Solvolysis of Haloallenes. Alkyl-Substituted Haloallenes

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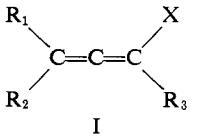
Abstract: The solvolysis of six trisubstituted haloallenes is reported. The solvent dependence and the activation parameters are found to be typical of SN1 reactions. The data are interpreted in terms of a unimolecular reaction proceeding *via* a charge-delocalized allenyl cation. Substitution of *tert*-butyl groups at the propargylic position of the cation encourages reaction at the allenyl position. The change in relative rate for phenyl substitution is interpreted in terms of steric inhibition of resonance in the cation.

Earlier work on the mechanism of triarylchloroallene solvolysis led us to an examination of the scope of the unimolecular solvolysis reaction of haloallenes. To this end six trisubstituted haloallenes, Ia–f, were synthesized as reported earlier[2,3] and their



I

a, $R_1 = R_2 = R_3 =$ *t*-butyl; X = Cl
b, $R_1 = R_3 =$ *t*-butyl; $R_2 = C_6H_5$; X = Cl
c, $R_1 = R_3 =$ *t*-butyl; $R_2 = C_6H_5$; X = Br
d, $R_1 = R_3 = C_6H_5$; $R_2 =$ *t*-butyl; X = Cl
e, $R_1 = R_2 =$ *t*-butyl; $R_3 = C_6H_5$; X = Cl
f, $R_1 = R_2 = C_6H_5$; $R_3 =$ *t*-butyl; X = Cl
g, $R_1 = R_2 = R_3 = C_6H_5$; X = Cl

behavior under solvolytic conditions was examined.

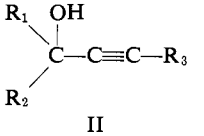
Results

The rate of HX appearance was measured conductometrically in triplicate. Excellent first-order rate plots were obtained to 90% reaction. The results of these studies are compiled in Table I.

From these data the activation parameters for the solvolysis of Ia in 50:50 acetone–water are calculated to be $\Delta H^{\pm} = 23.4 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\pm} = -5.0 \pm 0.5$ eu,[4] those for Ie under the same conditions are calculated to be $\Delta H^{\pm} = 20.2 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\pm} = -10.4 \pm 0.4$ eu,[4] and those for If in 60:40 acetone–water are calculated to be $\Delta H^{\pm} = 19.4 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\pm} = -11.7 \pm 0.4$ eu.[4]

An increase in solvent polarity results in an increase in the rate of solvolysis. The data in Table I yield the following *m* values when plotted against the Grunwald–Winstein *Y* values. For aqueous acetone mixtures Ia at 55°, $m = 1.22$; Ib at 35°, $m = 0.90$; Ic at 35°, $m = 1.04$; Id at 35°, $m = 0.95$; Ie at 35°, $m = 1.13$; If at 35°, $m = 0.87$. A comparison of the rates of solvolysis of Ib and c yields an element effect $k_{Br}/k_{Cl} = 56$.

When larger samples of Ia, b, d, and e are allowed to react under the conditions of the kinetic determinations, the corresponding propargyl alcohols, II, are



II

formed invariably as the major product. Thus, 1,3-di-*tert*-butyl-3-phenylchloroallene (Ib) and 1,3-diphenyl-3-*tert*-butylchloroallene (Id) yield 2,2,6,6-tetramethyl-3-phenyl-4-heptyn-3-ol (IIb) and 1,3-diphenyl-4,4-dimethyl-1-pentyn-3-ol (IId) in 72% and greater than 90% yields, respectively. No evidence of carbonyl absorption in the ir or of vinylic proton absorption in the nmr spectra of either crude product is observed. Similarly, from 1-phenyl-3,3-di-*tert*-butylchloroallene (Ie) an 89% yield of products is isolated. In addition to the absorptions corresponding to the propargyl alcohol, IIe, this material exhibits an α,β-unsaturated carbonyl absorption in the ir and a vinylic proton signal in the nmr as would be expected for 1-

Table I. Rates of Trisubstituted Halloallene[a] Solvolysis in Acetone–Water Solutions

Compd	Temp, °C	Solvent composition[b]	10^4k, sec^{-1}
Ia	44.79 ± 0.02	50:50	0.375 ± 0.002
		40:60	1.90 ± 0.57
	55.23 ± 0.02	60:40	0.251 ± 0.006
		50:50	1.31 ± 0.007
		40:60	7.10 ± 0.018
	64.64 ± 0.02	50:50	3.59 ± 0.101
Ib	35.20 ± 0.02	50:50	0.210 ± 0.003
		40:60	0.704 ± 0.002
Ic		60:40	2.77 ± 0.035
		50:50	11.7 ± 0.05
Id	35.20 ± 0.02	50:50	1.21 ± 0.012
		40:60	4.34 ± 0.096
Ie	25.00 ± 0.02	50:50	0.523 ± 0.003
		40:60	2.24 ± 0.042
	35.22 ± 0.02	60:40	0.345 ± 0.003
		50:50	1.64 ± 0.007
		40:60	7.47 ± 0.019
	44.80 ± 0.02	60:40	1.06 ± 0.007
		50:50	4.66 ± 0.035
If	25.04 ± 0.02	60:40	0.986 ± 0.009
	35.21 ± 0.02	60:40	2.97 ± 0.007
		50:50	9.99 ± 0.067
	44.79 ± 0.02	70:30	2.54 ± 0.007
		60:40	8.07 ± 0.032

[a] $2.7–6.4 \times 10^{-4}$ *M* in reactant. [b] Acetone–water (v/v).

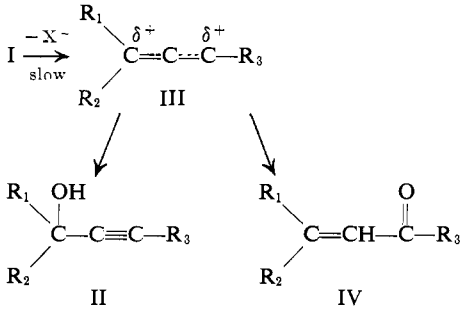
(1) National Science Foundation Undergraduate Research Participant, summer 1970.
(2) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Amer. Chem. Soc.*, **93**, 6989 (1971).
(3) Attempts at synthesizing several haloallenes containing alkyl groups other than *tert*-butyl by this method failed due to the apparent incursion of elimination reactions.
(4) Calculated at 25°.

phenyl-3-*tert*-butyl-4,4-dimethyl-2-penten-1-one. Using the hydroxylic proton signal as an internal standard the amount of ketone may be estimated as less than 5% of the isolated material.

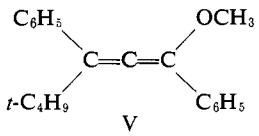
Two products are also formed upon solvolysis of tri-*tert*-butylchloroallene, Ia.[5] The material isolated (87% yield) after ten half-lives showed α,β-unsaturated carbonyl absorption and absorptions typical of a propargyl alcohol in the ir as well as an nmr spectrum consistent with a mixture of these two products. Nmr analysis of the isolated mixture showed the alcohol to be approximately 80% of the product. Within 2 days, a 10–15% yield of 2,2,6,6-tetramethyl-3-*tert*-butyl-4-heptyn-3-ol (IIa) crystallized from the crude material.

Discussion

These results parallel the data obtained in the solvolysis of triarylhaloallenes and illustrate the low reactivity of allenyl halides compared to saturated systems of comparable structure. The rate of solvolysis of α,α-dimethyl-γ-*tert*-butylpropargyl chloride in 80% aqueous ethanol[6] is over 300 times faster than the rate of solvolysis of tri-*tert*-butylchloroallene extrapolated to these conditions. These data may be interpreted in terms of slow formation of a resonance-stabilized allenyl cation, III, having two paths available for subsequent reaction. The observed dependence of the rate on solvent composition for each chloroallene studied is typical of an SN1 process as are the calculated activation parameters. These data are inconsistent with a direct displacement mechanism. The element effect measured here is in excellent agreement with that reported for the solvolysis of trianisylvinyl chloride and bromide, $k_{Br}/k_{Cl} = 58$.[7] These data rule out any nucleophilic addition–elimination mechanism in which the loss of halide ion is not rate limiting. While the present work does not rigorously exclude an addition–elimination sequence in which the nucleophilic addition of water is fast, such mechanisms are usually observed in reactions between nucleophiles of high carbon basicity and vinyl halides having high π-MO acidity.[8] Indeed trianisylvinyl bromide undergoes solvolysis in 80% aqueous ethanol in the presence of hydroxide ion at a rate at least 600 times faster[7] than the rate of nucleophilic addition–elimination of ethoxide ion to 1,1-dianisylvinyl bromide.[9a,b] Tri-*tert*-butylchloroallene, in which the π-electrophilicity is reduced, reacts over 15 times faster than trianisylvinyl bromide at a similar Y value and temperature. Thus the conditions under which the present reactions were accomplished as well as the observed kinetic behavior render this pathway highly unlikely.



Unlike the triarylchloroallene system, evidence of reaction at each end of the allenyl cation intermediate is found when the system is substituted with bulky groups in the 3 position. Our product studies indicate that the trisubstituted cation formed in these solvolysis reactions reacts preferentially at the electronically favored propargyl position. This is consistent with the expectation that the tertiary propargylic resonance structure makes a larger contribution to the hybrid than does the allenyl cation structure. Several reports have demonstrated the operation of steric control on the position of attack in substitution reactions of allenyl halides[10a,b] and propargyl halides.[11] Each of these reports considers only terminal haloallenes where substitution occurs *via* a zwitterion–carbene intermediate[12] and where steric effects inhibiting reaction at the allenyl position are minimized. Reaction of 3,3-di-*tert*-butylbromoallene, for example, with MeO^- in methanol yields a 9:1 ratio of allenyl to propargyl ethers as products[10b] while the silver oxide catalyzed hydrolysis of 1,3-di-*tert*-butyl-3-phenylbromoallene in moist acetone yields the corresponding propargyl alcohol exclusively.[13] Jacobs and Fenton[14] have suggested that steric effects are responsible for the exclusive formation of methyl 4,4-dimethyl-1,3-diphenyl-1,2-pentadienyl ether (V) from reaction of MeO^- with the corresponding allenyl bromide. Since this bromide does not react with sodium iodide in acetone, they further suggested that this product results from the preferential reaction at the allenyl end of a carbonium ion formed by ionization of the bromide. Such preference is apparently the result of steric hindrance at the propargyl position. Our product studies as well as the earlier work of Marvel, *et al.*,[13] indicate no reaction at the allenyl end of such cations unless two *tert*-butyl groups are present at the propargyl position. Since the conditions of these product studies are somewhat different and since no data concerning direct displacement reactions on trisubstituted haloallenes are presently available, further speculation seems unwarranted.



Steric effects of another variety apparently are operative in the solvolysis of haloallenes. Examination of Table II shows that substitutions in the 1 position (gem to Cl) have a somewhat different effect on the rate than do similar substitutions in the 3 position.

The C_6H_5/*tert*-butyl rate ratio (*cf.* Table II) obtained upon substitution of an aromatic ring for a *tert*-butyl

(5) No change in product distribution is observed if equimolar amounts of pyridine are present indicating the lack of any subsequent acid-catalyzed rearrangement of an initially formed propargyl alcohol.
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(13) J. H. Ford, C. D. Thompson, and C. S. Marvel, *ibid.*, **57**, 2619 (1935).
(14) T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, 30, 1808 (1965).

Table II. Relative Rates of $R_1R_2C{=}C{=}C(Cl)R_3$ Solvolysis in 50% Aqueous Acetone at 35°

Compd	R_1	R_2	R_3	k_{rel}
Ia	*t*-Bu	*t*-Bu	*t*-Bu	1.00[a]
Ib	*t*-Bu	C_6H_5	*t*-Bu	1.84
Id	*t*-Bu	C_6H_5	C_6H_5	10.6
Ie	*t*-Bu	*t*-Bu	C_6H_5	14.4
If	C_6H_5	C_6H_5	*t*-Bu	87.6
Ig	C_6H_5	C_6H_5	C_6H_5	345[b]

[a] Extrapolated at 35°. [b] Extrapolated from data in ref 2.

group in the 1 position of a haloallene is 14.4 (k_{Ie}/k_{Ia}), 5.8 (k_{Id}/k_{Ib}), or 3.9 (k_{Ig}/k_{If}) depending upon whether 0, 1, or 2 aromatic rings are present at the 3 position. This decrease in the rate ratio is consistent with an expected increase in delocalization of charge through the aromatic rings at C-3 with a resultant reduction of charge at position 1.

A similar interpretation may be advanced to explain the fact that the C_6H_5/*tert*-butyl rate ratio observed upon substitution of one aromatic ring for *tert*-butyl at position 3 is likewise dependent upon the substituent at C-1, C_6H_5/*tert*-butyl being 1.8 if *tert*-butyl is present at C-1 (k_{Ib}/k_{Ia}) and decreasing to 0.74 if an aromatic ring is the substituent at the 1 position (k_{Id}/k_{Ie}). Substitution of a second aromatic ring for *tert*-butyl at C-3 results in either a 47.6-fold enhancement (*tert*-butyl at C-1, (k_{If}/k_{Ib}) or a 32.5-fold rate increase (C_6H_5 at C-1, k_{Ig}/k_{Id}).

The substitution of a second aromatic ring for *tert*-butyl at C-3 causes a much larger increase in relative rate than is observed upon substitution of the first aromatic ring. Apparently, the bulky *tert*-butyl group prevents the first aromatic ring from completely achieving the coplanarity necessary for resonance stabilization. When two phenyls are present at C-3 both may obtain some degree of overlap with the electron-deficient π MO of the allenyl cation. A similar situation is observed in the structure of crystalline $(C_6H_5)_3C^+ClO_4^-$ where the aromatic rings are over 35° out of the plane defined by the central carbon and its three bonds.[15] The synthesis of compounds with structures having the necessary geometric constraints should provide the desired data. Work is in progress to this end.

Experimental Section

All melting points and boiling points are uncorrected. Ir spectra were obtained using a Perkin-Elmer Model 457 spectrophotometer. Nmr spectra were obtained using a Perkin-Elmer Model R-20B spectrometer. Acetone was purified according to Denoon[16] and stored over Linde 4A molecular sieves. Microanalyses were performed by Atlantic Microlabs, Atlanta, Ga. Benzophenone, di-*tert*-butyl ketone, and *tert*-butylacetylene were commercial samples used without further purification. Commercial phenylacetylene was distilled prior to use. Phenyl *tert*-butyl ketone was prepared according to the procedure of Marvel, *et al.*[13] As reported by other workers,[14,17,18] no evidence of contamination by the isomeric propargyl halides was to be found in the ir or nmr spectra of the haloallenes reported in this study. The detectable limit is estimated to be 2%.

2,2,6,6-Tetramethyl-3-*tert*-butyl-4-heptyn-3-ol (IIa) was prepared from reaction of *tert*-butylethynyllithium with di-*tert*-butyl ketone in hexane at 0° according to Olah and Pittman.[19] *tert*-Butylethynyllithium was prepared by dropwise addition of *tert*-butylacetylene (0.027 mol) in 10 ml of hexane to an equimolar amount of butyllithium in hexane. The cold solution was diluted with 17 ml of dry ether. Di-*tert*-butyl ketone (0.026 mol) in 25 ml of dry ether was added dropwise to the stirred organolithium solution. A N_2 atmosphere was maintained to this point. When the addition was complete, the solution was refluxed for 1 hr and hydrolyzed with distilled water, and ether layer was separated. The alcohol solidified upon distillation affording a 76% yield, mp 54–56°; ir (CCl_4) 3530 (OH) and 2210 (C≡C) cm^{-1}; nmr (CCl_4) δ 1.11 (s, 18), 1.23 (s, 9) and 1.65 (s, 1).

Table III. Spectral Analysis of Product Mixtures from Solvolysis of Trisubstituted Haloallenes

Haloallene	Ir, cm^{-1} [a]	Nmr, δ[a]	Alcohol: ketone[b]
Ia	2212 (C≡C)	1.12 (s)	4:1[c]
	1675 (C=O)	1.22 (s)	
		1.25 (s)	
		1.82 (s)	
		6.06 (s)	
Ib	2200 (C≡C)	0.95 (s)	*d*
	No carbonyl	1.26 (s)	
		2.02 (s)	
		7.3 (m)	
Id	2208 (C≡C)		*d*
	No carbonyl		
Ie	2210 (C≡C)	1.20 (s)	15:1
	1665 (C=O)	2.05 (s)	
		6.12 (s)	
		7.22 (m)	

[a] In CCl_4; all samples showed O–H absorption at 3550–3600 cm^{-1} in addition to those listed. [b] Estimated where possible by integration of either the vinyl proton signal or a *tert*-butyl signal of the product ketone not present in the alcohol spectrum. [c] Average of two separate runs, one containing an equimolar amount of pyridine. Estimated accuracy ±10%. [d] No evidence of ketone formation.

2,2,6,6-Tetramethyl-3-phenyl-4-heptyn-3-ol (IIb) was prepared as above, phenyl *tert*-butyl ketone being substituted for di-*tert*-butyl ketone. This procedure afforded a 70% yield of the desired alcohol, bp 130–131° (5 mm) [lit.[13] 125–128° (4 mm)]; ir (neat 3450 (O–H) and 2200 (C≡C) cm^{-1}; nmr (CCl_4) δ 0.95 (s, 9), 1.25 (s, 9), 2.2 (s, 1), and 7.3 (m, 5).

1,3-Diphenyl-4,4-dimethyl-1-pentyn-3-ol (IId) was prepared as above in 40% yield after several recrystallizations from ligroin; white needles, mp 65–66° [lit.[20] 68°]; ir (CCl_4) 3600 (O–H) and 2250 (C≡C) cm^{-1}; nmr (CCl_4) δ 1.09 (s, 9), 2.08 (s, 1), and 7.4 (m, 10).

1-Phenyl-3-*tert*-butyl-4,4-dimethyl-2-pentyn-1-ol (IIf) was prepared as above in 65% yield, bp 107° (0.5 mm); ir (neat) 3620 (O–H) and 2220 (C≡C) cm^{-1}; nmr (CCl_4) δ 1.20 (s, 18), 1.91 (3, 1), and 7.25 (m, 5).

1,1-Diphenyl-4,4-dimethyl-2-pentyn-1-ol (IIf) was prepared as above in 70% yield, bp 140° (1.3 mm) [lit.[21] 132–135° (0.5 mm)]; ir (neat) 3580 (O–H) and 2200 (C≡C) cm^{-1}

3-Chloro-2,2,6,6-tetramethyl-5-*tert*-butyl-3,4-heptadiene (Ia) was prepared from IIa according to the procedure described by Jacobs and Fenton for other similarly substituted chloroallenes.[14] Two distillations afforded a 45% yield of the desired chloroallene, bp 66–69° (1 mm); ir (neat) 1940 (C=C=C) cm^{-1}; nmr (CCl_4) δ 1.12 (s, 9) and 1.19 (s, 18).

Anal. Calcd for $C_{15}H_{27}Cl$: C, 74.23; H, 11.13; Cl, 14.64. Found: C, 74.50; H, 11.19; Cl, 14.39.

3-Chloro-2,2,6,6-tetramethyl-5-phenyl-3,4-heptadiene (Ib) was prepared as above from IIb in 60% yield, bp 76–77° (0.3 mm) [lit.[14] 105–108° (2–3 mm)]; ir (neat) 1960 (C=C=C) cm^{-1}; nmr (CCl_4) δ 1.15 (s, 9), 1.30 (s, 9), and 7.15 (m, 5).

Anal. Calcd for $C_{17}H_{23}Cl$: C, 77.71; H, 8.76; Cl, 13.52. Found: C, 77.49; H, 8.86; Cl, 13.60.

3-Bromo-2,2,6,6-tetramethyl-5-phenyl-3,4-hepadiene (Ic) was prepared according to the procedure of Marvel, *et al.*[13] Distillation afforded a 60% yield of the desired bromoallene, bp 130–131°

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(16) C. E. Denoon, *Org. Syn.*, 3, 16 (1955).
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(18) Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 24 (1959).
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(20) A. Willemart, *C. R. Acad. Sci.*, 200, 561 (1935).
(21) P. L. Salzburg and C. S. Marvel, *J. Amer. Chem. Soc.*, 50, 2842 (1928).

(6.8 mm) [lit.[13,14] 115–117° (1 mm), 107–109° (0.3–0.7 mm)]; ir (neat) 1950 (C=C=C) cm^{-1}.

1-Chloro-1,3-diphenyl-4,4-dimethyl-1,2-pentadiene (Id) was prepared according to the procedure reported earlier.[2,14] Distillation gave a 60% yield of the chloroallene, bp 130–131° (1 mm) [lit.[14,19] 145–147° (2–3 mm)]: ir (neat) 1920 (C=C=C) cm^{-1}; nmr (CCl_4) δ 1.25 (s, 9) and 7.3 (m, 10).

1-Chloro-1-phenyl-3-*tert*-butyl-4,4-dimethyl-1,2-pentadiene (Ie) was prepared in the above manner. Distillation afforded 62% of the desired chloroallene, bp 76–77° (0.3 mm); ir (neat) 1960 (C=C=C) cm^{-1}; nmr (CCl_4) δ 1.15 (s, 9), 1.30 (s, 9), 7.15 (m, 5).

Anal. Calcd for $C_{17}H_{23}Cl$: C, 77.71; H, 8.76; Cl, 13.52. Found: C, 77.77; H, 8.80; Cl, 13.51.

3-Chloro-1,1-diphenyl-4,4-dimethyl-1,2-pentadiene (If) was prepared as above in 80% yield, mp 37–40° (crystallized at −78° from ether); ir (CCl_4) 1945 (C=C=C) cm^{-1}.

Anal. Calcd for $C_{19}H_{19}Cl$: C, 80.71; H, 6.72; Cl, 12.57. Found: C, 80.56; H, 6.82; Cl, 12.67.

Product Studies. A 1-g sample of the chloroallene was transferred to 1 l. of an aqueous acetone solution thermostated at 35–55° depending upon the rate of solvolysis expected. After ten half-lives, 500 ml of distilled water was added and saturated with NaCl and the resulting solution extracted with five 200-ml portions of ether. The organic layer was dried over $MgSO_4$ and evaporated. Table III lists the spectral data obtained for each product study along with the nmr analysis of product mixtures when formed.

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Primary Amine Catalysis in the Dealdolization of Diacetone Alcohol

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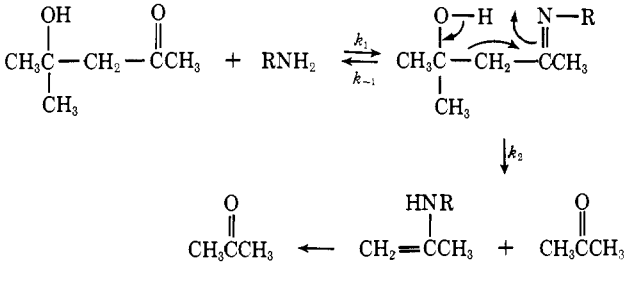
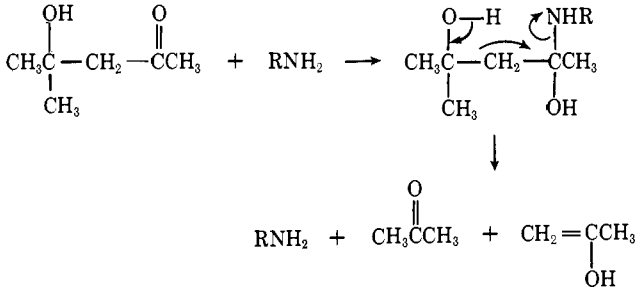
Abstract: The *n*-propylamine-catalyzed dealdolization of diacetone alcohol has been studied over the pH range 9.9–12.7 at 25°. The overall rate of reaction depends on a group with a pK_a of 10.9 which is assigned to the amine. The existence of a ketimine intermediate has been confirmed by direct spectral observation. This intermediate is formed rapidly and reversibly (K = 0.15 M^{-1}) from *n*-propylamine and diacetone alcohol, with subsequent decomposition in a slow step to give product acetone. An observed solvent isotope effect (k_{H_2O}/k_{D_2O} = 1.8) is dissected into a contribution due to the formation of the ketimine (K_{H_2O}/K_{D_2O} = 1.3) and an effect on the breakdown of the intermediate (k_{H_2O}/k_{D_2O} = 1.4). The small isotope effect on the breakdown indicates that proton transfer is probably not occurring in the transition state. The solvent effect on the decomposition of the ketimine is likewise small ($k_{H_2O}/k_{80\%\ ethanol}$ = 8) which suggests that the transition state is only slightly polar.

The catalysis of dealdolization reactions by primary amines is of considerable interest as a model for enzymatic aldol condensation since it has been shown that the terminal amino group of a lysine residue is covalently involved in the action of many of these enzymes.[1] The much greater effect of primary amines than secondary amines as catalysts for this reaction (tertiary amines are inactive) suggests[2] the involvement of a ketimine intermediate which decomposes to a molecule of acetone plus an enamine. Similar mechanisms have been postulated[3] for both enzymatic and nonenzymatic decarboxylations of β-keto acids.

Recently, it has been proposed[4] that primary amine catalysis of the dealdolization of diacetone alcohol may actually involve the intermediate formation of a reactive carbinolamine rather than a ketimine. This proposal was based primarily on extrapolations of data on rates of formation of ketimines which indicated that the rate of formation of a ketimine would be too slow to account for the observed catalysis.





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