with the alkene functionality also has a stabilizing effect (by about 2.4 kcal mol^{-1})[14] and it may be that the stabilization energies cited for mono-, di-, and trisubstituted alkenes are larger than the comparable values for 3-alkenones; however, it does not seem likely that the order would change. Secondly, β-methylation will stabilize the protonated 3-alkenone, particularly by increasing the contribution of resonance structure III, Scheme II. Since *both* the 3-alkenone and protonated 3-alkenone are stabilized by β-methylation, only a *difference* in the extent of stabilization will affect pK_a. Assuming that all the pK_a differences result from such a stabilization produces a net stabilization energy of the protonated 3-alkenones over the unprotonated of 0.7 and 1.4 kcal mol^{-1} on mono- and dimethylation, respectively. That is, the protonated–unprotonated energy difference for 4-methyl-3-penten-2-one is 0.7 kcal mol^{-1} less than that for 3-penten-2-one, which is 1.4 kcal mol^{-1} less than that for 3-buten-2-one. In general, then, protonated 3-alkenones are stabilized more than half again as much as unprotonated 3-alkenones on successive β-methylations.

It is tempting to invoke large solvation effects since a_W decreases from 0.5 to 10^{-3} over the range of acidity studied;[15] however, it must be remembered that plots of log [BH$^+$]/[B] vs. $-H_A$ were linear and of slope 1.0. This requires that medium effects (including solvation) on f_B/f_{BH^+} ratios be similar for protonation of amides and 3-alkenones. Thus the use of the acidity function method has precluded a discussion of solvation effects on pK_a values.

Finally, the effect of α-methylation is diminishingly small; but provided that the differences in Table I are real, they are in a reasonable direction. It appears that α-methylation decreases the acidity by about 0.1 pK_a unit. In view of the substituent effects discussed above and Scheme II, this 0.1 pK_a difference means that α-methylation stabilizes a 3-alkenone just slightly more than a protonated 3-alkenone. This is consistent with a significant but not predominant contribution of resonance structure III in Scheme II.

Conclusions

Protonation of acyclic α,β-unsaturated ketones in aqueous H_2SO_4 and $HClO_4$ follows the acidity function based on amide protonation, H_A, through 75% (12 M) H_2SO_4; plots of log [BH$^+$]/[B] vs. $-H_A$ produce straight lines of slope 1.0. This behavior differs from the protonation of benzophenones (H_B) or ethyl acetate (H_E) because of the way the changing nature of the conjugate acid resonance hybrid interacts with the changing medium.

Substitution of one methyl group for a hydrogen on the β carbon of the α,β-unsaturated carbonyl system increases pK_a by 1 unit; thus the conjugate acid of 3-buten-2-one has pK_a = −4.8, and the conjugate acid of 3-penten-2-one has pK_a = −3.8. 4-Methyl-3-penten-2-one is a remarkably basic ketone, being 10% protonated in 4.5 M (35%) $HClO_4$, pK_a = −2.9. The stabilization energies due to successive β-methyl substitution on the conjugate acids of homologues of 3-buten-2-one are estimated to be 1.4–3.9 and 0.7–1.7 kcal mol^{-1}. β-Methylation stabilizes the protonated 3-alkenones over the unprotonated by 1.4 and 0.7 kcal mol^{-1} for 3-buten-2-one/3-penten-2-one and 3-penten-2-one/4-methyl-3-penten-2-one, respectively.

Substitution of a methyl group for a hydrogen on the α carbon of the α,β-unsaturated carbonyl system has a barely discernible base-strengthening effect (0.2 pK_a unit).

α,β-Unsaturated ketones are remarkably basic, particularly when β-substituted; protonation is adequately described by the acidity function H_A.

Experimental Section

The compounds studied were purchased from Aldrich Chemical Co. and were purified by molecular distillation just prior to use. Ultraviolet spectra were obtained using a Cary Model 14 recording spectrophotometer. The general procedures used in determining pK_{BH^+} from the change in ultraviolet spectrum with changing acid concentration were similar to those used by us in a previous study of Hammett indicators.[7] The shift in λ_{max} on protonation of B to form BH$^+$ was 30–40 nm. At intermediate acidities where both B and BH$^+$ should be present, the characteristic "double humped" curve was observed. Solutions of BH$^+$ generated B quantitatively upon dilution. The general eq 1 was used to calculate [BH$^+$]/[B] whenever ϵ_B or ϵ_{BH^+} could be ignored relative to ϵ_e (cf. Table I).

$$\frac{[BH^+]}{[B]} = \frac{\epsilon_e - \epsilon_B}{\epsilon_{BH^+} - \epsilon_e} \qquad (1)$$

Values in brackets are molarities, ϵ represents molar absorptivity (e.g., ϵ_e is the molar absorptivity of an equilibrium mixture of B and BH$^+$ of comparable concentrations), and all values of ϵ are at the same wavelength.

Acknowledgments. Financial support from the Long Beach Heart Association and the California State University Long Beach Research Foundation is gratefully acknowledged.

Registry No.—3-Buten-2-one, 78-94-4; 3-methyl-3-buten-2-one, 814-78-8; 3-penten-2-one, 625-33-2; 3-methyl-3-penten-2-one, 565-62-8; 4-methyl-3-penten-2-one, 141-79-7.

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Medium Basicity Effects on the Transition State Structure of E2 Reactions. Kinetic Study of the Reaction of 1-Chloro-1-phenyl-2-arylethanes with Crown Ether Complexed Potassium *tert*-Butoxide in *tert*-Butyl Alcohol

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Received November 23, 1976

Lately[1] we have kinetically investigated the elimination reaction of 2-arylethyl bromides promoted by crown ether complexed *t*-BuOK in *t*-BuOH, and obtained data concerning the effect of base association on the transition state structure of this reaction.

Among others, two main observations have been made: (1) the reaction with complexed *t*-BuOK has an order in base significantly larger than one, (2) the transition state structure

Table I. Kinetic Data for the Elimination Reactions of 1-Phenyl-1-chloro-2-arylethanes Promoted by *t*-BuOK in *t*-BuOH in the Absence and in the Presence of 18-Crown-6 Ether at 30 °C

Registry no.	Substrate[a]	[*t*-BuOK], M	[18C6], M	k_1, s^{-1}	k_2, $M^{-1} s^{-1}$
4714-14-1	H	0.492		1.41×10^{-4}	2.86×10^{-4}
	H	0.665		2.00×10^{-4}	3.01×10^{-4}
22692-62-2	p-CH_3	0.501		6.56×10^{-5}	1.31×10^{-4}
	p-CH_3	0.665		8.78×10^{-5}	1.32×10^{-4}
4714-17-4	p-Cl	0.492		2.58×10^{-4}	5.23×10^{-4}
	p-Cl	0.665		3.49×10^{-4}	5.25×10^{-4}
4781-42-4	p-NO_2	0.095		1.71×10^{-2}	1.80×10^{-1}
	p-NO_2	0.376		6.53×10^{-2}	1.74×10^{-1}
	H	0.0105	0.0210	3.77×10^{-4}	0.0359
	p-CH_3	0.0105	0.0210	1.60×10^{-4}	0.0153
	p-Cl	0.0105	0.0210	3.83×10^{-3}	0.364
	p-NO_2	0.0105	0.0210	10.66	1016
	H	0.0442	0.0895	3.41×10^{-3}	0.0771
	p-CH_3	0.0442	0.0895	1.38×10^{-3}	0.0312
	p-Cl	0.0442	0.0895	3.37×10^{-2}	0.761
	H	0.0450	0.0905	3.96×10^{-3}	0.0880
	p-CH_3	0.0450	0.0905	1.51×10^{-3}	0.0337
	p-Cl	0.0450	0.0905	3.97×10^{-2}	0.883
	H	0.105	0.210	1.44×10^{-2}	0.137
	p-CH_3	0.105	0.210	5.85×10^{-3}	0.0557
	p-Cl	0.105	0.210	0.159	1.51

[a] H refers to 1-chloro-1,2-diphenylethane.

appears almost completely unaffected by the base association, the reaction with complexed *t*-BuOK exhibiting values of ρ, deuterium kinetic isotope effect, and leaving group effect very similar to those of the corresponding reaction carried out in the absence of crown ether.

In consideration of the interest of these results it seemed useful to obtain information on their degree of generality by studying a different series of substrates. In this note we report a kinetic study of the elimination from 1-chloro-1-phenyl-2-arylethanes promoted by *t*-BuOK and 18-crown-6 ether complexed *t*-BuOK in *t*-BuOH.

Results and Discussion

The reactions were followed by determining the formed *trans*-stilbene or substituted *trans*-stilbene spectrophotometrically, either in the presence or in the absence of 18-crown-6 ether (18C6). A stopped-flow spectrophotometer was used in the case of the reaction of 1-phenyl-1-chloro-2-*p*-nitrophenylethane with complexed *t*-BuOK. In each case, the UV spectrum, at infinity time, indicated a quantitative yield of olefin.

The concentration of *t*-BuOK was in the range 0.09–0.66 M in the experiments carried out without 18C6 and in the range 0.01–0.1 M when the crown ether was present. The base concentration was always in large excess with respect to that of the substrate (ca. 10^{-5} M) and first-order plots exhibited a satisfactory linearity. First-order and second-order rate constants (k_1 and k_2, respectively) are reported in Table I.

Also with this series of substrates the reaction with complexed *t*-BuOK exhibits an apparent order in base significantly larger than one. Accordingly, the data in Table I show that the k_2 values for eliminations carried out in the presence of 18C6 significantly increase by increasing base concentration. In contrast, no significant dependence on the base concentration is shown by the k_2 values for the reaction promoted by *t*-BuOK in the absence of 18C6. The apparent order in base for the reaction with complexed *t*-BuOK is ca. 1.5, a value very similar to that (1.4) determined for the reaction of 2-arylethyl bromides.[1] Thus, the peculiar kinetic aspect of eliminations promoted by crown ether complexed *t*-BuOK is fully confirmed.[2] Completely at variance with that observed in the reaction of 2-arylethyl bromides are, instead, the results concerning the effect of base association on the transition state structure, a very significant effect being observed in the eliminations from 1-chloro-1-phenyl-2-arylethanes. Accordingly, the Hammett reaction constant, ρ, is +2.20 (r = 0.996, S = 0.15) in the reaction promoted by *t*-BuOK in *t*-BuOH, and +3.40 (r = 0.999, S = 0.13) when the base is complexed *t*-BuOK. The latter value is evaluated using kinetic data obtained at the same base concentration (0.0105 M).[3,4] Thus, in going from associated to dissociated *t*-BuOK the elimination from 1-chloro-1-phenyl-2-arylethanes, unlike that from 2-arylethyl bromides, exhibits a substantial increase in the carbanion character of the transition state. A similar result has been recently found in the syn elimination from *trans*-2-arylcyclopentyl tosylates.[5] However, we feel that a syn mechanism of elimination is highly unlikely in our reaction, especially in the presence of a crown ether.

To explain the finding that the transition state of the eliminations from 2-arylethyl bromides promoted by *t*-BuOK is not significantly influenced by the medium basicity, it was suggested that in the transition state the base (whatever its state of association) is always the same species, partially neutralized *tert*-butoxide anion.[1,6] Clearly, the present results cast a serious doubt on the general validity of this suggestion.

According to recent work[7] it seems now well established that, in E2 reactions, structural changes can influence both the parallel and perpendicular modes of vibration of the transition state. In particular, the effects of structural changes which stabilize products or reactants are mainly felt along the parallel mode of vibration of the transition state (parallel effects) and lead to a transition state more "reactant-like" or "product-like", respectively. On the other hand, effects increasing the stability of the carbanion or the carbocation, which would be formed if the reaction were stepwise, manifest itself mainly along the perpendicular mode of vibration of the transition state (perpendicular effects) and make the transition state more "carbanion-like" or more "carbocation-like", respectively. When both parallel and perpendicular effects have to be taken into account it is very difficult to determine which effect will be the dominating one and, consequently, to predict the changes in the transition state geometry. However, it has been recently suggested that perpendicular effects should prevail for "reactant-like" or "product-like" transition states whereas parallel effects should predominate when the transition state is "carbanion-like" or "carbocation-like".[7c]

In going from associated to dissociated *t*-BuOK there is a significant increase[8] in medium basicity and this structural change should favor both the product and the carbanion.[7b] Therefore, both parallel and perpendicular effects may play a role in determining the sensitivity of the transition state structure to changes in medium basicity. On this basis, the different behaviors of the reactions of 2-arylethyl bromides and 1-chloro-1-phenyl-2-arylethanes could be tentatively explained by suggesting a more "reactant-like" transition state for the latter reaction, owing to the much larger stability of the formed olefin,[9] and, consequently, a greater importance of the perpendicular effects. Thus, an increase in the medium basicity could increase the carbanion character of the transition state in the case of the eliminations from 1-chloro-1-phenyl-2-arylethanes and have practically no effect in the case of the eliminations from 2-arylethyl bromides.

Whatever the correct explanation, the present results clearly support the suggestion[7c,d] that the sensitivity of the transition state of an E2 reaction to structural changes can depend on the character of the transition state itself and its position in More O'Ferrall's potential energy diagram.[7b] It appears therefore particularly dangerous to draw general conclusions concerning this problem from the results of only one series of substrates.

The comparison of the data reported here with the corresponding ones relative to the reaction of 2-phenylethyl chloride[1] allow us to evaluate the kinetic effect of an α-phenyl group in these eliminations. It is interesting to note that the introduction of an α-phenyl group produces a significant rate-retarding effect (ca. two-fold, after consideration of the statistical factor[10]) in the reaction promoted by complexed *t*-BuOK, whereas no kinetic effect is found in the reaction carried out in the presence of crown ether. These findings compare with the six-fold accelerating effect observed (at 50°C) in the eliminations promoted by EtONa in EtOH.[11]

Experimental Section

Materials. 1-Chloro-1-phenyl-2-arylethanes were available from a previous study.[11]

18-Crown-6 ether (18C6) was a commercial product (Fluka) purified by crystallization from *n*-hexane, mp 38.5–39.5 °C (lit.[12] mp 39.5–40.5 °C).

Base–Solvent Solution. *tert*-Butyl alcohol was distilled after treatment with potassium metal. Solution of alkoxide was obtained by reaction, under nitrogen, of freshly cut potassium with *tert*-butyl alcohol.

Kinetic Studies. For all compounds but 1-chloro-1-phenyl-2-*p*-nitrophenylethane, kinetics were carried out in a stoppered two-limb silica cell, either in the presence or in the absence of 18C6. In one limb was placed the substrate solution (1 mL) and in the other the base solution (1 mL). The cell was placed in the thermostated compartment of a Beckman DB-GT spectrophotometer. After ca. 0.5 h the solutions were mixed thoroughly and the cell was rapidly placed again in the compartment of the spectrophotometer. Absorbances were measured at the following wavelengths (nm): 298 for *trans*-stilbene; 299 for *p*-chloro-*trans*-stilbene; 298 for *p*-methyl-*trans*-stilbene; and 348 for *p*-nitro-*trans*-stilbene.

In the experiments with complexed base the reference cell contained a solution of potassium *tert*-butoxide and 18C6 in *tert*-butyl alcohol at the same concentration used in the kinetic run, to compensate for the significant absorption by complexed *t*-BuOK. At the wavelengths used for measurements in this study, the compensation was effective in the range 0.01–0.1 M of *t*-BuOK–18C6 concentration.

The elimination from 1-chloro-1-phenyl-2-*p*-nitrophenylethane, in the presence of 18C6, was followed on a Durrum-Gibson D-110 stopped-flow spectrophotometer.

The yield of olefin was determined from the value of D_∞ (optical density at infinite time) and pseudo-first-order rate constants were determined from the slope of a plot of log $(D_\infty - D_t)$ against time. Second-order rate constants, k_2, were obtained by dividing the first-order rate constants by the base concentration.

Acknowledgment. This work was carried out with the financial support of the Italian National Research Council (C.N.R.).

Registry No.—*trans*-Stilbene, 103-30-0; *p*-chloro-*trans*-stilbene, 1657-50-7; *p*-methyl-*trans*-stilbene, 1860-17-9; *p*-nitro-*trans*-stilbene, 1694-20-8; 18-crown-6 ether, 17455-13-9.

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Acceleration of an Allylic Rearrangement by the Cyclopropyl Substituent. Reaction Conditions to Prevent Ring Opening[1]

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Received July 2, 1976

Although it is well known[2] that the cyclopropyl group has a remarkable ability to stabilize an α positive charge, there are conflicting data in the chemical literature as to whether the cyclopropyl or phenyl substituent is better able to delocalize a positive charge on an adjacent carbon. For example, it has been reported[3] that methyl cyclopropyl ketone is more basic than methyl isopropyl ketone and significantly more basic than acetophenone in H_2SO_4–H_2O or CF_3CO_2H–H_2SO_4 solutions, indicating that the cyclopropyl group is better able to delocalize an adjacent positive charge than is a phenyl group. On the other hand, Olah and White have demonstrated[4] that a phenyl group is considerably more effective than cyclopropyl in stabilizing an α carbonium ion by measuring the ^{13}C NMR chemical shifts of the sp^2 carbon in related cyclopropyl- and phenyl-substituted carbonium ions. This note discusses a series of experiments involving the acid-catalyzed rearrangement of tertiary vinyl carbinols (**2**) in acetic acid that not only demonstrates the remarkable ability of the cyclopropyl substituent to stabilize an adjacent cationic center but also provides some evidence concerning the nature of the reaction intermediate vs. the question of cyclopropane ring opening.

The acid-catalyzed ring opening of cyclopropanoids is a well-known reaction. For example, the Julia synthesis[5] of homoallylic halides is dependent on such cyclopropyl ring cleavage (eq 1). However, as Breslow has noted in his review of rearrangements of small ring compounds,[6] it is possible for