comes from a consideration of the predicted rate for enolization of VI. The previously published data on the hydroxybutanones I, II, and III show clearly that the rate of enolization is not appreciably influenced by the electron-withdrawing or electron-donating groups in the benzene ring. Therefore, the inductive influence of the additional phenyl group in VI will be negligible.

Consideration of the possible steric influence on enolization suggest that the additional phenyl group will have a retarding effect. The rate of enolization (halogenation) of isovalerophenone is only one-third that of *n*-valerophenone,[12] a reflection of the change to a carbon skeleton branched at the β-carbon to the carbonyl group. Thus, these facts suggest that VI should undergo reaction no faster than V, and probably substantially more slowly, were enolization the rate controlling step for VI. In fact, VI undergoes dehydration from three to fifty times faster than V.

Inasmuch as the close energetic similarity of a benzhydryl cation and a *p*-methoxybenzyl cation suggested the desirability of the present study, it is of value to compare the rates of reaction of VI with III. Relevant data are summarized in Table II. The increase in the rate of dehydration, at an H_0 of -2, caused by the change to the carbonium ion mechanism, consists of a factor of 15 for the pair I, III and of a factor of 25 for the pair V, VI. The rate of dehydration of VI was found to be only one-third that of III. This decrease in rate may be attributed to either, or both, of the following causes. Estimates suggest a somewhat

TABLE II

RATES OF DEHYDRATION OF VARIOUS β-HYDROXY KETONES AT $H_0 = -2.0$

($T = 25.00°$)

Hydroxy ketone	log k, sec.$^{-1}$	Relative rate
I	−3.78	4.8
II	−3.78	4.8
III	−2.60	72
IV	−4.40	1.2
V	−4.46	1
VI	−3.06	25

lessened stability for the carbonium ion derived from VI compared to that originating from III. A further decrease in the rate of dehydration may be expected from consideration of the transition state of step 3 of the carbonium ion mechanism. The energy requirements of this step might well be increased in the reaction of VI, for two reasons. Due to electronic effects, the α-proton which is lost in the rate-determining step 3 is abstracted less rapidly in VI than in III[13]; the rate of proton loss is also likely to be reduced by the unfavorable *cis* interactions between a benzene ring and a benzoyl group developing in the transition state. Evidence for the presence of *cis* interactions in the product, β-phenylchalcone, has been obtained both from the ultraviolet spectrum[14] and from the measured basicity[15] of β-phenylchalcone. A similar reduction in rate, a factor of 60, is found in comparing the rates of dehydration of III and IV. Again a necessary *cis* interaction develops at the transition state.

(12) D. P. Evans, *J. Chem. Soc.*, 785 (1936); D. P. Evans and J. J. Gordon, *ibid.*, 1434 (1938).

(13) That the α-proton is less acidic when it is located alpha to a benzoyl group (as in VI) than when it is found alpha to an acetyl group (as in III) is evidenced by the lowered rate of dehydration *via* the enolization mechanism of the hydroxypropixphenone V from that of the corresponding hydroxybutanone I.

(14) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955).

Experimental

β,β-Diphenyl-β-hydroxypropiophenone was prepared by a Grignard reaction of phenylmagnesium bromide on 1,3-diphenyl-1,3-propanedione as described by Vorländer, *et al.*[16]

Kinetic Measurements.—Preparation of optical solutions and spectral measurements were carried out as previously described.[10] All measurements were carried out in a thermostated compartment block. The ultraviolet spectrum of the solution after ten half-lives of reaction corresponded exactly to that of the product, β-phenylchalcone, at the same acid concentration; it was found to remain constant for an additional period of ten half-lives. No competing cleavage reaction was observed.

Acknowledgment.—Grateful acknowledgment is made for partial support of this work by a grant from the Petroleum Research Fund administered by the American Chemical Society, and for a grant from the National Science Foundation (G-13125).

(15) D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

(16) D. Vorländer, J. Osterburg, and O. Meye, *Ber.*, **56**, 1138 (1923).

Transmission of Electronic Effects by the Acetylenic Group. Rates of Alkaline Hydrolysis of *m*- and *p*-Substituted Ethyl Phenylpropiolates

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Several pieces of evidence suggest that the acetylenic unit (−C≡C−) is a poorer transmittor of electronic effects than the *trans* ethylenic group (H>C=C<H). Resonance effects on the heats of hydrogenation of substituted acetylenes are slightly smaller than those in olefin hydrogenation,[22] thus suggesting that π bond interactions involving sp hybridized carbon are weaker than those of sp^2 carbon under these conditions. Similarly, ionization constants of 3-substituted propiolic acids,[26] rates of hydrolysis of the corresponding ethyl esters,[26] dipole moment measurements on substituted acetylenes,[26] and estimates of polarizibility[3] all confirm the same conclusion. Hammett ρ values of 0.41[4] and 0.69[5] have been reported for the ionization of phenylpropiolic acids in 50% ethanol. The value of 0.466 has been given for the ionization of cinnamic acids in water,[6] but this value is probably increased by 40–60% by a change to 50% ethanol (*cf.* benzoic acids[6]), and any comparison is equivocal. One definite anomaly is the reported[4] value of 1.91 for the saponification of a series of ethyl phenylpropiolates, which is nearly 50%

(1) Present address: Chemistry Department, University of Houston, Houston 4, Tex.

(2)(a) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1608 (1959); (b) M. Charton, *J. Org. Chem.*, **26**, 735 (1961).

(3) H. Sinn, *Z. Elektrochem.*, **61**, 989 (1961); J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **57**, 3454 (1953).

(4) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(5) I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958).

(6) H. H. Jaffé, *Chem. Rev.*, **73**, 191 (1953).

larger than the corresponding value of 1.314[7] for cinnamate hydrolysis in the same solvent, 87.8% ethanol. This difference, only a small part of which can be due to the different temperatures (20° *vs.* 30°) of the two studies, has been attributed[4,8] to an especially large "field effect" through the linear system. There then remains an uncertainty as to which systems may reasonably be expected to show this large effect.

It is surprising that phenylpropiolic acid and ester series do not show abnormal σ-values. If, in fact, transmission of electronic effects from the phenyl ring to the functional group is largely a "field" or inductive effect, this should be reflected in σ-values which approach Taft's σ^0 based on benzene derivatives having nonconjugated side-chain functional groups.[9] This does not appear to be true in the preceding cases, nor in the shielding of acetylenic protons in the phenylacetylenes.[10] Rates of alkaline hydrolysis of the ethyl phenylpropiolates have, therefore, been redetermined on a more extensive series than previously studied.[4] A lower temperature (10°) and greater dilution have been used to permit more accurate determination of these fast rates (Table I).

TABLE I

RATES OF ALKALINE HYDROLYSIS OF ETHYL PHENYLPROPIOLATES[a] IN 87.8% ETHANOL AT 10°

Substituent	$k \times 10^2$ l. mole^{-1} sec.$^{-1}$
p-CH_3	1.19
H	1.61
p-F	2.08[b]
p-Cl	3.13
m-Cl	4.48
p-NO_2	12.0

[a] Prepared by the methods of M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955). Initial [KOH] = 0.02 *M*, [RCOOEt] = 0.012 *M*. The kinetic method is that reported in ref. 7. [b] *Anal.* Calcd. for $C_{11}H_9O_2F$: C, 68.74; H, 4.72. Found: C, 69.02; H, 4.90.

About 20% of the *p*-nitro ester is diverted to an ester of much lower reactivity, probably the ethoxycinnamate. Nevertheless, it has been possible to obtain consistent rate constants corresponding with more than 90% of the desired reaction. *The value of ρ is 1.10.* Five of the points (excepting H) of the plot of log *k vs.* ordinary σ-values fall on a straight line with such precision that no deviation is detectable graphically. The unsubstituted compound falls slightly off this line. All points have been weighed equally in determining ρ; the average deviation from the best line is about 0.01 σ-unit. Making use of σ-values derived from the saponification of ethyl cinnamates in 87.8% ethanol[11] the average deviation in σ is only 0.005 unit, which indicates a close correspondence of the resonance-inductive balance in the two systems. While it would have been desirable to include additional compounds having "reliable" *meta* substituents[12] in this study, it was not found possible to obtain by published procedures samples of sufficient homogeneity to increase confidence in the determined value of ρ.

(7) J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961).
(8) R. E. Dessy and J.-Y. Kim, *J. Am. Chem. Soc.*, **83**, 1167 (1961).
(9) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).
(10) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963).
(11) K. Kindler, *Ber.*, **69**, 2792 (1936).
(12) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

The earlier value of ρ for ethyl phenylpropiolate saponification, based on four points fitting with rather poor precision, appears to be in error.[13] *There is now no substantiated case in which the acetylenic unit transmits electronic effects better than, or, as well as, a trans ethylenic unit.*

Acknowledgment.—The author wishes to thank Dr. Jordan J. Bloomfield and Mr. Scott Cohen for furnishing several of the compounds.

(13) The new value of ρ appears to give a much improved fit of Miller's ρ–ρ relationship. (S. I. Miller, unpublished studies.)

Investigations in Heterocycles. XIV. 2- and 3-Azaoctahydroindolo[2,3*a*]quinolizines[1]

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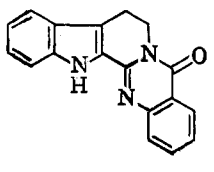
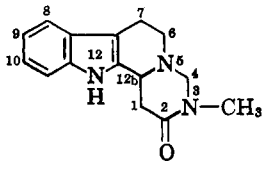
In a recent report[2] from our Laboratory, there was outlined the synthesis of a variety of tetracyclic and pentacyclic indolo[2,3*a*]quinolizines related to naturally occurring substances. It was of particular interest to prepare tetracyclic indolo[2,3*a*]quinolizines containing a nitrogen atom in ring E, compounds bearing a formal resemblance to Rutecarpine (I). Thus, as previously described,[2] II was converted to its N-methyl amide III which was allowed to react with formaldehyde in refluxing ethyl alcohol with a trace of alkaline catalyst to afford 3-methyl-3-aza-1,2,3,4-6,7,12,12b-octahydro-2-oxoindolo[2,3*a*] quinolizine (IV). It was also pointed out at the time that condensation of III with a variety of aromatic aldehydes yielded the corresponding 4-aryl derivatives of IV.



I



IV

It appeared now that a further extension to modifications of IV would be (a) the preparation of similar tetracyclic indoles with a keto group in position 4 and substituents other than a methyl group at the 3-aza position, and (b) the preparation of a 2-azaoctahydroindolo[2,3*a*]quinolizine. The synthesis of some of these compounds, as outlined in Scheme I, serves as the subject of this note.

Compound II proved very useful in these studies, since it readily underwent condensation with alkyl and aryl isocyanates in cyclohexane to form the corresponding urea derivatives which were converted to the 2,4-dioxo-3-substituted 3-azaoctahydroindolo[2,3*a*]quinolizine in refluxing ethyl alcohol containing small amounts

(1) This subject was discussed in part by G. deS. in a Symposium Lecture on the Chemistry of Nitrogen Heterocycles sponsored by the Medicinal Chemistry Division of the 141st National Meeting of the American Chemical Society, Washington, D. C., March 27, 1962.
(2) G. deStevens, H. Lukaszewski, M. Sklar, A. Halamandaris, and H. M Blatter, *J. Org. Chem.*, **25**, 2457 (1962).