from the alkali-insoluble part. It gave m.p. 95–97° on recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.66; H, 5.83.

A compound, m.p. 125–127°, was isolated from the alkali-soluble part.

Anal. Calcd. for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 60.09; H, 4.45.

The Mechanism of Dehydration of β,β-Diphenyl-β-hydroxypropiophenone[1]

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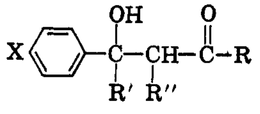
It previously has been demonstrated[3] that, depending on structure, two different mechanisms are available for the dehydration of β-hydroxy ketones. Thus, 4-phenyl-4-hydroxy-2-butanone (I),[3] 4-(*p*-nitrophenyl)-4-hydroxy-2-butanone (II)[3] and β-phenyl-β-hydroxypropiophenone (V)[4] undergo dehydration *via* a mechanism involving a rate-determining enolization step, while 4-(*p*-methoxyphenyl)-4-hydroxy-2-butanone (III)[3] and 4-(*p*-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone (IV)[5] dehydrate *via* a carbonium ion mechanism. The change in mechanism is manifested by a different dependence of the rate on the acidity function H_0 (the carbonium ion mechanism is characterized by linear correlation with H_0 with slope greater than unity) and by different entropies of activation (the carbonium ion mechanism has a less negative entropy by a magnitude corresponding to the absence of involvement of water in the transition state).



I, R = CH_3 R′ = H; R″ = H; X = H
II, R = CH_3 R′ = H; R″ = H; X = NO_2
III, R = CH_3 R′ = H; R″ = H; X = OCH_3
IV, R = CH; R′ = H; R″ = CH_3; X = OCH_3
V, R = C_6H_5; R′ = H; R″ = H; X = H
VI, R = C_6H_5; R′ = C_6H_5; R″ = H; X = H

It was of interest to study the effect that the introduction of a phenyl substituent on the β-position of V would have on the mechanism of the dehydration reaction. The stability of the 1,1-diphenylethyl cation is quite similar to that of the (*p*-methoxyphenyl)ethyl carbonium ion, as estimated from solvolytic data.[6] From the published results of Deno and co-workers[7-9] on arylcarbonium ion equilibria, it is evident that the two carbonium ions are formed, to the extent of 50% from their corresponding alcohols, at 72% and 65% sulfuric acid, respectively. On the basis of these stability estimates for the carbonium ions derived from III and VI, it was expected that the dehydration mechanism would change from the enolization mechanism found in V to a carbonium ion mechanism for β,β-diphenyl-β-hydroxypropiophenone (VI). We have, in fact, found this to be the case.

Rates of dehydration for VI were measured under conditions similar to those used previously. In order to facilitate solubility of VI in the reaction medium, we used a 5% dioxane–95% aqueous sulfuric acid medium. This solvent system has been shown[10] to be useful for H_0 comparisons, and the H_0 scale established in it. Even so it was necessary to carry out measurements with extremely dilute solutions of VI (about 10^{-6} *M*) using 10-cm. cells.

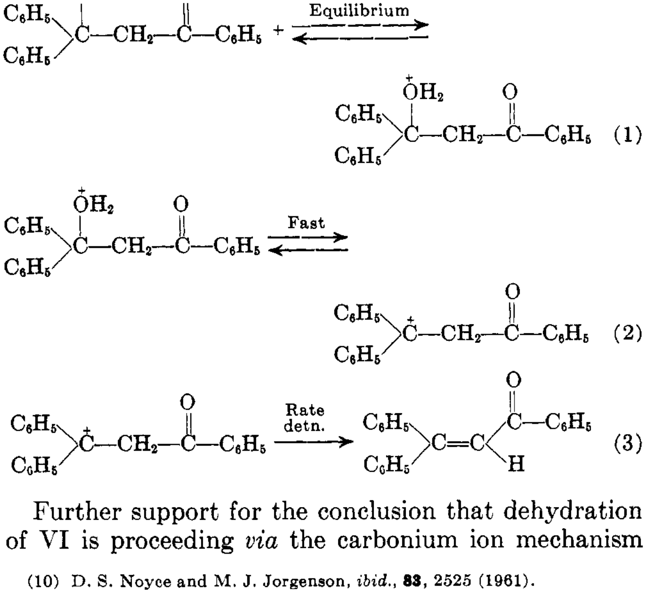
TABLE I

RATE OF DEHYDRATION OF β,β-DIPHENYL-β-HYDROXYPROPIOPHENONE in 5% DIOXANE–95% AQUEOUS SULFURIC ACID

H_2SO_4, *M*	H_0	k, sec.$^{-1}$	log *k* + H
		(T = 25.00°)	
1.42	−0.45	1.54×10^{-1}	−5.26
2.56	−1.04	6.20×10^{-1}	−5.25
2.87[a]	−1.15	$8.50 \pm 0.10 \times 10^{-2}$[b]	−5.22
3.35	−1.42	1.80×10^{-4}	−5.17
3.94	−1.71	4.12×10^{-4}	−5.10
4.26	−1.87	7.0×10^{-4}	−5.03
4.84	−2.13	1.05×10^{-3}	−5.11
		(T = 45.00°)	
2.87[a]	−1.15	8.60×10^{-4}	

[a] $\Delta H^* = 21.2$ kcal.; $\Delta S^* = -10.9$ e.u. [b] Average of two runs.

The measured rates (Table I) show smooth correlation with the acidity function, the slope of log *k vs.* H_0 being 1.15. From the temperature coefficient of the rate the entropy of activation (at H_0 = 0) was determined. The value, −11, is similar to that obtained for other dehydration reactions proceeding *via* a carbonium ion mechanism.[3,11] These two facts provide a sound basis for suggesting that β,β-diphenyl-β-hydroxypropiophenone undergoes dehydration *via* the carbonium ion mechanism, namely, equations 1–3.



Further support for the conclusion that dehydration of VI is proceeding *via* the carbonium ion mechanism

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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 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.

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

Experimental

β,β-Diphenyl-β-hydroxypropiophenone was prepared by a Grignard reaction of phenylmagnesium bromide on 1,3-dipheny-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.

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(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.

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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 $(-C\equiv C-)$ 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%

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

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