xaoxaeicosane, 56930-39-3; tetraethylene glycol dichloride, 638-56-2; tetraethylene glycol dimercaptan, 2781-02-4.

References and Notes

(1) Presented at the 5th International Congress of Heterocyclic Chemistry, Ljubljana, Yugoslavia, July 13, 1975.

(2) Supported by the National Science Foundation Grant GP 33536-X and National Institutes of Health Grant GM 18811.

(3) J. S. Bradshaw, J. Y. Hui, B. L. Haymore, J. J. Christensen, and R. M. Izatt, *J. Heterocycl. Chem.*, **10**, 1 (1973).

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(10) See for example, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", McGraw-Hill, New York, N.Y., 1968, p 220.

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Loss of Water from Ketones in Isobutane Chemical Ionization Mass Spectrometry

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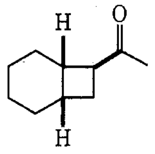
Isobutane CI mass spectra are reported for 38 ketones containing zero, one, or two carbon–carbon double bonds as the only additional functional groups. An enhanced loss of water in these compounds can be correlated with the structural feature that an allylic hydrogen atom be available and able to approach within 2 Å of the carbonyl oxygen. α,β-Unsaturated ketones fail to show enhanced loss of water, even when this feature is present. Experiments with deuterium-labeled ketones demonstrate that scrambling of hydrogen is rapid relative to loss of water.

Earlier examination of the isobutane chemical ionization (CI) mass spectra of the bicyclic ketones **1–6** revealed a noteworthy variation in the intensity of the $(M + 1 - 18)^+$ ions formed on loss of water from the protonated ketone.[1] Significant loss of water occurs only from the unsaturated, endo-substituted ketones **5** and **6**, and we suggested that this result reflected the availability in only these two members of the series of a reactive, allylic hydrogen atom which is accessible to the carbonyl oxygen atom. Through a six-membered (**5**) or seven-membered (**6**) transition state this allylic hydrogen could approach the protonated oxygen atom and be lost subsequently as water. These observations encouraged us to examine the CI mass spectra of a variety of other ketones in order to determine the generality of this process and to study the structural factors influencing it. The results, which are presented in Table I, are discussed below.



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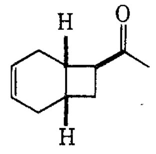

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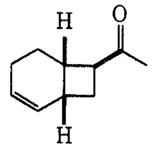

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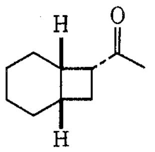

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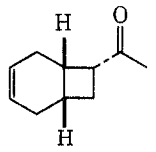

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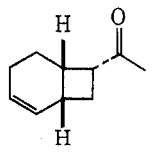


6

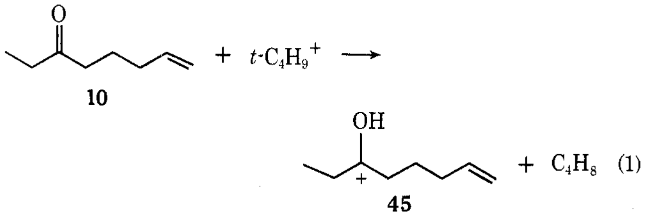
The data in Table I are from the isobutane CI mass spectra of 38 monoketones containing zero, one, or two carbon–carbon double bonds as the only additional functional groups. The results indicate that under these conditions enhanced loss of water can be correlated with three structural requirements. (1) Allylic hydrogens are necessary. Table I contains many pairs of ketones in which the only structural difference involved is the presence or absence of a double bond which provides activation for an appropriately placed (see below) allylic hydrogen. In nearly all cases there is a significant increase in intensity of the $(M + 1 - 18)^+$ ion when allylic hydrogen is present, and many of the ketones lacking the activating double bond show no detectable $(M + 1 - 18)^+$ ion at all.

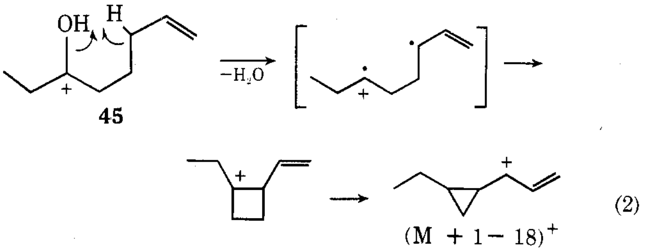
(2) The allylic hydrogen must be geometrically accessible to the carbonyl oxygen atom. Loss of water occurs only in those ketones of Table I in which allylic hydrogen can approach oxygen closer than 2 Å, as measured on Dreiding models.[2] Thus no $(M + 1 - 18)^+$ ion is seen in **25** or **27**, in which the distance from oxygen to the β allylic hydrogen is ~2.3 or ~2.5 Å, respectively. Furthermore, there is a qualitative correlation between the intensity of the $(M + 1 - 18)^+$ ion and the expected facility with which the two centers can be brought together. Loss of water is greatest with γ allylic hydrogen, which requires a sterically and entropically favorable six-membered transition state. A related effect is apparent in ketones involving more distant allylic hydrogen. In both **22** and **40** a δ allylic hydrogen is present, but the $(M + 1 - 18)^+$ ion is nearly eight times as intense in **22**, in which the activating double bond is situated between the reacting centers rather than beyond the hydrogen atom as it is in **40**. This location of the double bond in **22** presumably facilitates formation of the seven-membered transition state by reduction of the available rotational degrees of freedom in the chain. A similar comparison may be made between **24** and **42**, where the allylic hydrogen is in the ϵ position. It is also noteworthy that for allylic hydrogen more distant than γ there is little effect of increasing number of methylene groups between the allylic hydrogen and the carbonyl group (compare **40**, **42**, **44**).

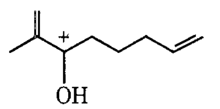
(3) The presence of a double bond conjugated with the carbonyl group prevents loss of water. This is true whether the double bond is involved in or independent of the allylic activation. Thus, while **10** shows a substantial $(M + 1 - 18)^+$ ion, introduction of an α methylene group to form **11** or **12** effectively suppresses this fragmentation. Mesityl oxide (**33**) and phorone (**34**) provide examples in which allylic activation of a favorably situated γ hydrogen is due to the conjugated double bond, but no significant loss of water occurs.

We have also determined the methane CI mass spectra of most of these ketones. Under these more energetic conditions none of the correlations discussed above is applicable. With methane as the ionizing gas compounds having only saturated hydrogen yield an $(M + 1 - 18)^+$ ion, and α,β-unsaturated ketones behave just as saturated or nonconjugated ketones. Thus, while both methane and isobutane CI mass spectra provide examples of extensive loss of water from ketones, only the milder conditions employing isobutane offer discrimination between saturated and unsaturated systems.

The failure of conjugated ketones to show loss of water in their isobutane CI spectra may result from the fact that on protonation they yield resonance-stabilized ions that are somewhat less reactive. This interpretation can be supported by mechanistic and thermochemical considerations. We suggest that the reaction in which water is lost from the ketones may be represented as shown in eq 1 and 2 for **10**. In the case of an α,β-unsaturated ketone the ion produced by the reaction analogous to eq 1 may be represented by **46**, which is protonated **11**, and in which the charge is allylically stabilized. From tabulated values of heats of formation[3] one can show that a secondary allylic ion such as 1-buten-3-yl (**47**) is 19 kcal/mol more stable than a secondary alkyl carbonium ion such as 2-butyl. The difference in energies of **45** and **46** will be similar, although not identical because of the stabilizing effect of the hydroxyl group present in these ions. We suggest that the energy of ions such as **46** is sufficiently low markedly to inhibit their further decomposition as represented in eq 2.







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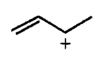
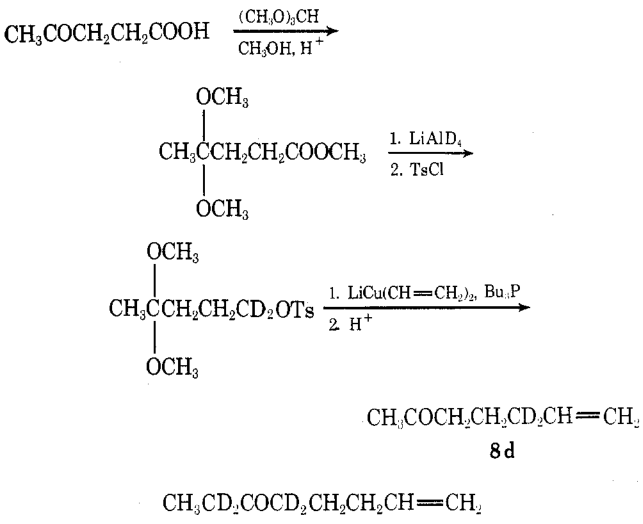


47

The example used in eq 2 permits the formation of an $(M + 1 - 18)^+$ ion wherein stabilization is afforded by both allylic and cyclopropylcarbinyl interaction. For ketones in which the allylic hydrogen is farther removed from the carbonyl group, the cyclic ion analogous to that initially formed in eq 2. will be larger than cyclobutyl, and subsequent reactions of the ions will be different from those represented in eq 2. However, simple mechanisms, generally involving hydride shifts, are available whereby low energy allylic $(M + 1 - 18)^+$ ions may be formed. It should be noted that while these structural requirements suffice to account for nearly all of the results of Table I, there are exceptions. Ketones **36**, **37**, and **38**, all 2-isopropenylcyclohexanones, fail to show significant $(M + 1 - 18)^+$ ions, although by the above criteria they should do so. This structural type appears to involve considerations which are as yet undefined, although one possibility is that the cyclization step (eq 2) here would lead to a strained 1-bicyclo[4.2.0]octyl ion.

Scheme I



$$CH_3COCH_2CH_2COOH \xrightarrow[CH_3OH,\ H^+]{(CH_3O)_3CH} CH_3\overset{OCH_3}{\underset{OCH_3}{C}}CH_2CH_2COOCH_3 \xrightarrow[2.\ TsCl]{1.\ LiAlD_4} CH_3\overset{OCH_3}{\underset{OCH_3}{C}}CH_2CH_2CD_2OTs \xrightarrow[2.\ H^+]{1.\ LiCu(CH{=}CH_2)_2,\ Bu_3P} CH_3COCH_2CH_2CD_2CH{=}CH_2$$

8d

$CH_3CD_2COCD_2CH_2CH_2CH{=}CH_2$

10d

Other mechanisms can be written to account for loss of water in the isobutane CI spectra. For example, initial interaction of the required double bond with the protonated carbonyl group is attractive and has plausible analogy in the nucleophilic attack of an olefin on a carbonium ion, a process well known in solution chemistry. However, adoption of any mechanism involving specific participation of the double bond necessarily implies a different mechanism for loss of water in the methane CI spectra of saturated ketones. In the absence of information distinguishing the isobutane and methane processes mechanistically it seems preferable to write a single mechanism applicable to both.

With an interest in demonstrating directly that allylic hydrogen is lost in formation of the $(M + 1 - 18)^+$ ion, we prepared labeled **8d** from levulinic acid as shown in Scheme I, as well as α-labeled **10d** (84% d_4, 15% d_3) by treatment of **10** with potassium carbonate in ethanol-*O-d* containing deuterium oxide. Isobutane CI mass spectra of **8d** and **10d** showed approximately statistical loss of HOD, indicating that hydrogen scrambling is rapid relative to loss of water. Such rapid hydrogen scrambling prior to fragmentation precludes use of deuterium-labeled species as mechanistic probes.

Experimental Section

Materials and Equipment. Spectra were determined on samples purified by vapor phase chromatography using a Varian Aerograph Model 700 Autoprep or Model A-90-P3 with one of the following columns: A, 25% QF-1, 10 ft; B, 25% QF-1, 20 ft; C, 25% SE-30, 10 ft; D, 10% SE-30, 15 ft; E, 25% Carbowax 1500, 10 ft; F, 25% Carbowax 20M, 10 ft; G, 25% Carbowax 20M, 20 ft; H, 25% DEGS, 20 ft. All columns were prepared using 60–80 Chromosorb W in 0.375 in. aluminum tubing. The column oven was operated at 85–

Table I
Loss of Water from Ketones in Isobutane Chemical Ionization

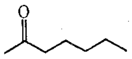
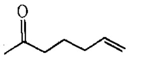
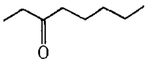
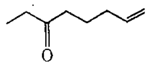
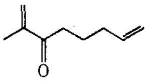
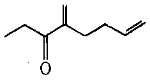
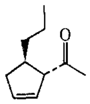
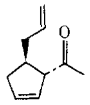
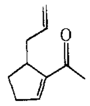
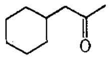
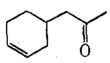
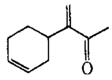
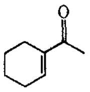
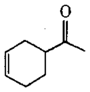
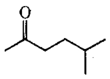
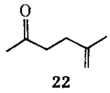
		Rel intensity[a]			
Structure	Mol wt	$(M + 1)^+$	$(M + 1 - 18)^+$	100 × $(M + 1 - 18)^+/(M + 1)^+$	Other major ions (>0.02) present, (rel intensity)[a]
 7	114	0.92			116 (0.065)
 8	112	0.77	0.174	23	114 (0.040)
 9	128	0.88			130 (0.066)
 10	126	0.75	0.13	17	128 (0.057)
 11	138	0.82	0.003	0.4	140 (0.094) 81 (0.025) 71 (0.024)
 12	138	0.79			140 (0.074) 111 (0.078)
 13	152	0.60	0.004	0.7	155 (0.040) 154 (0.089) 152 (0.038) 151 (0.055) 125 (0.021) 109 (0.084)
 14	150	0.55	0.072	13	152 (0.067) 150 (0.024) 133 (0.072) 107 (0.083)
 15	150	0.73	0.003	0.4	152 (0.069) 150 (0.032) 149 (0.057) 109 (0.033)
 16	140	0.87			142 (0.075)
 17	138	0.51	0.20	39	153 (0.046) 140 (0.046) 81 (0.032) 80 (0.038) 71 (0.027)
 18	152	0.88	0.004	0.4	152 (0.074)
 19	124	0.85			126 (0.062) 124 (0.029)
 20	124	0.79			126 (0.074) 124 (0.040) 81 (0.026) 71 (0.028)
 21	114	0.88	0.007	0.8	116 (0.059)
 22	112	0.61	0.23	37	114 (0.039) 112 (0.020) 95 (0.23)

Table I
(*Continued*)

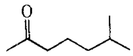
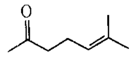
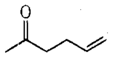
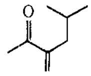
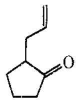
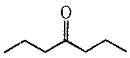
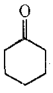
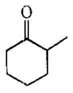
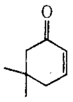
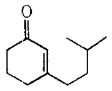
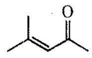
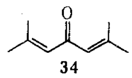
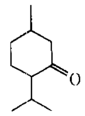
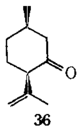
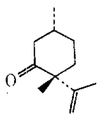
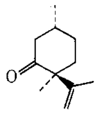
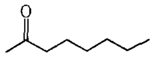
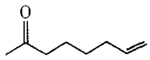
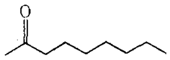
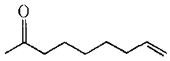
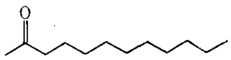
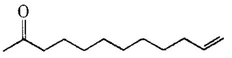
Structure	Mol wt	Rel intensity[a]		100 × $(M + 1 - 18)^+/(M + 1)^+$	Other major ions (>0.02) present, (rel intensity)[a]
		$(M + 1)^+$	$(M + 1 - 18)^+$		
 23	128	0.80	0.05	5.7	130 (0.065) 111 (0.046) 85 (0.026) 71 (0.041)
 24	126	0.64	0.21	33	128 (0.052) 126 (0.020) 108 (0.022) 71 (0.020) 69 (0.022)
 25	98	0.95			100 (0.045)
 26	126	0.88			128 (0.071) 126 (0.024)
 27	124	0.81			126 (0.073) 124 (0.029) 81 (0.025)
 28	114	0.88			116 (0.056) 71 (0.026)
 29	98	0.90	0.012	1.3	100 (0.059)
 30	112	0.88	0.003	0.3	114 (0.068) 112 (0.026)
 31	124	0.85			126 (0.079) 71 (0.025)
 32	166	0.82			168 (0.096) 71 (0.022)
 33	98	0.79	0.012	1.5	100 (0.047) 98 (0.036) 85 (0.022) 83 (0.028) 71 (0.027)
 34	138	0.72			140 (0.053) 83 (0.20)
 35	154	0.70	0.026	3.7	156 (0.078) 154 (0.027) 112 (0.033) 81 (0.020)
 36	152	0.73	0.004	0.5	154 (0.077) 152 (0.041) 81 (0.022)
 37	166	0.57			181 (0.10) 169 (0.024) 168 (0.077) 166 (0.028) 139 (0.051) 83 (0.024) 81 (0.020)

Table I
(Continued)

Structure	Mol wt	Rel intensity[a] (M + 1)$^+$	Rel intensity[a] (M + 1 − 18)$^+$	100 × (M + 1 − 18)$^+$/(M + 1)$^+$	Other major ions (>0.02) present, (rel intensity)[a]
 38	166	0.62			168 (0.063) 166 (0.029) 153 (0.070) 139 (0.033) 83 (0.020)
 39	128	0.93			130 (0.059)
 40	126	0.89	0.042	4.7	128 (0.059)
 41	142	0.92			144 (0.070)
 42	140	0.87	0.040	4.6	142 (0.064) 123 (0.040) 81 (0.022)
 43	184	0.81			186 (0.097) 85 (0.026) 71 (0.020)
 44	182	0.83	0.056	6.8	184 (0.078)

[a] Average of two scans.

200°, and helium carrier gas flow rate was 100–150 ml/min. Unless otherwise noted, ir and NMR spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237B spectrophotometer and the latter on a Varian HR-200 (220 MHz) spectrometer. Solutions were dried over Na_2SO_4; melting points are corrected; boiling points are uncorrected. Mass spectra were obtained with a Du Pont 21-492 *mass spectrometer at resolution* 1000, source temperature 200°C, and 200 eV ionizing voltage. Samples were introduced via a glass batch inlet system at 200°C. Isobutane and methane reactants were Matheson Instrument Grade gas. The repellers were used to optimize the ion current, and were typically maintained at zero voltage. The pressure of the source could not be measured, but was about 0.5–1.0 Torr based on prior experience. The intensities reported have not been corrected for ^{13}C isotope contributions. Data were obtained with an AEI DS-30 to which our own CI programs have been added. A peak with relative intensity of 0.001 would typically be three times stronger than the computer threshold level.

Ketones **7**, **9**, **16**, **19**, **21–25**, **28–30**, **33–35**, **39**, **41**, and **43** were available commercially. Ketones **14–15**,[4] **17–18**,[4] **20**,[5] **26**,[5] and **27**[4] were on hand from previous investigations. The preparation of ketones **10**,[6] **31**,[7] **32**,[8] **36**,[9] **37–38**,[10] **40**,[11] **42**,[12] and **44**[12] has been previously described; the remaining ketones, **8**, **11**, **12**, and **13**, were synthesized as described below and were obtained as colorless oils.

6-Hepten-2-one (8). This compound was prepared by the method of LeBel and co-workers[11] and in the following way. A solution of levulinic acid (7 g) in 30 ml of dry methanol and 60 ml of methyl orthoformate was treated under nitrogen with 4 ml of acetyl chloride and then allowed to stand at room temperature for 72 hr. It was then poured into pentane containing excess solid anhydrous sodium carbonate and then allowed to stand overnight. Removal of the solid followed by evaporation of the pentane under reduced pressure left an oil (crude methyl levulinate dimethyl ketal) which was dissolved in 50 ml of ether and added dropwise under nitrogen to 2.0 g of lithium aluminum hydride. The reaction mixture was worked up with 15% aqueous sodium hydroxide[13] and the lithium salts were removed by filtration. Concentration of the solution under reduced pressure afforded 4,4-dimethoxy-1-pentanol in good yield; ir 3600–3200 (br), 2950, 2825, 1375 and 1050 cm^{-1}. The crude ketal alcohol was taken up in 25 ml of dry pyridine, 20 g of tosyl chloride in 10 ml of pyridine was added, and the mixture was then allowed to stand at 4° for 6 hr at which time crystals of pyridine hydrochloride were present. The mixture was poured into water and extracted three times with ether. The combined ether layers were washed with saturated sodium bicarbonate, 10% hydrochloric acid, and brine, then dried and evaporated to afford the tosylate: ir 3070, 2990, 2975, 2825, 1580, 1440, 1375, 1190, 1180 and 700 cm^{-1}.

Following the procedure of Johnson[14] a solution of 3 g (0.011 mol) of the tosylate in 5 ml of dry tetrahydrofuran was added to a stirred solution of lithium divinylcuprate tributylphosphine complex (0.020 mol).[15] The mixture was stirred at 0° for 2 hr, poured into saturated ammonium chloride, and then extracted with ether. The ether was dried and the solvent was removed through a Vigreux column. The oily residue was distilled to afford ketone **8** which was identical with an authentic sample:[11] ir 2990, 2980, 1715, 1640, 1380, 1180, 995, and 905 cm^{-1}; NMR δ 1.63 (m, 2 H), 2.01 (m, partially obscured by singlet, 2 H), 2.05 (s, 3 H), 2.36 (t, J = 6 Hz, 2 H), 4.95 (m, 2 H), and 5.71 (m, 1 H).

6-Hepten-2-one-*5,5-d*$_2$ (8d). The labeled ketone was prepared from levulinic acid exactly as ketone **8** except that lithium aluminum deuteride was used: ir 2965, 1715, 1640, 1405, 1360, 1160, 995, and 905 cm^{-1}; NMR δ 1.62 (t, J = 7 Hz, 2 H), 2.05 (s, 3 H), 2.34 (t, J = 7 Hz, 2 H), 4.93 (m, 2 H), 5.68 (dd, J = 15 and 10 Hz, 1 H); mass spectrum *m/e* 114.1019 (M$^+$, calcd for $C_7H_{10}D_2O$, 114.1014).

7-Octen-3-one-*2,2,4,4-d*$_4$ (10d). Ketone **10**[6,16] (~175 mg) was treated with a mixture of EtOD (6 ml), D_2O (2 ml), and K_2CO_3 (300 mg) under nitrogen for 24 hr. The mixture was extracted with pentane, dried, and evaporated to an oil. VPC purification on column D afforded ketone **10d**: ir 3080, 2980, 2940, 1720, 1640, 1450, 1400, and 900 cm^{-1}; NMR δ 0.98 (s, 3 H), 1.60 (t, J = 7 Hz, 2 H), 1.98 (m, 2 H), 4.90 (m, 2 H) and 5.67 (m, 1 H); mass spectrum *m/e* 130.1308 (M$^+$, calcd for $C_8H_{10}D_4O$, 130.1315).

2-Methylene-7-octen-3-one (11) and 4-Methylene-7-octen-3-one (12). These ketones were prepared from **10** using piperidine hydrochloride and 37% formalin according to a procedure previously described[5] for closely related compounds. Purification on column G yielded analytically pure samples of **12** and **11** in that order. Characterization data for **11**: ir 3075, 2975, 2920, 1685 (s), 1645, 1635, 1450, 1360, 1070, 980, 920, 905 cm^{-1}; NMR δ 1.69 (tt,

$J_1 = J_2 = 7.5$ Hz, 2 H), 1.83 (br s, 3 H), 2.06 (m, 2 H), 2.61 (t, $J =$ 7.5 Hz, 2 H), 4.89–5.03 (m, 2 H), 5.65–5.83 (m, 1 H), 5.68 (m, 1 H), 5.85 (m, 1 H); mass spectrum *m/e* 138.1072 (M^+, calcd for $C_9H_{14}O$, 138.1044). Characterization data for **12:** ir 3080, 2980, 2940, 1685 (s), 1645, 1630, 1445, 1415, 1375, 1110, 985, 920, 905 cm^{-1}; mass spectrum *m/e* 138.1056 (M^+, calcd for $C_9H_{14}O$, 138.1044).[16]

Methyl *trans*-5-Propyl-2-cyclopenten-1-yl Ketone (13). A solution of 43 mg of the allyl-substituted ketone **14**[4] was hydrogenated (7 ml of hydrogen) at 1 atm in 2 ml of methanol containing a few milligrams of Pd/$BaSO_4$. Usual work-up and separation on column E afforded **13** as the major product: ir 1710 cm^{-1}; NMR δ 0.92 (t, $J = 6$ Hz, 3 H), 1.66 (m, 4 H), 1.68 (m, 1 H), 1.77 (m, 1 H), 2.05 (m, 4 H), 2.52 (m, 1 H), and 5.51 (m, 2 H); mass spectrum *m/e* 152.1201 (M^+, calcd for $C_{10}H_{16}O$, 152.1201).

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Registry No.—**7**, 110-43-0; **8**; 21889-88-3; **8d**, 56960-41-9; **9**, 106-68-3; **10**, 39256-98-9; **10d**, 56960-42-0; **11**, 56960-43-1; **12**, 56960-44-2; **13**, 56960-45-3; **14**, 52358-90-4; **15**, 52502-24-6; **16**, 103-78-6; **17**, 24476-16-2; **18**, 52358-85-7; **19**, 932-66-1; **20**, 7353-76-6; **21**, 110-12-3; **22**, 3240-09-3; **23**, 928-68-7; **24**, 110-93-0; **25**, 109-49-9; **26**, 1187-87-7; **27**, 30079-93-7; **28**, 123-19-3; **29**, 108-94-1; **30**, 583-60-8; **31**, 4694-17-1; **32**, 29843-84-3; **33**, 141-79-7; **34**, 504-20-1; **35**, 10458-14-7; **36**, 17882-43-8; **37**, 23733-70-2; **38**, 57029-74-0; **39**, 111-13-7; **40**, 3664-60-6; **41**, 821-55-6; **42**, 5009-32-5; **43**, 6175-49-1; **44**, 5009-33-6; levulinic acid, 123-76-2; acetyl chloride, 75-36-5; methyl levulinate dimethyl ketal, 52128-61-7; lithium aluminum hydride, 16853-85-3; 4,4-dimethoxy-1-pentanol, 56960-46-4; tosyl chloride, 98-59-9; 4,4-dimethoxy-1-pentyl tosylate, 56960-47-5; lithium aluminum deuteride, 14128-54-2; EtOD; 925-93-9.

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(16) We thank Dr. R. A. Cormier for preparation of **10–12**.

Notes

The α Effect and Ring-Induced Acceleration of Hydrolysis at a Sulfinyl Center. Buffer and Nucleophile Effects in the Hydrolysis of Diphenyl Sulfite

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Although considerable work on the hydroxide ion and hydronium ion catalyzed hydrolyses of diaryl sulfites, including diphenyl sulfite (**1**), has been described,[1] to date there is a dearth of quantitative information on the susceptibility of the sulfinyl centers in these compounds to reaction with nucleophiles in general. Knowledge of the transition-state properties in the reactions of **1** with nucleophiles is fundamental to an understanding of the large enhancement seen in the value of k_{HO^-} (but not k_{H^+}) when the hydrolysis of catechol cyclic sulfite is compared to that of **1**. In addition, the mechanistic aspects of the sulfitase activity of pepsin attend clarification. In connection with the latter, some studies of the reactions of a series of carboxylate ion with **1** have been made but only over a limited p*K* range of catalysts. We now wish to report a study of the reactivity of **1** in water containing 9.1% (v/v) of CH_3CN at 25°C over a wide pH span and for a broad range of buffer species. The observed rate constants, k_{obsd}, for the hydrolysis of **1** catalyzed by the more basic buffers (e.g., carbonate) show contributions from first-order terms in hydroxide ion and the free base form of the buffer, but no catalysis by acidic buffer species. Thus, k_B (the second-order rate constant for attack by the free base form of the buffer) is obtained readily as the slope of a plot of the values of k_{obsd} vs. the concentration of buffer present as the free base. The intercept of this plot is the solvolytic rate constant (k_{solv}) for that pH. Less basic buffers (e.g., formate) show contributions to k_{obsd} not only from k_{solv} and k_B but also from catalysis by the acidic forms of the buffer (k_A). In these cases, the values of k_{solv} were obtained as the intercepts at zero buffer concentration of plots of k_{obsd} vs. total buffer concentration. The slopes of such graphs were replotted at a constant total buffer concentration against the mole fraction of buffer present in the free base state to give k_A and k_B, as illustrated in Figure 1 for formate buffer. Similar plots for more basic species such as carbonate showed k_A negligible compared to k_B. Values of k_A and k_B for the nucleophiles studied, along with additional data from the literature, are collected in Table I.

By plotting the values of k_{solv} calculated at zero buffer concentration vs. pH, the pH profile of Figure 2 was constructed for the hydrolysis of **1**. From a comparison with