The rates of isomerization decrease in the same order. The rates of the cyclopentenylphenols are unexpectedly the slowest. One might have expected an isomerization slower than that of allylphenol (because the two added methylene groups supply electrons), but faster than that of the crotylphenols, because the anions from cyclopentenylphenols are presumably more favored relative to olefin than $CH_3—\overset{\ominus}{C}H—CH{=}CH—Ar$ which has diminished hyperconjugation. This failure in the equilibrium–rate parallelism is reminiscent of the nitroalkyls,[8] where the acidities increase from nitromethane to nitroethane to 2-nitropropane, and the rates of ionization decrease. Presumably, there is steric hindrance to the approach of a hydroxide ion to the α-carbon atom of the cyclopentenyl phenolate. As judged by ultraviolet spectra, however, there is little steric inhibition of conjugation in the *o*- and *p*-1-cyclopentenylphenols.

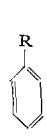
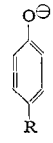
At equilibrium, I–VI are almost completely isomerized. Bateman and Cunneen[9] have recently discussed the importance of hyperconjugation as well as conjugation in isomerizations of alkenylbenzenes and their data also show the great retardation of the reaction of crotyl- compared to allyl-aromatics. Table I lists the equilibrium concentrations of the conjugated isomers in the isomerizations of alkenylbenzenes, alkenylphenols and unsaturated acids. With the phenolate, presumably resonance contributions of structures such as XVIIIa shift the equilibria further toward conjugation than in alkenylbenzenes.



XVIII XVIIIa

TABLE I

% CONJUGATE ISOMER

R	R-CO_2		
$-CH_2—CH{=}CH_2$	98[a]	100	95
$-CH_2—CH{=}CH—CH_3$	68[a]	82	95
$-CH_2—CH{=}C(CH_3)_2$	22[b]	57	90

[a] R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 614 (1934). [b] R. P. Linstead, *ibid.*, 1603 (1930).

It also seemed of interest to compare the isomerization of *o*-allylphenol with that of 2-allyl-3,5-dimethylphenol (XIX). The ultraviolet spectrum of the product XX has a long wave length maximum which is weaker and at shorter wave length than in other conjugated *o*-alkenylphenols and, as the nor-

(8) S. H. Maron and V. K. LaMer, THIS JOURNAL, **60**, 2588 (1938).
(9) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 2283 (1951).

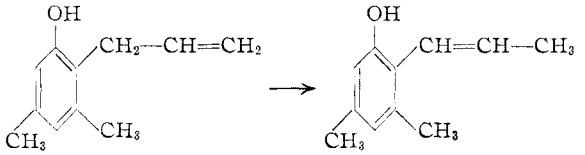
TABLE II

CONJUGATED PHENOLS

Phenols	M.p., °C.	Solvent of crys.	λmax,[c,d] mμ (log e)	λmin, mμ (log e)	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
o-1-Butenyl-	−3 to −1	.....	250(4.04); 303(3.62)	234(3.86); 273(3.20)	$C_{10}H_{12}O$	81.04	80.81	8.16	8.12
p-1-Butenyl-	85–86	Heptane	261(4.29); 285(infl. 3.47)	227.5(3.47)	$C_{10}H_{12}O$	81.04	80.63	8.16	8.10
o-3-Methyl-1-butenyl-	Liquid[b]	.....	253(3.95); 285(infl. 3.45); 301(3.54)	235(3.75); 274(3.37)	$C_{11}H_{14}O$	81.44	81.24	8.69	8.75
p-3-Methyl-1-butenyl-	83–84	Heptane	261(4.27); 298(infl. 3.36)	228(3.50)	$C_{11}H_{14}O$	81.44	81.16	8.69	8.78
o-1-Cyclopentenyl-	48–49	Heptane	227.5(3.87); 253(3.88); 295(3.59); 304(infl. 3.50)	237(3.77); 274(3.31)	$C_{11}H_{12}O$	82.46	82.12	7.55	7.80
p-1-Cyclopentenyl-[a]	149	Aq. ethanol	262.5(4.27); 290(infl. 3.43)	227.5(3.36)	$C_{11}H_{12}O$				

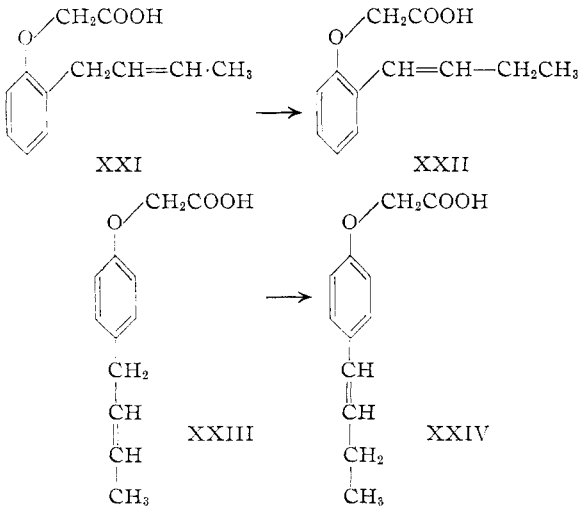
[a] See ref. 4. [b] This probably contained some of the unconjugated isomer. [c] EtOH–0.1% acetic acid. [d] These spectra will be discussed in detail in a paper with Prof. M. G. Ettlinger, in preparation.

mal effect of the methyl groups would be bathochromic, some steric interference is indicated; thus, there must be less assist from conjugation. The effect of hyperconjugation is as in *o*-allylphenol, and the reaction proceeds almost as easily.



XIX XX

That the difficulty of isomerizing the phenolate is primarily due to the necessarily close approach of a hydroxide ion to the α-carbon atom, and hence to a center of partial negative charge at the *o*- or *p*-carbon atom, was shown by the facile isomerizations of the crotylphenoxyacetic acids XXI and XXIII under the relatively mild conditions required to isomerize *o*-allylphenol.



XXI XXII XXIII XXIV

Experimental

Table II lists the physical constants of the conjugated phenols made from I–VI. *p*-Crotylphenol[3] (IV), crystallized from heptane, is a crystalline solid, m.p. 39°. The conjugated *p*-cyclopentenylphenol was identical with the compound prepared previously[4] in the isomerization catalyzed by palladium-on-charcoal.

Mixtures of 10 g. each of I–VI, 10 g. of potassium hydroxide and 30 cc. of methanol were heated with solvent take-off until the flask temperature reached 110°. The clear solutions were then refluxed at 110° under inert gas for 100 hours. The percentage conjugation of I–VI, estimated by ultraviolet spectra, were found to be 80, 3, 60, 30, 3–4 and 1–2%, respectively.

When 0.1 mole each of I–VI was heated in solutions of potassium hydroxide (10 g.) in diethylene glycol[10] (100 cc.) at 165–170° for one hour, no isomerizations were observable. *o*-Allylphenol and XIX are largely isomerized under these conditions.

When each of I–VI was heated with an equal weight of potassium hydroxide at 200° for 4 hours, each of the conjugated phenols was obtained in better than 80% yields. With equal weights of sodium hydroxide or with small amounts of potassium hydroxide, there was little or no isomerization. To illustrate the need for excess alkali further, 14.8 g. (0.1 mole) each of I and IV was heated with 33.5 g. (0.6 mole) of potassium hydroxide in methanol, and 29.6 g. (0.2 mole) each of I and IV was heated with 13.4 g. (0.2 mole) of potassium hydroxide in methanol. Each mixture was treated as in the first experiments described, and was heated in the same oil-bath at 110° for 40 hours. There was *no* isomerization of the phenols treated with equivalent amounts of alkali; and 68% in the *o*-crotylphenol (I) and 36% in the *p*-crotylphenol (IV) treated with excess alkali.

The conjugated phenols are unstable in air, but stable under nitrogen in the icebox. Exposed to air, the conjugated phenols' ultraviolet spectra show diminishing intensities of the maxima at 250–263 mμ characteristic of conjugation, and the emergence of maxima suggesting the formation of unconjugated phenols or phenyl ethers. Thus, when a sample of *p*-1-butenylphenol was exposed to air for two months, the maximum at 261 mμ originally of log *e* 4.29 had a log *e* 3.9, and there was a new maximum at 227.5 mμ, log *e* 3.85, and new minima at 222.5 mμ (3.84) and 242.5 mμ (3.65).

***p*-Crotylphenyl Allyl Ether.**—The reaction of allyl chloride with aqueous sodium *p*-crotylphenolate quantitatively yielded the ether, a colorless oil, b.p. 85–87° (0.5 mm.), m.p. −25 to −23°, $n^{25}D$ 1.523.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.76; H, 8.66.

2-Allyl-4-crotylphenol.—Heating the ether at 200° for three hours yielded (95%) the phenol, b.p. 87–88° (0.1 mm.), $n^{25}D$ 1.540.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.18; H, 8.60.

2-Allyl-4-crotylphenyl Allyl Ether.—This compound prepared similarly is a colorless oil, b.p. 116–119° (0.7 mm.), $n^{25}D$ 1.524.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.71; H, 9.00.

The Claisen rearrangement (200°, 3 hours) of this ether yielded (95%) **2,6-diallyl-4-crotylphenol** (VII), a colorless oil, b.p. 122–125° (0.6 mm.), $n^{25}D$ 1.5392. Its infrared spectrum in carbon disulfide shows strong bands at *ca.* 10.0 and 11.0 μ indicative of terminal unsaturation R—CH=CH_2, and at 10.37 μ indicative of a trans double bond R—CH=CH—R.[11]

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.00, 84.25; H, 9.03, 9.05.

The reaction of 2,6-diallyl-4-crotylphenol with an equal weight of potassium hydroxide in methanol at 110° as above (6 hours) yielded as the sole product **2,6-dipropenyl-4-crotyl-**

(10) J. H. Fletcher and D. S. Tarbell, THIS JOURNAL, **65**, 1431 (1943).

(11) H. W. Thompson and D. H. Whiffen, *J. Chem. Soc.*, 1412 (1948); N. Sheppard and G. Sutherland, *Proc. Roy. Soc. (London)*, **A196**, 195 (1949).

TABLE III

	M.p., °C.	Solvent of cryst.	Analyses,[a] % Found C	H	0.1% HOAc–EtOH λ_{max}, mμ (log ϵ)	λ_{min}
XXI[b]	135–136	Water	69.80	7.00		
XXII	101–102	Heptane	69.61	6.91	252.5(4.14), 297.5(3.63)	232.5(3.89), 274(3.31)
XXIII[c]	80–81	Water	69.84	6.80		
XXIV[d]	128–129	Aq. ethanol	69.72	7.16	260(4.37), 287(infl., 3.42) 302.5(infl., 3.17)	226.5(3.51)

[a] Calcd. $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. [b] Prepared from crude *o*-crotylphenol; XXI is the only isomer sparingly soluble in toluene–heptane. [c] Prepared from *p*-crotylphenol, m.p. 39°. [d] Prepared both by alkali isomerization of XXIII and from *p*-1-butenylphenol, m.p. 85–86°.

phenol (VIII) which formed white clusters of soft needles from heptane and melts at 60°. Its infrared spectrum in carbon disulfide shows no bands at 10.0 and 11.0 μ and a strong band at 10.35 μ.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.77, 84.07; H, 8.82, 8.98. $\lambda_{max}^{EtOH-0.1\% HOAc}$ 237.5 mμ (log e 4.61); 257.5 mμ (infl. log e 4.09); 324 mμ (log e 3.69). λ_{min} 295 mμ (log e 3.30).

2,6-Dipropenylphenol (IX) prepared similarly from 2,6-diallylphenol[12] forms white needles from heptane and melts at 77–78°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 8.67. $\lambda_{max}^{EtOH-0.1\% HOAc}$ 237.5 mμ (log e 4.60); 255 mμ (infl., log e 4.02); 317.5 mμ (log e 3.67). λ_{min} 287.5 mμ (log e 3.29).

2-Propenyl-3,5-dimethylphenol (XX).—2-Allyl-3,5-dimethylphenol[13] (XIX) was treated with an equal weight of potassium hydroxide in methanol at 110° for 20 hours to form XX in good yield. The product formed soft needles from heptane, m.p. 69–70°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.70. XIX: $\lambda_{max}^{EtOH-0.1\% HOAc}$ 216 mμ (log e 4.04), 277 mμ (infl., log e 3.26) 283 mμ (log e 3.29). XX: $\lambda_{max}^{EtOH-0.1\% HOAc}$ 220 mμ (log e 4.38); 254 mμ (log e 4.00); 297 mμ (log e 3.42). λ_{min} 239 mμ (log e 3.87); 279 mμ (log e 3.24).

Butenylphenoxyacetic Acids (XXI–XXIV).—When the mixture of I and IV made by the reaction[3] of phenol with butadiene is treated with chloroacetic acid, the *ortho* isomer XXI is easily separated from XXIII through the former's lesser solubility in toluene and heptane. The acids XXI and XXIII were isomerized to XXII and XXIV, respectively, in methanolic potassium hydroxide (110°, 6 hours). The physical constants of the isomers are listed in Table III.

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(12) K. v. Auwers, *Ann.*, **422**, 174 (1920).

(13) K. v. Auwers and E. Borsche, *Ber.*, **48**, 1716 (1915).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

2-Acylstyrenes from 3,4-Dihydroisoquinolines[1]

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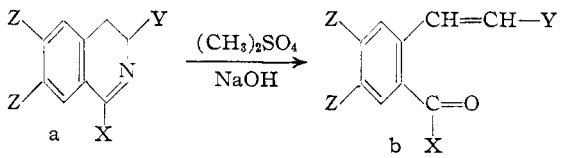
Further examples of 2-acylstyrenes from 3,4-dihydroisoquinolines are reported.

Earlier work showed that aqueous alkali and dimethyl sulfate converted 1-trimethoxyphenyl-6,7-methylenedioxy-3,4-dihydroisoquinoline (Ia) to 2-trimethoxybenzoyl - 4,5 - methylenedioxystyrene (Ib).[3] The present paper describes applications of this reaction to other dihydroisoquinolines. Table I lists the compounds tried, the acylstyrene products, and the yields obtained.

Where there is no substituent on the dihydroisoquinoline 1-position, the product is an aldehyde. For example, 6,7-dimethoxy-3,4-dihydroisoquinoline (IIa) yielded 2-formyl-4,5-dimethoxystyrene (IIb), and cotarnine (Xa) yielded 2-formyl-3-methoxy-4,5-methylenedioxystyrene (Xb).[4] The yields, despite alkaline conditions conducive to Cannizzaro disproportionation, were acceptable. Attempted conversion of the 2-formyl-4,5-dimethoxystyrene to 2-acetyl-4,5-dimethoxystyrene with diazomethane[5] failed. Silver oxide oxidation to 2-carboxy-4,5-dimethoxystyrene, however, proceeded without dif-

TABLE I

ACYLSTYRENES FROM DIHYDROISOQUINOLINES



	X	Y	Z	Yield, %
I	$(CH_3O)_3C_6H_2$	H	$-OCH_2O-$	98[3]
II	H	H	CH_3O	69
III	CH_3	H	H	70
IV	CH_3	H	CH_3O	49
V	C_6H_5	H	H	54
VI	C_6H_5	H	CH_3O	70
VII	$C_6H_5CH_2$	H	H	55
VIII	C_6H_5	CH_3	H	90
IX	C_6H_5	$COOCH_3$	CH_3O	41

(1) Some of the material in this paper was abstracted from the thesis submitted by Edward M. Healy to the Graduate School of Boston University in partial fulfillment of the requirements for the Doctoral degree, 1953.

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(3) W. J. Gensler and C. M. Samour, THIS JOURNAL, **73**, 5555 (1951).

(4) W. H. Perkin, Jr., *J. Chem. Soc.*, **109**, 815 (1916).

(5) *Cf.* C. D. Gutsche, Chapter 8 of R. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954.