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A Base-promoted 1,4-Elimination Reaction. Influence of Solvent and Base on Rate and Deuterium Isotope Effect

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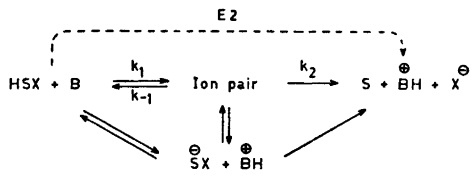
The 1,4-elimination reactions of 3-(2-acetoxy-2-propyl)indene (*B*) promoted by sodium methoxide and tertiary amines have been studied in various protic solvents. We found unusually small deuterium isotope effects ($k_H/k_D = 0.9-2$) with tertiary amines as the promoting bases in solvents ranging in polarity from *t*-BuOH to a mixture of methanol/water. Even in a mixture of 82.5 % DMSO in methanol the deuterium isotope effect did not change significantly. These observations suggest that the 1,4-elimination with these amines takes place by a mechanism in which ion pairs are reversibly formed.

The isotope effect on the 1,4-elimination reaction with NaOMe in methanol was determined to be 7.6, a value consistent with an irreversible *E1cB*-mechanism. The isotope effect for a closely related 1,2-elimination, *i.e.* the reaction of 1-(2-acetoxy-2-propyl)indene (*A*) with NaOMe in methanol, was 6.5.

Stepwise base-promoted elimination reactions (*E1cB*) can be classified mechanistically on the basis of: (a) the extent of the dissociation of the proton from the substrate, and (b) the degree to which the dissociation is reversible under the reaction conditions. According to this view there exists a spectrum of mechanisms ranging from the one extreme with a non-steady-state concentration of the intermediate anion to the other extreme with SX^- reacting irreversibly to form products.[1]



Scheme 1.

Mechanisms in which the anion is reversibly formed in steady-state concentration can be placed between these extremes. As in proton transfer reactions, the intermediate has been suggested in some elimination reactions to be a tightly solvated anion or an ion pair. Strong indications for the existence of the ion-pair mechanism, $(E1cB)_{ip}$, have been obtained recently.[1-5]

Criteria of the $(E1cB)_{ip}$-mechanism have been a low deuterium isotope effect in combination with the absence of significant deuterium exchange and the absence of a negative salt effect. Miller and coworkers [3] used these criteria in their mechanistic interpretation of the elimination of HBr from *cis*-1,2-dibromoethene with triethylamine in dimethylformamide. The isotope effect found was 1.00, and there was neither rate retardation nor hydrogen exchange when triethylammonium or triethylammonium-*d* bromide was present during the reaction.

The above mentioned ion pairs should not be confused with two other types of ion pairs sometimes discussed in connection with elimination reactions: (a) the promoting agent is an ion pair, *e.g.* *t*-BuOK, (b) the substrate and leaving group form a carbonium ion ion-pair. Rappoport and coworkers [6] have proposed ion pairs as intermediates in reactions involving tertiary-amine promoted elimination of HCN from acidic substrates (tri- and tetra-cyano-substituted ethanes) but in these reactions the intermediates are rather stable and are formed in non-steady-state concentrations.

The above discussion applies to 1,4- as well as 1,2-elimination reactions. Very few examples of 1,4-elimination reactions are described in the literature. No conclusive evidence for such

a one-step reaction has been published.[5,7–11] Cristol and coworkers [7,8] have studied 1,4-elimination from *cis*- and *trans*-9,10-di-X-dihydroanthracene derivatives (X = halogen, OH, OAc, and OCOPh) with sodium hydroxide in ethanolic dioxane or pure ethanol. *syn*-1,4-Elimination was found to be preferred. The reactions are presumably stepwise, at least the reactions with the diols. Naphthalene tetrachlorides with sodium methoxide in methanol/acetone gave 1,2- and 1,4-elimination of HCl.[9] 1,4-Elimination was also found in reactions of 1-chloro-2-alkylperfluorocyclobutene and -pentene in KOH/EtOH or MeOH.[10] These two substrates have free rotation around the $C_\gamma - C_\delta$ bond and mixtures of *cis*- and *trans*-olefin were formed. No incorporation of deuterium in the recovered butene-substrate was observed when the reaction was performed in MeOD.

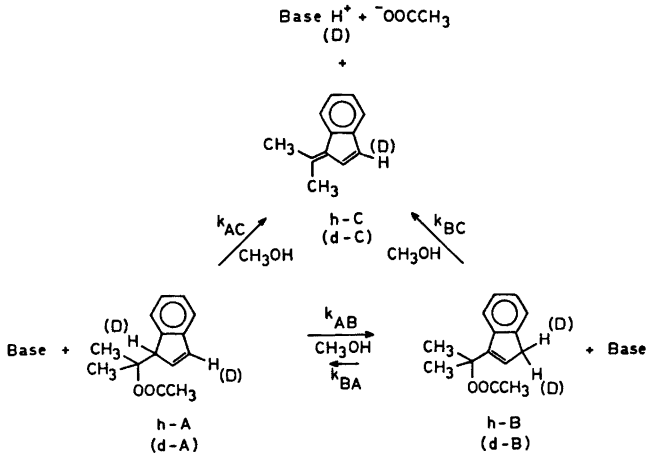
We have recently reported methoxide-promoted 1,4-elimination reactions in methanol from 3-(1-acetoxyethyl)indene and compared the product composition (of *cis*- and *trans*-olefin) and the deuterium isotope effect with the results obtained with non-stereospecific 1,2-elimination from *erythro*- and *threo*-1-(1-acetoxyethyl)indene.[11]

Our laboratories have also reported base-catalysed 1,3-proton transfer competing with 1,2- and 1,4-elimination reactions (Scheme 2) and found not only unusually small but also unusually large isotope effects.[5] The 1,3-proton transfer reaction, which has been indicated to proceed *via* at least one ion-pair intermediate, was used as an ion-pair probe. The results with *N*-ethylpiperidine (EP) as the catalytic and elimination promoting base suggested that all three reactions had at least one ion pair in common.

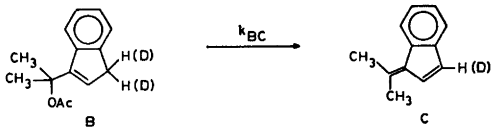
The goal of the present work has been to get further indications for (or against) the suggestion that *B* and tertiary amines react by an ion pair mechanism. Mechanistically interesting questions are, *e.g.*, how the base structure and solvent affect the reversibility of the ion-pair formation and the rate of the dissociation step. Thus the 1,4-elimination of HOAc from *B* was studied in various protic solvents and with several bases.

RESULTS AND DISCUSSION

The 1,4-elimination reactions of 3-(2-acetoxy-2-propyl)indene (*B*) with the tertiary amines triethylamine (TEA) and *N*-ethyl-*N*,*N*-diisopropylamine (EDIPA) have been studied in different protic solvents in the presence of the corresponding ammonium acetate. *B* has also been reacted with sodium methoxide in methanol. The only product of these reactions was 1-isopropylideneindene (*C*) (Scheme 3). The kinetics of the reactions were studied using a sampling – quench – extraction – ^{1}H NMR procedure and/or UV-spectrophotometry. The reactions are shown to be "true" 1,4-elimination reactions, *i.e.* the reactions are not mixtures



Scheme 2.



Scheme 3.

of 1,3-proton transfer and 1,2-elimination. This publication includes a discussion of results obtained recently with *B* in methanol with the bases TEA, *N*-ethylpiperidine (EP) and 1,4-diazabicyclo[2.2.2]-octane (DABCO).[5]

I. 1,4-Elimination reactions with tertiary amines. When a methanol solution of *B* was reacted with tertiary amines of varying base strength and causing different degrees of steric hindrance, the product *C* was obtained (Table 1, run 1 – 4). The weakest base, DABCO, gave the lowest elimination rate and TEA the highest. Large steric hindrance reduced the rate and increased the small isotope effect (Tables 1 and 2, run 4 compared with runs 2 and 3). All deuterium isotope effects are small and consistent with mechanisms involving reversible formation of intermediates (Table 2). However, an alternative explanation of the small isotope effects is the *E2*-mechanism that has a transition state which is highly asymmetric and/or non-linear with respect to proton transfer.[12] The fact that DABCO, the weakest base, was the worst promoting agent is consistent with the ion-pair mechanism, because protonated DABCO is a stronger acid than the other protonated amines and therefore is expected to yield faster ion-pair collapse to starting material (k_{-1} in Scheme 1).[13]

Buffers were added to the reaction solutions to lower the methoxide ion concentration. As the rate data (Table 1) show, the methoxide ion is not the active base when enough buffer is added. Another reason for adding trialkylammonium acetates was to allow for detection of dissociated states.

Lowering the polarity of the solvent is predicted to decrease the elimination rate because the rate determining transition state is expected to be more polar than the initial state. It is also reasonable to predict a larger ratio of ion-pair collapse/ion-pair elimination (*i.e.* k_{-1}/k_2 in Scheme 1) causing the deuterium isotope effect to decrease. Experimentally this behaviour was also found when *B* was reacted with TEA in *t*-BuOH (Tables 1 and 2, run 7) instead of methanol. The rate was decreased about six times and the isotope effect from 1.3 to 0.9. When the polarity of the solvent was increased by addition of water to the methanol, the rate and the isotope effect were increased from 1.3 to 2.0.

An often used method for increasing the basicity of a protic base solution is to add DMSO.[14] When the reaction with TEA was carried out in a mixture of 82.5 % DMSO in methanol, the rate was increased by a factor of 24 but the isotope effect was only slightly enhanced. This experiment illustrates the difficulty in predicting isotope effects when a mechanism with more than one transition state is involved.

The isotope effect on the dissociation step (k_2 in Scheme 1) is expected to be very small since the major bond-breaking and bond-forming process involving the proton ought to be passed once the ion pair is formed. Corrections for the secondary isotope effects expected (see part II) would result in somewhat smaller primary isotope effects. This means that not only the primary isotope effect on the rate of the reaction with TEA in *t*-BuOH, but also the effect with DABCO in methanol ought to be significantly < 1. Thus the ionization transition states for the reaction with these amines ought to be ion-pair-like because inverse isotope effects are commonly interpreted with very product-like transition states involving stronger bonding of the hydrogen in products than in reactants.[15]

The above mentioned ion pairs are expected to be contact ion pairs. An interesting question concerning Scheme 1 is whether the ion pairs eliminate by a one- or multistep process. The incorporation of protium in *d-C* (at the 3 position) when using TEA and EP in methanol was 7.4 ± 3 % and 2.0 ± 3 %, respectively. This could be due to exchange with solvent-separated and/or free ions. However, even if the existence of ions could be shown, this does not necessarily prove that the elimination from the ion pair(s) is stepwise.[16] No incorporation, *i.e.* 0 ± 2 %, of protium in *d-B* could be detected for any of the reactions after 40 – 60 % reaction to *d-C* as determined by ^{1}H NMR spectroscopy.

Table 1. Reactions with *B* and tertiary amines; kinetic data. Initial substrate conc. in the UV-cell was 8×10^{-5} M, otherwise 0.03 M.

Run No.	Initial concentration Base/M	Buffer/M	k_{BC}[a] 10^{-5} M^{-1} s^{-1}	Rel. rate[e]
DABCO in MeOH at 20.00(3) °C; ^{1}H NMR				
1-h[b,c]	0.500	0.030	$0.78(^{+10}_{-14})$[d]	1.0
1-d[c]	0.500	0.030	$0.87(^{+4}_{-12})$[d]	
EP in MeOH at 30.00(3) °C; ^{1}H NMR				
2-h[c]	1.000	0.030	8.88(22)	5.7
2-d[c]	1.000	0.030	6.52(16)	
TEA in MeOH at 29.99(3) °C; ^{1}H NMR				
3-h[c]	1.00	0.030	13.5(3)	8.7
3-d[c]	1.00	0.030	10.7(3)	
EDIPA in MeOH at 29.91(7) °C; UV				
4-h	1.035	0	8.11(41)	
4-h	1.036	0.003	3.67(18)	
4-h	1.019	0.015	2.88(14)	
4-h	1.038	0.030	2.88(14)	1.8
4-d	1.038	0.030	1.65(8)	
EDIPA in MeOH at 30.00(7) °C; ^{1}H NMR				
4-h[f]	1.036	0.030	3.06(31)	
4-h[f]	0.8288	0.030	3.6(4)	
4-d[f]	0.8288	0.030	2.18(22)	
TEA in MeOH/DMSO (82.5 wt % DMSO) at 29.91(7) °C; UV				
5-h	0.1018	0	434(22)	
5-h	0.08684	0.013	466(23)	300
5-d	0.08684	0.013	320(16)	
5-d	0.1241	0.018	321(16)	
TEA in MeOH/DMSO (80.5 wt % DMSO) at 19.99(7) °C; ^{1}H NMR				
5-h[f]	0.0674	0.028	304(30)	390
5-d[f]	0.0674	0.028	217(22)	
TEA in MeOH/H_2O (33.5 wt % H_2O) at 29.91(7) °C; UV				
6-h	0.9792	0	84.9(40)	
6-h	0.9693	0.015	62.5(31)	
6-h	0.9856	0.029	62.9(32)	41
6-h	0.9856	0.029	63.7(32)	
6-d	0.9856	0.029	31.8(16)	
6-d	0.9856	0.029	32.0(16)	
TEA in MeOH/H_2O (33.5 wt % H_2O) at 29.91(7) °C; ^{1}H NMR				
6-h[f]	0.9395	0.058	65.5(66)	
6-d[f]	0.9395	0.058	34.9(35)	
TEA in *t*-BuOH at 30.00(7) °C; ^{1}H NMR				
7-h	1.025	0.015	2.0(2)	
7-h	1.010	0.030	2.17(13)	1.4
7-d	1.010	0.030	2.40(13)	

[a] Estimated errors are considered as maximum errors. [b] Bengtsson, S. unpublished results. [c] Ref. 5. [d] When calculating the rate constants with DABCO, the rates have been divided by the statistical factor 2. [e] When calculating relative rates, the factor 2 has been used to convert rate constants from 20 to 30 °C. [f] One-point-kinetics.

Table 2. Reactions with *B* and tertiary amines; deuterium isotope effects (calculated from the data in Table 1) and protium incorporation.

No.	Analytical method	Solvent	Base	Initial base conc. /M	Initial buffer conc. /M	Temp./°C	k_{BC}^{H}/k_{BC}^{D}	Incorporation of protium
1	^{1}H NMR	MeOH	DABCO	0.5	0.030	20	0.9(2)	
2	^{1}H NMR	MeOH	EP	1.0	0.030	30	1.36(7)	2 ±3 % in *d-C*
3	^{1}H NMR	MeOH	TEA	1.0	0.030	30	1.26(7)	7.4±3 % in *d-C*
4	UV	MeOH	EDIPA	1.0	0.030	30	1.75(10)	
4	^{1}H NMR	MeOH	EDIPA	0.8	0.030	30	1.7(2)	0 ±2 % in *d-B*
5	UV	MeOH/DMSO	TEA	0.1	0.013	30	1.45(10)	
5	^{1}H NMR	MeOH/DMSO	TEA	0.1	0.028	20	1.4(2)	0 ±2 % in *d-B*
6	UV	MeOH/H_2O	TEA	1.0	0.029	30	1.98(10)	
6	^{1}H NMR	MeOH/H_2O	TEA	0.9	0.058	30	1.9(2)	0 ±2 % in *d-B*
7	^{1}H NMR	*t*-BuOH	TEA	1.0	0.030	30	0.9(1)	0 ±2 % in *d-B*

Table 3. Reactions with *A* and *B* in NaOMe/MeOH; kinetic data and deuterium isotope effects.

Substrate	Initial base conc./M	k_{BC} (or k_{AC})/ 10^{-3} M^{-1} s^{-1}	k_H/k_D
0.02654 M;[a] 19.97(7) °C; ^{1}H NMR			
h-B	0.02642	13.6(8)	7.9(10)
0.02699 M;[a] 19.97(7) °C; ^{1}H NMR			
d-B	0.02642	1.73(10)	
0.03327 M;[a] 30.00(7) °C; ^{1}H NMR			
h-B	0.02905	39.6(24)	7.6(10)
0.02615 M;[a] 30.00(7) °C; ^{1}H NMR			
d-B	0.02905	5.20(30)	
0.8×10^{-4} M;[a] 29.91(7) °C; UV			
h-B[b]	0.01053	41.3(20)	7.6(4)
h-B	0.01053	39.8(20)	
d-B	0.01052	5.45(27)	
d-B	0.01321	5.26(27)	
h-A	0.01053	15.9(8)	6.5(3)
h-A	0.01322	16.0(8)	
h-A	0.01322	16.1(8)	
d-A	0.01322	2.46(12)	
d-A	0.01322	2.48(12)	
d-A	0.01053	2.43(12)	

[a] Initial substrate concentration. [b] Initial substrate concentration 1.8×10^{-4} M.

II. Reactions with sodium methoxide. When sodium methoxide is used instead of tertiary amines in methanol, the rate is increased drastically. The large isotope effect (7.6) shows that the transfer of the proton from the substrate to the base is involved in the rate determining step. The 1,2-elimination from 1-(2-acetoxy-2-propyl)indene (*A*) has also been studied. The elimination rate was about 20 % smaller with this substrate (per proton) and the isotope effect was 6.5 (Table 3). No competing 1,3-proton transfer was involved in the reactions of either *A* or *B*, because no trace of *A* or *B* was observed when a deficiency of base was used. Thus *A* gives exclusively 1,2-elimination and *B* exclusively 1,4-elimination.

As *d-B* is a 1,1-di-*d*-substituted compound, a secondary isotope effect >1 is expected.[17] Correction for this secondary isotope effect should result in a somewhat smaller primary isotope effect for *B* than observed. The magnitude of secondary isotope effects of this type has been determined for hydroxide catalysed ionization of nitroalkanes. At 25 °C the value was 1.18 for $CH_3CD_2NO_2$ and 1.14 for the corresponding reaction with $PhCD_2NO_2$.[18] If the isotope effect obtained with *B* (7.6) is corrected by a factor of this magnitude, a primary isotope effect of about 6.5 is obtained 7.6/1.16 = 6.5). Thus the primary isotope effects for the 1,2- and 1,4-elimination are similar.

The value of the equilibrium constant, $[B]_{eq}/[A]_{eq}$ is 19 in methanol at 30 °C.[5a] Thus the acidity of *A* and *B* is of about the same magnitude. The pK_a of NaOMe in methanol (= 18.1)[19a] should not differ much from the pK_a's of the substrates *A* and *B*. Large isotope effects are therefore expected if the reactions are stepwise.[15,19] On the other hand, *E2*-reactions

on the borderline *E1cB–E2* probably have rather small isotope effects.[20,21] Furthermore, some incorporation of protium in *d-C* (5.4 ± 4.0 %) has been observed when a 0.05 M solution of *d-B* was reacted with NaOMe.

The small difference in rate between the 1,2- and 1,4-elimination (per proton) and the large and similar primary isotope effects in connection with the small incorporation of protium in *d-C* suggest that *A* and *B* react by irreversible *E1cB*-mechanisms. The hypothesis that ions are involved in the reactions is also supported by the fact that the *A* and *B* resembling substrates, *erythro-* and *threo*-1-(1-acetoxyethyl)-indenes and 3-(1-acetoxyethyl)indene, react non-stereospecifically with NaOMe in methanol.[11]

Study of the stereochemistry of the reactions discussed under I and II is not possible with the substrates *A* and *B*. Work is in progress in our laboratories on the stereochemistry and other mechanistic aspects of *E1cB*-reactions.

EXPERIMENTAL

Syntheses

3-(2-Acetoxy-2-propyl)indene (*h-B*) and the corresponding 1,1-di-*d* compound (*d-B*) were prepared according to methods published previously.[5a] ^{1}H NMR spectra of *h-* and *d-B* showed no impurities. The deuterium content of *d-B* was 98.2 ± 1.0 atom-% in the 1 position as determined by ^{1}H NMR spectroscopy.

Kinetics

General. All kinetic runs were made at constant temperature in a thermostat (Heto 01 PT 623) or in a jacketed cell of quartz (Hellma 160 B) coupled to the thermostat with an insulated tubing. The temperature of the bath was measured with a calibrated mercury thermometer with an absolute accuracy of ± 0.05 °C. The deviation of the temperature during all runs was < 0.02 °C. Thus the absolute temperature of the bath was t ± 0.07 °C. When the deuterium isotope effects were measured, the temperature deviation was smaller, < 0.02 °C, because the settings of the thermostat were not changed between the runs.

The NMR spectra were recorded with a Varian A 60 D ^{1}H NMR spectrometer. The time was measured with a chronometer or, in the UV-kinetics, with the time scale of the recorder. All glassware, except the UV-cell, was cleaned with chromic acid and rinsed with water, dilute ammonium hydroxide, and distilled water before drying at 150 °C at least over night.

Solvents and bases. Methanol (Fluka spectrograde quality) stored over 3 Å molecular sieves was used without further purification. Dimethyl sulfoxide (Merck spectrograde quality) was distilled at reduced pressure and the centercut stored in a dry nitrogen atmosphere over 3 Å molecular sieves. *t*-BuOH (Merck *p.a.*) was purified by blowing dry oxygen for 24 h through the liquid in which pure-cut pieces of sodium had been dissolved. After distillation using a Widmer column, the center cut was dried and distilled from calcium hydride and then stored under dry nitrogen over molecular sieves. Distilled water was boiled before use. Triethylamine (BDH, > 99 %) was first dried over KOH and then purified by two methods. Distillation through a "spinning-band" column (Nester-Faust) and distillation from *p*-bromobenzoyl chloride in a dry nitrogen atmosphere using a Vigreux column produced amine of equal purity (< 0.009 % diethylamine in the distillate). The former method was also used to purify *N*-ethyl-*N*,*N*-diisopropylamine (Fluka, > 98 %). After distillation the amine contained < 0.003 % diisopropylamine. The analysis were made by GLC on a 2.5 m × 3 mm steel column packed with 20 % Ucon LB-550-X, 20 % KOH on Chromosorb P 80/100, 180 kPa N_2 at 80 °C. The amines were stored over 3 Å molecular sieves under dry nitrogen. A stock solution of NaOMe was prepared by adding methanol-washed pure-cut pieces of sodium to dry methanol. The concentration was determined by titration of aliquots of this stock solution with 0.1 M HCl.

The substrates, bases and solvents (except the methanol) were stored in the freezer.

Quench-extraction-^{1}H NMR procedures. (a) TEA as base in t-*BuOH.* The substrate was weighed into the reaction flask and dissolved in thermostated acetic acid-*t*-BuOH solution (10 ml), and a thermostated solution of TEA in *t*-BuOH (20 ml) was added with a pipette. When sampling, the reaction solution (10 ml) was withdrawn with a pipette and rapidly transferred to a 60 ml stop-cocked centrifuge tube containing CCl_4 (1 ml), 1 M HCl (30 ml) and ice (10 g). The mixture was shaken for 1 min, centrifuged and the organic layer transferred to an NMR tube. The methyl region was integrated and the mol-% of each of the two components of the mixture was evaluated. The analytical procedure has previously been calibrated.[5a]

(b) NaOMe as base in methanol. Thermostated methanol (30 ml) was transferred with a pipette to one of the two compartments of the reaction vessel. The other compartment was filled with thermostated base solution (10 ml). After 10 min in the thermostat the solutions were mixed by shaking the flask. The sampling-quench-extraction-^{1}H NMR procedure

was the same as in (a), but only one extraction with CCl_4 (0.6 ml) was necessary.

(c) One-point kinetics. The substrate was weighed into a 10 ml narrow-necked flask. This flask was then filled with thermostated base solution (containing buffer) and the chronometer was started The same base solution was used both in the reactions with *h-B* and *d-B*. The procedure was otherwise the same as in (b).

Kinetics studied with UV-spectrophotometry. The UV-spectra of *B* and *C* in methanol solution and in MeOH/DMSO were recorded using a Pye Unicam 1800 A spectrophotometer. *C* had absorption maximum at 306.5 nm in pure methanol and at 308 nm in MeOH/DMSO. *B* had no absorption at these wavelengths.

The reactions were run in a thermostated jacketed cell. The absorbance at the absorption maximum was followed as a function of time using a recorder. The reactions were started outside the spectrophotometer in a water thermostat. Solutions of substrate and base were thermostated and transferred with pipettes to a flask. Reaction solution was transferred to the cell with a pasteur pipette.

Evaluation of rate constants and estimation of errors. (a) Quench–extraction–^1H NMR-procedure. The elimination reactions consumed base, but at infinite time the base concentration had diminished by only 3 %. Thus the reactions are expected to show near pseudo-first-order behaviour, and the rate constants were obtained from the slopes of plots ln (mol-% *B*) *versus* time.

(b) UV-kinetics. The reactions are expected to show near first order behaviour, because $[\text{base}]_0/[\text{substrate}]_0 > 10^4$ and 10^2, respectively. Thus ln $(A_\infty - A)$ was plotted *versus* time and the rate constants were evaluated from the slopes. The estimated errors are considered as maximal errors including random errors and maximal systematic errors.

Determination of protium incorporation in d-C. To attain a value of the protium incorporation in *d-C* with NaOMe as base, a 0.05 M solution of *d-B* was run $10t_{\frac{1}{2}}$ (otherwise the same conditions as in the kinetic runs). This solution (20 ml) was then quenched and prepared as in the kinetic experiments. The area under the 2 and 3 protons was compared with the area of the methyl protons. The 2 position was assumed to contain no deuterium. As ^1H NMR reference a solution of *h-C*, obtained as above, was used. The protium content in *d-C* obtained from *d-B* was 5.4 ± 4.0 % in the 3 position.

No incorporation of protium in the 1 position in *d-B* could be detected during the kinetic runs with amines and NaOMe after 40–60 % reaction as determined by ^1H NMR (*i.e.* 0 ± 2 %).

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REFERENCES

1. Bordwell, F. G. *Acc. Chem. Res. 5* (1972) 374.
2. Bordwell, F. G., Weinstock, J. and Sullivan, T. F. *J. Am. Chem. Soc. 93* (1971) 4728.
3. Kwok, W. K., Lee, W. G. and Miller, S. I. *J. Am. Chem. Soc. 91* (1969) 468.
4. Fiandanese, V., Marchese, G. and Naso, F. *J. Chem. Soc. Perkin 2* (1973) 1538.
5. a. Ahlberg, P. *Chem. Scr. 4* (1973) 33; b. Ahlberg, P. and Bengtsson, S. *Ibid. 6* (1974) 45; c, Ahlberg, P. *Ibid. 8* (1975) 49; d. Thibblin, A., Bengtsson, S. and Ahlberg, P. *To be published.*
6. Ahlbeck, M., Hoz, S. and Rappoport, Z. *J. Chem. Soc. Perkin 2* (1972) 1248, (1975) 628.
7. Cristol, S. J., Barasch, W. and Tieman, C. H. *J. Am. Chem. Soc. 77* (1955) 583.
8. Cristol, S. J. *Acc. Chem. Res. 4* (1971) 393.
9. de la Mare, P.B.D., Koeningsberger, R. and Lomas, J. S. *J. Chem. Soc. B* (1966) 834.
10. Park, J. D. and McMurtry, R. J. *J. Org. Chem. 32* (1967) 2397.
11. a. Thibblin, A. and Ahlberg, P. *Acta Chem. Scand. B 28* (1974) 818; b. Thibblin, A. and Ahlberg, P. *To be published.*
12. Saunders, Jr., W. H. *Chem. Scr. 8* (1975) 27.
13. Bell, R. P. *The Proton in Chemistry*, Chapman and Hall, London 1973, p. 207.
14. Cockerill, A. F., Rottschaefer, S. and Saunders, Jr., W. H. *J. Am. Chem. Soc. 89* (1967) 901.
15. Saunders, Jr., W. H. *Acc. Chem. Res. 9* (1976) 19.
16. Breslow, R. *Tetrahedron Lett.* (1964) 399.
17. Alder, R. W., Baker, R. and Brown, J. M. *Mechanism in Organic Chemistry*, Wiley-Interscience, New York 1971, p. 18.
18. Jones, J. R. *The Ionisation of Carbon Acids*, Academic, London and New York 1973, p. 150.
19. a. McLennan, D. J. and Wong, R. J. *Tetrahedron Lett.* (1972) 2887; b. McLennan, D. J. and Wong, R. J. *J. Chem. Soc. Perkin 2* (1974) 526.
20. More O'Ferrall, R. A. and Slae, S. *J. Chem. Soc. B* (1970) 268, 274.
21. Bordwell, F. G. *Acc. Chem. Res. 3* (1970) 281.

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