phatic alcohols is a procedure of sufficient utility and generality to be added to those previously available for the reduction of carbonyl groups to methylene groups.

Experimental Section

Materials. $LiEt_3BH$ and $LiEt_3BD$ were purchased as 1 M solutions in THF from Aldrich Chemical Co. Reactant alcohols were either commercially available or prepared by unexceptional procedures. The mesylates were made by a standard literature method;[25] in all cases IR and NMR established the absence of reactant alcohol after the esterification.

General Procedure for Reductions. To a dry, N_2-flushed, round-bottom flask equipped with reflux condenser, magnetic stir bar, and rubber stopple was introduced by syringe x mmol of mesylate and x mL of dry THF. With stirring, $2.1x$ mL of a 1 M $LiEt_3BH$ solution in THF was added in one portion by syringe. The resulting reaction was stirred under N_2 for the time period and at the temperature recorded in Table I for each mesylate. A useful signal of reaction progress was found to be formation of lithium methanesulfonate, which precipitated.

After the reduction period, the vessel was cooled in an ice bath and excess hydride quenched by dropwise addition of water. The organoboranes were oxidized by adding $0.7x$ mL of 3 N NaOH, followed by the slow, dropwise addition of $0.7x$ mL of 30% H_2O_2. The ice bath was removed and the reaction mixture refluxed for 1 h. VPC analyses were measured from the THF layer of the cooled product mixture.[26]

Isolation of products was accomplished by pouring the reaction mixture into $10x$ mL of water, extraction with pentane, washing to remove dissolved THF, drying ($MgSO_4$), and concentration to the crude product by flash distillation. Final purification for structural studies was accomplished using standard preparative VPC techniques.

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Registry No.—Heptane, 142-82-5; neopentane, 463-82-1; *exo*-2-methylnorbornane, 872-78-6; *endo*-2-methylnorbornane, 765-90-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; cyclooctane, 292-64-8; norbornane, 279-23-2; 1,5-diphenylpentane, 1718-50-9.

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(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of New Mexico Research Allocations Committee for the support of this research.
(3) American Chemical Society Petroleum Research Fund Undergraduate Scholar, 1975–1976.
(4) Conventional procedures are compiled in (a) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, New York, N.Y., 1972; (b) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971. More recently developed methods include use of sodium cyanoborohydride or tetrabutylammonium cyanoborohydride,[5] reduction of the tetramethylphosphorodiamidate derivative of the corresponding alcohol,[6] treatment of mesylates or halides with copper hydride reagents,[7] and formation of the tosylhydrazone followed by reduction with catecholborane or other active hydrides.[8]
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(26) Control experiments established the absence of product alkane and internal standard in the lower layer. Internal standards were either introduced at this point or before reduction; no difference in calculated yields was noted.

The Basicity of Enones. Substituent Effects and the Correlation of Protonation with H_A

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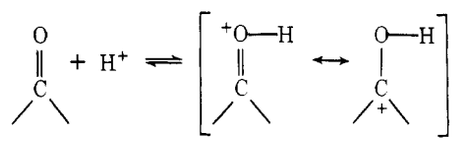
The basicity of carbonyl compounds is of considerable interest since most acid-catalyzed reactions proceed via a preequilibrium protonation of the carbonyl group, followed by some sort of nucleophilic attack.

Scheme I



Arnett has recently reported thermodynamic pK_as for 52 protonated carbonyl compounds, based on heats of ionization in fluorosulfonic acid.[1] Of particular interest to a kinetic study we carried out[2] are the basicities of α,β-unsaturated ketones. These compounds as a class are much more basic than other ketones by 3–5 pK_a units.[1] There have been several recent reports of basicity studies on a series of alicyclic α,β-unsaturated ketones.[3,4] However, the only reported pK_a value for a protonated noncyclic α,β-unsaturated ketone is 2.4 for 4-methyl-3-penten-2-one.[1,5] We wish to report pK_as for several α,β-unsaturated ketones demonstrating a sizable substituent effect on pK_a.

Acidity Dependence. Table I presents pK_a values measured in aqueous $HClO_4$ and H_2SO_4 solutions. Plots of log $[BH^+]/[B]$ vs. $-H_A$ gave straight lines of slope 1.0 for 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one; thus protonation of acyclic α,β-unsaturated ketones follows the acidity function based on amide protonation (H_A)[9] at least through 75% (12 M) H_2SO_4 and 65% (10.5 M) $HClO_4$. This result is consistent with previous studies on cyclopentenones and cyclohexenones.[4]

It is striking that protonation of 3-alkenones follows H_A so closely throughout such a broad range of acidity. This requires that the f_B/f_{BH^+} ratio for the protonation of amides and

Table I. pK_a Values for Protonated 3-Alkenones[a]

Compd	Acid	Method	pK_a
3-Buten-2-one	H_2SO_4	*b*	−4.8
3-Methyl-3-buten-2-one	H_2SO_4	*b*	−4.6
3-Penten-2-one	H_2SO_4	*b*	−3.8
	$HClO_4$	*b*	−3.4
3-Methyl-3-penten-2-one	H_2SO_4	*b*	−3.7
	H_2SO_4	*c*	−3.5
4-Methyl-3-penten-2-one	$HClO_4$	*b*	−2.9
	$HClO_4$	*c*	−2.9
	$HClO_4$	*d*	−2.6

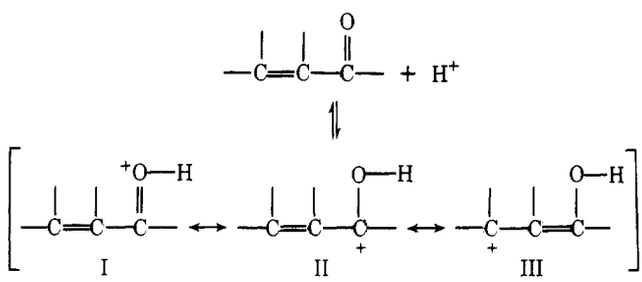
[a] Measured using a standard spectrophotometric method.[7] [b] pK_a was taken as the inflection point on the sigmoidal λ_{max} vs. $-H_A$ plot. [c] pK_a was taken as the point in the log $[BH^+]/[B]$ vs. $-H_A$ line where log $[BH^+]/[B] = 0$. The slope of the line was 1.0. [d] pK_a was calculated by the Bunnett–Olson method.[8]

Table II. Selected Values of H_A, H_E, H_B, and H_0 in H_2SO_4

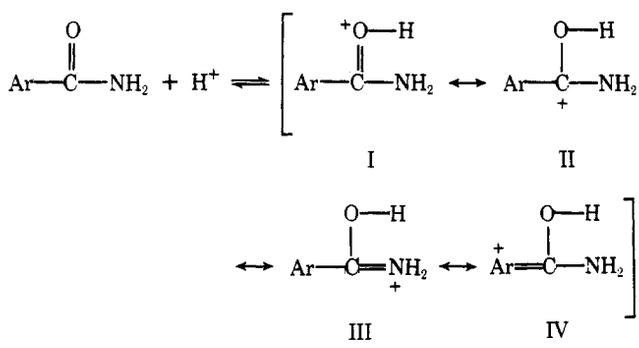
% H_2SO_4	$-H_A$[a]	$-H_E$[b]	$-H_B$[c]	$-H_0$[d]
40	2.00		2.44	2.41
50	2.51		3.49	3.38
60	3.07	2.2	4.46	4.46
70	3.77	2.8	5.38	5.80
80	4.59	3.5	6.35	7.34

[a] Reference 9. The amide protonation scale is anchored by the overlap method to 4-nitroaniline. [b] Reference 11. The ester protonation scale is based on the protonation of ethyl acetate. pK_{BH^+} for ethyl acetate was taken as −3.45 (obtained via Bunnett–Olson calculation). [c] Reference 10. The benzophenone protonation scale is anchored by the overlap method to H_0 scale[16] below 60% H_2SO_4. [d] Reference 12. Primary aniline protonation scale.

Scheme II



Scheme III



$$-H_A = \log a_{H^+} f_B / f_{BH^+}$$

α,β-unsaturated ketones be similarly affected by changes in medium (changes in solvation). This is a rather surprising result, since it would appear that protonation of 3-alkenones is more similar to protonation of benzophenones (H_B)[10] than to amide (H_A)[9] or ester (H_E)[11] protonation. Table II compiles values of these acidity functions over the range of 40–80% H_2SO_4; clearly $d(-H_A)/d(\%\ H_2SO_4) \simeq d(-H_E)/d(\%\ H_2SO_4) < d(-H_B)/d(\%\ H_2SO_4) < d(-H_0)/d(\%\ H_2SO_4)$. Thus it is certain that protonation of α,β-unsaturated ketones follows H_A and perhaps H_E, but not H_B or H_0.

It is interesting to note that the main difference between the H_A and H_E functions is the value at a given acidity *rather* than a difference in medium dependence. For example, if H_E had been anchored to the H_A scale at 60% H_2SO_4, $H_E = 4.4$ in 80% H_2SO_4 compared with $H_A = 4.6$ [i.e., $d(H_E)/d(\%\ H_2SO_4) = 0.9\ d(H_A)/d(\%\ H_2SO_4)$]. It is also interesting that Bunnett–Olson calculations for 3-alkenone protonation produce a pK_a value 0.3 pK_a units less than values calculated from H_A; this difference is in the same direction as the difference between the H_A and H_E acidity scales, but it is about one-half to one-third the magnitude. Evidently (a) the H_A and H_E scales could be commonly anchored and the differences in the absolute values would diminish,[13] or (b) protonation of 3-alkenones follows an acidity function with a medium dependence equal to that of H_A but of magnitude intermediate to H_E and H_A.

A brief rationale as to why Scheme I follows H_A rather than H_B: for the more basic 3-alkenones (e.g., 4-methyl-3-penten-2-one), canonical form III of Scheme II contributes much more to the hybrid structure than is the case for the less basic 3-alkenones (e.g., 3-buten-2-one). For the more basic benzamides, canonical form IV of Scheme III contributes much more to the hybrid structure than is the case for the less basic benzamides (ones with several nitro substituents in the aryl group). The net effect for both types of compounds is an increasing importance of canonical forms I and II (Schemes II and III) as the basicity diminishes. This trend is less pronounced for the amides than for the benzophenones because of the importance of canonical form III of Scheme III (i.e., the effect of several nitro groups in Ar is less important for benzamides because IV is less important overall). Thus the shallower acidity dependence of Schemes II and III compared with H_B or H_0 is attributable to f_B/f_{BH^+} decreasing for amide, ester, and 3-alkenone carbonyl protonation relative to f_B/f_{BH^+} changes for protonation of benzophenones or primary nitroanilines. This is consistent with the greater solvation of protonated benzamides, esters, and 3-alkenones. It is tempting to ascribe the relatively similar protonation behavior of esters, benzamides, and 3-alkenones to a common importance of canonical forms I and II in Schemes II and III; however, as discussed above in comparing the H_A and H_B functions, the situation is considerably more complex.

Substituent Effects on pK_{BH^+}. Two effects are evident from the pK_a values in Table I. First, methylation β to the carbonyl of an α,β-unsaturated ketone markedly enhances the basicity (e.g., 3-buten-2-one is half protonated in 14.5 M H_2SO_4 whereas 3-penten-2-one is half protonated in 11.5 M H_2SO_4). Second, methylation α to the carbonyl of an α,β-unsaturated ketone has little or no effect on the basicity. These two observations are discussed separately below.

4-Methyl-3-penten-2-one is a remarkably basic ketone: it is about 10% protonated in 4.5 M (35%) $HClO_4$ (cf. H_B, the acidity function based on benzophenone protonation, Table II). This large β-methylation effect is ascribable to a substituent effect. Two factors must be kept in mind: First, methylation of a carbon–carbon double bond stabilizes alkenes; e.g., for several classes of alkenes, trisubstituted are more stable than disubstituted by about 1 kcal mol^{-1}, disubstituted are more stable than monosubstituted by about 2.5 kcal mol^{-1}, and monosubstituted are more stable than ethylene by about 2.5 kcal mol^{-1}.[14] Of course, conjugation of a carbonyl group

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).

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

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.

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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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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