easily or because the leaving group is a soft nucleophile), then the transition states for aryl and alkyl thiol anions may differ markedly even though the nucleophiles are equally basic.

The reactions of thiol anions with oxygen esters are good examples of the case where the rates correlate well with the basicity alone, reflecting the hardness of the electrophile.[6,29] The reactions of thiol anions with 2,4-dinitrophenyl iodide, on the other hand, show an enormous deviation from the ratio of rates expected based on thiol pK_a. For this reaction, thiophenoxide is 13 000 times faster than methyl thiol anion even though the latter is 10 000 times more basic.[26] The reaction of thiols with **1**, exhibiting a modest enhancement of rates for aryl thiol anions, may well be a case between these two extremes.

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Leaving-Group Effects and Ion-Pair Intermediates in Base-Promoted Elimination Competing with Base-Catalyzed 1,3-Proton Transfer

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Abstract: Reaction of 1-(2-X-2-propyl)indene(*h*-**1**-X) (X = Cl, OAc, OMe, or Me) with tertiary amines or sodium methoxide in methanol results in base-promoted 1,2-elimination and/or base-catalyzed 1,3-proton transfer. On passing from *h*-**1**-Me to *h*-**1**-Cl the total reaction rate was found to increase 615 and 470 times using triethylamine or sodium methoxide, respectively. In spite of this large rate increase, the rearrangement rate was found to decrease drastically when X was changed from OMe to OAc or Cl using NaOMe as base. This shows that the elimination and rearrangement are coupled via a common intermediate(s). The kinetic deuterium isotope effects on the total reaction rates were large indicating irreversible formation of the intermediates which presumably are of the ion-pair and carbanion type, respectively. The results thus suggest that with tertiary amines the elimination of **1**-Cl is an $(E1cB)_{ip,I}$ reaction, i.e., it proceeds via irreversibly formed ion-pair intermediates as previously was shown for **1**-OAc. With sodium methoxide the elimination mechanism for **1**-Cl, as for **1**-OAc, is $(E1cB)_I$.

The 1,3-proton transfer reaction (Scheme I) is a useful carbanion and ion-pair probe in elimination reactions. This reaction was used to show that ion pairs are intermediates in some 1,2- and 1,4-elimination reactions.[1] The main evidence was the unusually large kinetic deuterium isotope effects on the 1,3-proton transfer reaction when competing with 1,2-elimination. The results also gave experimental support to the hypothesis of the existence of two ion-pair intermediates in 1,3-proton transfer reactions.[1d] Stepwise base-promoted elimination has recently been reviewed by Bordwell.[2]

The allylic system used in this investigation is the indene system substituted as shown in Scheme II. Substituent (potential leaving-group) effects on the 1,3-proton transfer reaction in a similar system were previously studied in these laboratories but without interference of total bond breaking to the leaving group.[3] The study showed that electron-withdrawing substituents enhance the rearrangement rate. Results contrary to this are presented in this report which show that when the group X is an efficient leaving group, the rearrangement rate decreases drastically, although the total rate increases. These substituent and leaving-group effects are discussed in terms of free energy relationships (FER). Such relationships have been used previously in attempts to distinguish one-step and multistep elimination reactions.[4]

A common view is that stepwise base-promoted elimination does not involve significant weakening of the bond to the leaving group in the proton-removal step.[5] The leaving group is assumed to interact only inductively with the reaction center. In this work a unifying view is taken. The substituent or leaving-group effects are discussed in terms of varying degree of

Table I. Initial Reaction Conditions and Analytical Methods Used for the Reactions of **1**-Cl, **1**-OMe, and **1**-Me in Methanol at 30.00 ± 0.03 °C

Base	Base concn, M	Buffer concn, M	Substr concn, M	Anal. method
P	1.000	0 or 0.030	0.005	^{1}H NMR
TEA	0.8950	0.030	0.005	^{1}H NMR
	0.8950	0.030	8×10^{-5}	UV[a]
EP	1.000	0.030	0.005	^{1}H NMR
NaOMe	0.1060 or 0.01060		0.005	^{1}H NMR
	0.01060		8×10^{-5}	UV[a]

[a] The UV method was used only for the kinetics of **1**-Cl.

bond breaking to X in the transition state of the proton-abstraction process. Thus the same interaction mechanism is assumed to operate whether the reaction is a one-step or multistep reaction.

Results and Discussion

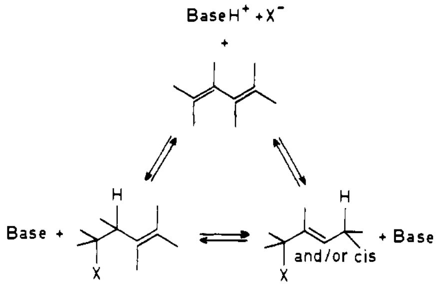
Reactions. The reaction of 1-(2-X-2-propyl)indene (*h*-**1**-X) (X = Cl, OAc, OMe, or Me) or 1-(2-X-2-propyl-*1,3*-d_2)indene (*d*-**1**-X) in methanol with the tertiary amines pyridine (P), triethylamine (TEA), or *N*-ethylpiperidine (EP), or sodium methoxide, produced 3-(2-X-2-propyl)indene (*h*-**2**-X) and/or 1-isopropylideneindene (*h*-**3**), or the corresponding deuterated compounds *d*-**2**-X and *d*-**3**, respectively (Scheme II). The reaction solutions of the stronger amines TEA and EP were buffered with TEAH$^+$OAc$^-$ and EPH$^+$OAc$^-$, respectively, to exclude the methoxide ion as the active base.[1] The kinetics of the reactions was evaluated using the analytical methods presented in Table I.

The dominant isomer in the tautomeric equilibrium was found to be **2**-X (X = OAc, OMe, or Me). The equilibrium constants $K_{eq}{}^{X} = [h\text{-}\mathbf{2}\text{-X}]_{eq}/[h\text{-}\mathbf{1}\text{-X}]_{eq}$ at 30.00 ± 0.03 °C were $K_{eq}{}^{OAc} = 19.9 \pm 2.0$ (1 M pyridine as catalyst),[1d] $K_{eq}{}^{OMe} = 49 \pm 10$ (0.1 M NaOMe), and $K_{eq}{}^{Me} = 30 \pm 5$ (0.1 M NaOMe). The latter was also measured at 40.00 ± 0.03 °C: $K_{eq}{}^{Me} = 23 \pm 4$ (0.1 M NaOMe). It was not possible to measure the equilibrium constant for the interconversion of the chlorides. The thermodynamic equilibria exclusively favor **3**, and no trace of the eliminating substrates was found after long reaction times. The elimination reactions of the ethers have, however, not been followed to completeness.

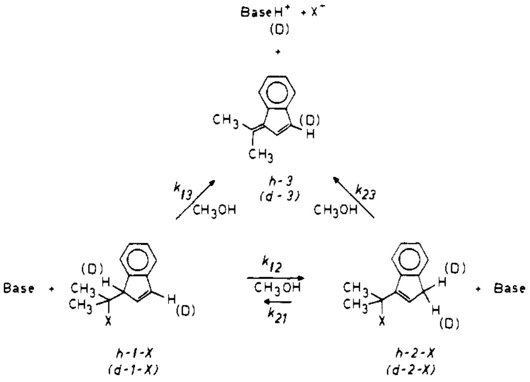
The reaction rate constants and the kinetic deuterium isotope effects are collected in Tables II–IV. Detectable amounts of rearrangement product were not found in the reactions of **1**-Cl with TEA, EP, or NaOMe, or in the reaction of **1**-OAc with NaOMe. The values of $k_{12}{}^{H}$ for these reactions presented in Table IV are the estimated maximum values.

When using P as base in the reaction of **1**-Cl, a small amount of rearrangement accompanied the elimination. However, direct observation of **2**-Cl was not possible since the rearrangement product rapidly reacts with the solvent to form **2**-OMe as the main product, which a separate experiment using **2**-Cl as reactant showed.[7] The kinetics of the reaction of *d*-**1**-Cl and P is complex since side reactions (mainly substitution by solvent) compete with elimination and rearrangement.

Scheme I



Scheme II



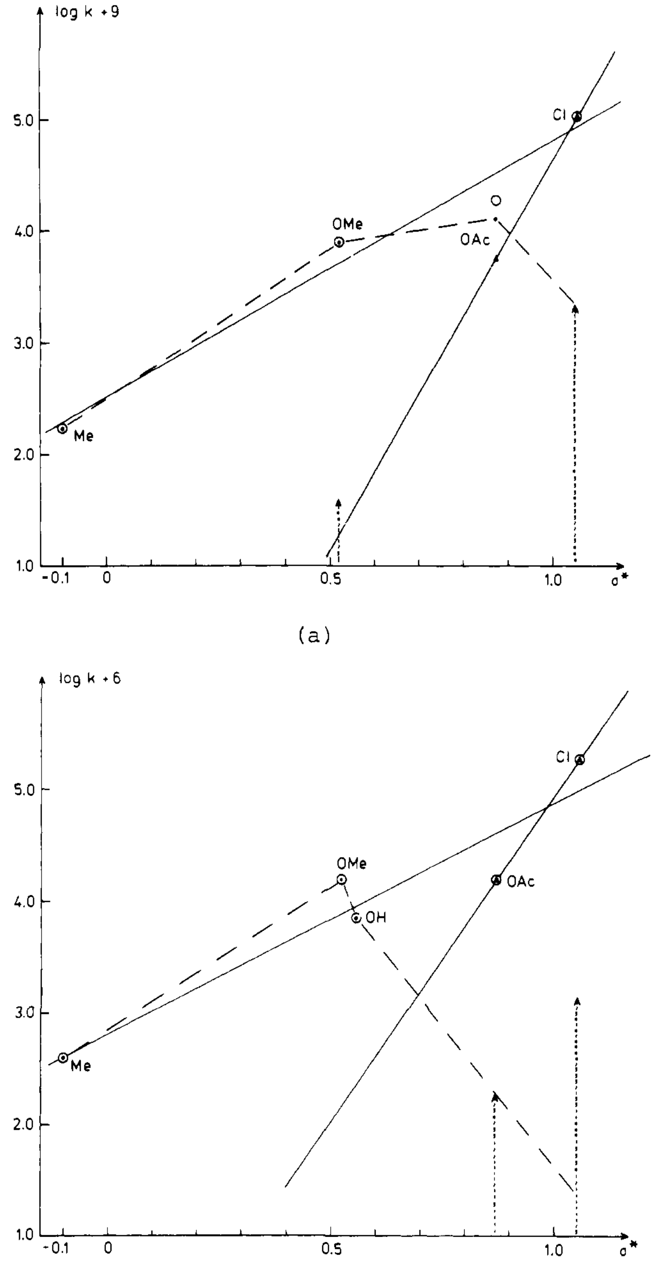
Mechanistic Interpretation of the Results. The large isotope effects (Table III) show that transfer of the proton is involved in the rate-determining step. Consequently, the question arises whether the elimination reactions are of the E2 or the irreversible, stepwise type.

In order to distinguish between one- and two-step elimination mechanisms, the logarithms of $(k_{12} + k_{13})$, k_{12}, and k_{13}, respectively (Table IV) vs. σ^{*8} have been plotted using the data for the reactions with TEA and NaOMe. As shown in Figure 1, there is a linear correlation between log $(k_{12} + k_{13})$ and σ^*, and between log k_{13} and σ^*. The positive slopes (ρ^*) of the lines indicate that the substituents interact with an electron-rich reaction center. An interpretation is that $(k_{12} + k_{13})$ is the ionization rate of the substrates. This is true at least for the noneliminating substrate **1**-Me, and for **1**-OMe and **1**-OH which predominantly rearrange under the reaction conditions. The plot for $(k_{12} + k_{13})$ does not contradict the hypothesis that **1**-OAc and **1**-Cl react stepwise to produce **3**.

Table II. Rate Constants[g] $k_{12} + k_{13}$ ($\text{M}^{-1}\,\text{s}^{-1}/10^{-6}$) for Reaction of *h*-**1**-X in Methanol at 30.00 ± 0.03 °C

	Base			
Substrate	P	TEA	EP	NaOMe
h-**1**-Cl	7.53 ± 0.38	105.6 ± 1.1	120 ± 4	183 700 ± 1900
d-**1**-Cl		12.6 ± 0.5	15.2 ± 0.5	25 850 ± 300
h-**1**-OAc	0.573 ± 0.023[a]	18.7 ± 0.7[b]	19.3 ± 0.3[c]	16 000 ± 800
d-**1**-OAc		2.58 ± 0.10[b]	2.75 ± 0.04[c]	2460 ± 12[d]
h-**1**-OMe		8.01 ± 0.30	(20.4 ± 0.5)[e]	16 300 ± 1000
d-**1**-OMe		1.04 ± 0.04	(2.86 ± 0.07)[e]	
h-**1**-OH				7100[f]
h-**1**-Me		0.172 ± 0.006 (0.447 ± 0.018)[e]		390 ± 16

[a] With buffer: 0.589 ± 0.024. [b] Reference 1a. [c] Reference 1d. [d] Reference 1c. [e] At 40.00 ± 0.03 °C. [f] Extrapolated from the rate constant measured at 32.5 °C.[6] [g] The averages from two or more kinetic runs.



(a)

(b)

Figure 1. Reaction of 1-(2-X-2-propyl)indene in (a) TEA/MeOH; (b) MeONa/MeOH. Plot of log k vs. σ^*; $k = k_{12} + k_{13}$ (○), $k = k_{12}$ (•), and $k = k_{13}$ (▲), respectively. The arrow heads represent the maximum rate of rearrangement or elimination.

We have recently reported substituent effects on TEA-catalyzed 1,3-proton transfer in the closely related system 1-(X-methyl)indene in benzene.[3] The substituent effects on the rearrangement, which was not accompanied by elimination, gave a qualitatively similar picture to that for ($k_{12} + k_{13}$) in this paper, i.e., electron-withdrawing groups substantially accelerate the base-catalyzed rearrangement.

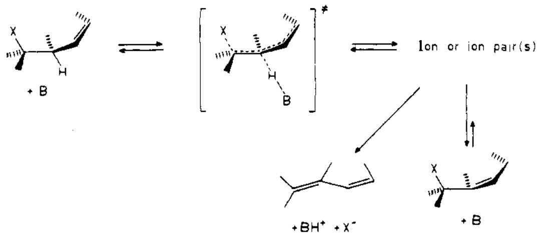
It is concluded from the following that the elimination reactions of **1**-OAc and **1**-Cl are indeed stepwise. Although the total reaction rate increases substantially when passing from *h*-**1**-Me to *h*-**1**-Cl, the rearrangement rate decreases drastically when X is changed from OMe to OAc and/or Cl (Figure 1). Thus, rather than increasing the rearrangement rate as expected if the reactions were parallel, there is a drastic decrease in rearrangement rate (Figure 1) showing that the rearrangement and the elimination reactions are coupled via a common intermediate(s). Presumably this intermediate(s) is of the carbanion or ion-pair type (Scheme III).

Table III. Isotope Effects [$(k_{12}^{H} + k_{13}^{H})/(k_{12}^{D} + k_{13}^{D})$] on the Reactions of **1**-X in Methanol at 30.00 ± 0.03 °C

Substituent X	Base TEA	EP	NaOMe
Cl	8.4 ± 0.4	7.9 ± 0.5	7.1 ± 0.2
OAc	7.3 ± 0.6[a]	7.0 ± 0.2[b]	6.5 ± 0.3[c]
OMe	7.7 ± 0.6	(7.1 ± 0.4)[d]	

[a] Reference 1a. [b] Reference 1d. [c] Reference 1c. [d] At 40.00 ± 0.03 °C.

Scheme III



The substituent effects on ($k_{12} + k_{13}$) could be interpreted by a recently proposed molecular orbital model.[3,9] Accordingly, a substituent more electronegative than H interacts positively with the carbanionic center and results in energy lowering. This hyperconjugative interaction favours a syn or anti positioning of the proton-abstracting base and the electronegative group X in the transition state. A consequence of this theoretical model is that partial bond breaking to the electron-withdrawing group occurs in the proton-removal step and the reaction step is thus considered to be concerted.[10] This gives a unifying view of the interaction mechanism in one-step (E2) and multistep elimination reactions. Both reaction types thus involve (1) partial bond breaking to the leaving group in the proton-abstraction process, (2) some double-bond character of the C_α–C_β bond, and (3) a preferred periplanar positioning between the base and the leaving group.

Free-energy relationships have been used previously in attempts to distinguish between the E2 and E1cB mechanism.[4] In these studies hydrogen exchange was compared with elimination. The most recent study has been done by More O'Ferrall and Warren,[4c] who plotted log k vs. σ^*, where k represents the rate of hydrogen exchange and/or elimination of 9-(X-methyl)fluorene in MeONa/MeOH. The points corresponding to X = Me, H, Ph, and OH gave a good straight line with a slope of 2.25 (ρ^*). The eliminating substrates, for example, X = Cl or Br, were found to react much faster than predicted from the line and these reactions were therefore concluded to be E2 reactions. However, if all points are used, a regression line with quite a different slope ($\rho^* \approx 3.5$) is obtained and then only the points corresponding to the bromo and hydroxy compounds are situated considerably aside of the line. It is reasonable that a smaller ρ^* value is obtained with the indene system ($\rho^* = 2.1$ with NaOMe) compared with the fluorene system since indene is about three pK_a units more acidic than fluorene.

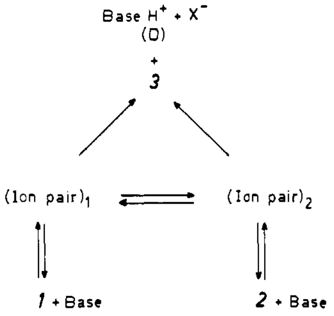
One may question the assumption that a good linear relationship should be obtained for proton-abstraction reactions with substrates of the type X–C–C–H where X is an electron-withdrawing group. The interaction between the reaction center and the substituent/leaving group could be expected to differ from that of the reactions used to determine the substituent constants. Furthermore, a plot of log k vs. σ^* does not take into consideration the steric effects of the substituents,[8a] or the fact that the rate-determining step can change.

Table IV. Rate Constants in $M^{-1}\ s^{-1}/10^{-6}$ for Reactions of *h*-**1**-X in Methanol at 30.00 ± 0.03 °C

Substituent X	Base	k_{12}^H	k_{13}^H	k_{12}^H/k_{13}^H	$(k_{12}^H + k_{13}^H)_{rel}$
Cl	P	0.20	7.33	0.03	13
OAc	P	0.55	0.04	14	1
Cl	TEA	<2.2	105.6	<0.021	615
OAc	TEA	13.0[a]	5.67[a]	2.3	109
OMe	TEA	8.01	<0.04	>200	47
Me	TEA	0.172			1
Cl	EP	<2.5	120	<0.021	6.2
OAc	EP	14.8[b]	4.49[b]	3.3	1
OMe	EP	(20.4)[c]	(<0.1)[c]	(>200)	
Cl	MeONa	<1410	183 700	<0.008	471
OAc	MeONa	<200	16 000[d]	<0.012	41
OMe	MeONa	16 300	250	66	42
OH	MeONa	7100[e]			18
Me	MeONa	390			1

[a] Reference 1a. [b] Reference 1d. [c] At 40.00 ± 0.03 °C. [d] Reference 1c. [e] Extrapolated from the rate constant measured at 32.5 °C.[6]

Scheme IV



Obviously, the results show a common intermediate(s) for the rearrangement and elimination reactions. The intermediates in all the reactions with tertiary amines are presumably of the ion-pair type. We have recently shown ion-pair intermediates in the reactions of **1**-OAc and **2**-OAc with tertiary amines.[1] Evidence was found that 1,2- and 1,4-elimination and the 1,3-proton transfer are coupled via two ion-pair intermediates as shown in Scheme IV.[1d] The main evidence was the unusually large deuterium isotope effects on the rearrangement, e.g., $k_{12}^H/k_{12}^D = 18.1 \pm 1.1$ with quinuclidine as base. The cause of the amplified rearrangement isotope effects was competition between two processes with different isotope effects (the elimination and collapse of the ion pairs) which follows a rate-determining ionization step. The 1,4-elimination isotope effects were found to be small, e.g., 1.63 ± 0.03 with quinuclidine, and unaccompanied by significant D-H exchange.[1d] The reactions of **1**-Cl, **1**-OMe, and **1**-Me presented in this study are consistent with the Scheme IV mechanism.

The larger k_{12}/k_{13} ratio (Table IV) obtained with P than with TEA or EP is consistent with the ion-pair mechanism since the collapse from the ion pair is predicted to be fastest from the strongest acid, i.e., PH^+.[11]

It had been of interest to have an estimate of the isotope effect, which we expect to be exceptionally large, in the pyridine-catalyzed 1,3-proton transfer reaction of **1**-Cl. As was pointed out recently,[1d] the isotope effect on the rearrangement rate is predicted to increase when the 1,3-proton transfer is slowed down compared with the competing elimination process, i.e., when $k_{12}^H \ll k_{13}^H$.

The experiments do not indicate which type of mechanism the ion pairs utilize for the elimination process. Some incorporation of protium in *d*-**3** formed from *d*-**2**-OAc has been found previously at high buffer concentrations,[1] which could indicate the intermediacy of carbanions in the elimination process or buffer participation in electrophilic substitution on the ion pair(s).

The common intermediate indicated in the reactions with sodium methoxide is reasonably a carbanion. We have previously found indication of such an intermediate in the elimination reactions of **1**-OAc and **2**-OAc.[1c] The nonstereospecific elimination of HOAc in a closely related system, the diastereomeric 1-(1-acetoxyethyl)indenes in MeONa/MeOH, has also been discussed in terms of carbanion intermediates.[12]

Experimental Section

General. The ^{1}H NMR analyses were made with a JEOL FX 100 spectrometer equipped with a 5-mm dual probe. A Varian Cary 118 spectrophotometer was used for the UV kinetics.

Methanol (Fluka for UV spectroscopy) stored over 0.3-nm molecular sieves (Merck or Fluka) was used without further purification. The purification of triethylamine[1c] and *N*-ethylpiperidine[1d] have been described before. Pyridine (Mallinckrodt analytical reagent) was distilled from calcium hydride in a dry nitrogen atmosphere. The center cut was stored under dry nitrogen over 0.3-nm molecular sieves. GLC[1c] and ^{1}H NMR established the high purity of the amines. All bases were stored in the deep freeze 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 0.05 M HCl.

1-(2-Chloro-2-propyl)indene (*h*-1-Cl). A solution of 9.0 g of 1-(2-hydroxy-2-propyl)indene[1a] in 50 mL of $CHCl_3$ (p.a.) was shaken for 30 s with 45 mL of concentrated HCl saturated with anhydrous zinc(II) chloride. The organic phase was washed with water and then three times with diluted $NaHCO_3$ solution and finally several times with water. After evaporation of the chloroform, the residue was distilled through a short Vigreux column, yield usually >50% of isolated material, bp 64–66 °C (13 Pa). ^{1}H NMR showed the compound to be free from rearranged and eliminated material and other impurities: MS (IP, 70 eV) *m/e* 192 (M); ^{1}H NMR (100 MHz, CCl_4) δ 1.68 (3 H, s), 1.69 (3 H, s), 4.00 (1 H, t, *J* small), 6.64 (1 H, dd, *J* = 5.7 and 2.1 Hz), 6.96 (1 H, dd, *J* = 5.7 and 2.1 Hz, and further small coupling), 7.16–7.42 (3 H, complex), 7.77–7.89 (1 H, complex).

1-(2-Chloro-2-propyl-*1,3*-d_2)indene (*d*-1-Cl) was prepared from 1-(2-hydroxy-2-propyl-*1,3*-d_2)indene[1a] according to the method above. ^{1}H NMR established the high purity. The deuterium content was 98.2 ± 1.0 atom % (in the 1 and 3 positions, ^{1}H NMR).[1a]

3-(2-Hydroxy-2-propyl)indene. In 150 mL of dry pyridine (distilled from CaH_2) 51.0 g of 1-(2-hydroxy-2-propyl)indene[6] was dissolved. The reaction mixture was heated under dry nitrogen and, after 136 h at 70 °C, a mixture was obtained containing about 9% of unrearranged material and traces of eliminated material. The product mixture was poured onto ice and, after addition of 150 mL of water, extraction was performed with 3 × 200 mL of ether. The combined ether extracts were washed, first with 100 mL of water, then with 2 M HCl until acidic, and finally with four further portions of HCl. The organic phase was washed with water until neutral and then with saturated sodium chloride solution. Evaporation of the ether gave a solid residue which was recrystallized three times from pentane, yield 31.5 g (62%), mp 78–79 °C. The product was free both from unrearranged and eliminated material as well as from any other impurity (^{1}H NMR): ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.65 (6 H, s), 1.77 (1 H, s), 3.32 (2 H, d, J small), 6.36 (1 H, t, J small), 7.11–7.75 (4 H, complex).

3-(2-Hydroxy-2-propyl-*1,1*-d_2)indene was prepared from 1-(2-hydroxy-2-propyl-*1,3*-d_2)indene[1a] according to the method above. ^{1}H NMR showed that the product was pure.

3-(2-Chloro-2-propyl)indene (*h*-2-Cl). 3-(2-Hydroxy-2-propyl)-indene (5.0 g) was dissolved in 28 mL of $CHCl_3$ (p.a.) and shaken for 30 s with 25 mL of concentrated HCl saturated with zinc(II) chloride. The organic phase was washed with water until neutral and then with two further portions of water. After washing with saturated sodium chloride solution, the chloroform was removed under vacuum, yield 4.0 g (72%). The product decomposed on distillation but, as shown by ^{1}H NMR, the undistilled product had a high purity: ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.03 (6 H, s), 3.38 (2 H, d, J small), 6.42 (1 H, t, J small), 7.10–7.90 (4 H, complex).

3-(2-Chloro-2-propyl-*1,1*-d_2)indene (*d*-2-Cl) was prepared from 3-(2-hydroxy-2-propyl-*1,1*-d_2)indene according to the method above. ^{1}H NMR established the high purity of the undistilled product. The deuterium content was 98.3 ± 1.0 atom % (in the 1 position).[1a]

1-*tert*-Butylindene (*h*-1-Me) was prepared from 4,4-dimethyl-3-phenylpentanoic acid according to a method previously reported for 1-methylindene:[13] yield 64% isolated material of high purity (^{1}H NMR); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.02 (9 H, s), 3.27 (1 H, t, J small), 6.53 (1 H, dd, J = 5.7 and 2.0 Hz), 6.80 (1 H, dd, J = 5.7 and 2.0 Hz, and further coupled 0.7 Hz), 7.03–7.58 (4 H, complex).

The syntheses, purification, and deuterium content of 1-(2-acetoxy-2-propyl)indene (*h*-**1**-OAc), 3-(2-acetoxy-2-propyl)indene (*h*-**2**-OAc) and the corresponding dideuterated compounds *d*-**1**-OAc and *d*-**2**-OAc have been reported previously.[1a]

Kinetics. All glassware was cleaned with chromic acid and rinsed with water, dilute ammonium hydroxide, and distilled water before drying at 150 °C at least overnight. The kinetic runs were performed at constant temperature in a HETO 01 PT 623 thermostat or in a jacketed UV cell (10 mm, Hellma 160B) thermostated with water via a short insulated tubing. The UV-cell holder was thermostated with water from a second thermostat. The temperature was measured with a calibrated mercury thermometer with an absolute accuracy of ±0.02 °C. During the runs the temperature of the bath did not deviate more than 0.01 °C from the average value (t), and thus the absolute temperature was $t \pm 0.03$ °C.

In the UV kinetics the absorbance at an absorption maximum (307 nm) of the product **3** was measured as a function of time using the recorder of the spectrometer. The reactions were started in the following way. The cell was filled with base solution and after thermostating for 30 min 1 μL of a solution of the substrate in methanol was added. Before initiating measurements, the solution was homogenized by inverting the cell several times.

The quench–extraction ^{1}H NMR procedure has been described previously.[1a] The following modifications were used: the substrate was weighted into the reaction flask and thermostated base solution was added; aliquots of 5 mL of reaction solution were quenched; 0.5 mL of CCl_4 was used for the extraction; 0.1 mL of C_6D_6 was added to the CCl_4 solution in the NMR tube.

The equilibrium constants for *h*-**1**-OMe and *h*-**1**-Me were obtained from kinetic runs which exceeded 10 half-lifetimes.

Evaluation of Rate Constants and Estimation of Errors. The reactions showed first-order behavior since $[\text{base}]_0/[\text{substrate}]_0 \geqslant 132$ in the elimination reactions. Thus ln $(A_\infty - A)$ was plotted vs. time and the rate constants were evaluated from the slopes and the measured equilibrium constants. The rate constant for the elimination reaction of *h*-**1**-ome with NaOMe was evaluated from the slope (Δ absorbance/Δt) of the recorder trace at the beginning of the reaction using the molar absorbance of *h*-**3** determined in a separate experiment.

All estimated errors are considered as maximum errors derived from maximum systematic errors and random errors. The maximum errors of the directly measured quantities were thus allowed to propagate as systematic errors into derived quantities. However, since only one stock solution for each base buffer was used in all kinetic measurements, the error of the base concentration was not included in the error calculation. This error was ≤0.1% in the concentration of the amines and ≤0.4% in NaOMe.

The value for σ^*_{OAc} was obtained using the relation $\sigma^* = (1/0.45) \times \sigma^{\mathrm{I}}$.[8b]

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