

water and diethyl ether added, the ether extract washed with water and dried over magnesium sulfate. Evaporation of the ether gave the crude 6,6-dimethylundeca-1,10-diyne (7.6 g = 65 %) which was found by IR spectroscopy to contain no dibromide and was used in the next step without further purification.

13,13-Dimethylcyclohexadeca-1,8-diyne. To a stirred solution of sodamide, made from sodium (2.02 g = 0.088 mol) in liquid ammonia (600 ml), was added 6,6-dimethylundeca-1,10-diyne (7.5 g = 0.044 mol). After 1 h 1,5-dibromopentane (12 g) was added and the stirring continued for 8 d under refluxing ammonia. The ammonia was slowly evaporated, the residue dissolved in water and the water solution extracted with ether. The ether extracts were dried with magnesium sulfate, and the ether evaporated. The crude reaction product (7.3 g) was purified on an alumina column, and by elution with a benzene/pentane 1/3 solution was obtained the 13,13-dimethylcyclohexadeca-1,8-diyne (1.5 g = 15 %), m.p. 26 °C. (Found: C 88.33; H 11.45. Mol. w. 244 (by mass spectrometry). Calc. for $C_{18}H_{28}$: C 88.45; H 11.55. Mol. w. 244).

6,6,15,15-Tetramethylcyclo-octadeca-1,10-diyne. 6,6-Dimethylundeca-1,10-diyne (8.5 g = 0.05 mol) was added to a solution of sodamide, made from sodium (2.3 g = 0.1 mol) in liquid ammonia (600 ml) and stirred for 1.5 h.

4,4-Dimethyl-1,7-dibromoheptane (14.3 g = 0.05 mol) was added and the reaction mixture was stirred and refluxed for 5 d. Dry diethyl ether (500 ml) was added, the ammonia evaporated and the ether solution stirred at room temperature for 2 d. Water was added, the ether solution washed with more water, dried with magnesium sulfate. After evaporation of ether the crystalline residue (8.5 g) was dissolved in pentane and purified through a short alumina column. After recrystallization with ethanol was obtained: 6,6,15,15-tetramethylcyclo-octadeca-1,10-diyne (3.0 g = 21 %, 8.5 g = 59 % yield as crystalline reaction product), m.p. 91 °C. (Found: C 87.79; H 12.04. Mol. w. 300 (by mass spectrometry. Calc. for $C_{22}H_{36}$: C 87.92; H 12.08. Mol. w. 300).

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Base-promoted Non-stereospecific 1,2- and 1,4-Elimination Reactions

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The stereochemistry of elimination reactions from the two diastereomeric 1-(1-acetoxyethyl)indenes (A_1 and A_2) and from 3-(1-acetoxyethyl)indene (B) have been studied in $MeO^-/MeOH$. The mechanisms of the elimination reactions are discussed.

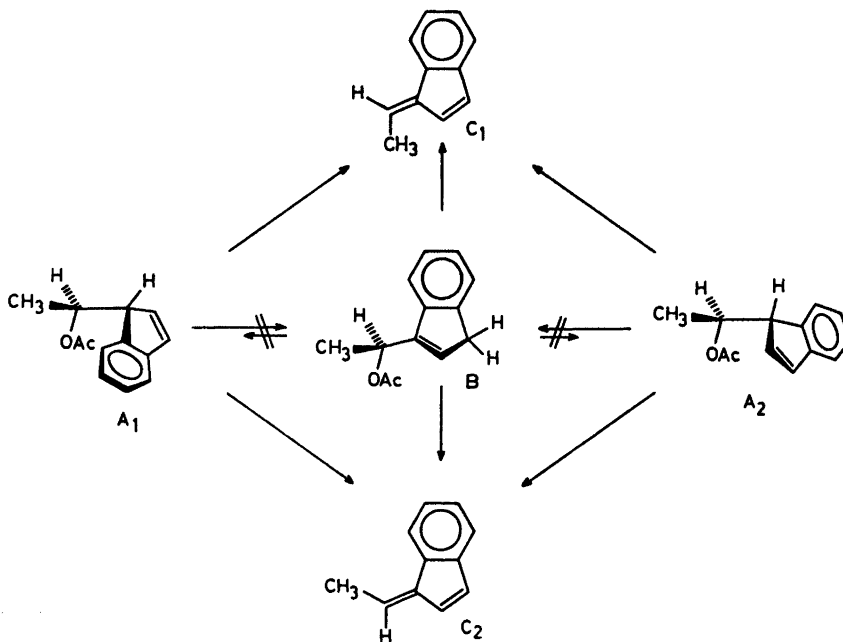
When a methanol solution 0.03 M in substrate was reacted with KOMe or NaOMe (0.06 M) at 30 °C, *trans*- and *cis*-1-ethylideneindene (C_1 and C_2) were obtained (Scheme 1). The proportions varied considerably with the substrate structure (A_1 , A_2 , and B). The thermodynamic equilibria exclusively favour C_1 and C_2 , no trace of A_1 , A_2 , or B being observed after long reaction times. Neither any epimerization of A_1 or A_2 nor any 1,3-proton transfer to B could be observed when a deficiency of base was used. The reactions were studied using a quench-extraction-NMR procedure. The results are given in Table 1.

Table 1. Product compositions obtained with A_1 , A_2 , and B in $MeO^-/MeOH$ at 29.96 ± 0.07 °C.

Initial substrate conc. 0.03 M	Initial [NaOMe] M	Initial [KOMe] M	100 C_2 / $C_1 + C_2$
A_1	0.06		37.1 ± 2.0
A_1		0.06	37.0 ± 2.0
A_2	0.06		8.1 ± 2.0
A_2		0.06	8.2 ± 2.0
B	0.06		22.6 ± 2.0
B		0.06	22.5 ± 2.0
A_1^a	0.02		38 ± 3
A_2		0.01	7.4 ± 2.0

^a 0.05 M.

A preliminary correlation between diastereomers and structures (A_1 and A_2) has been made assuming *anti* elimination from substrate A_2 to be favoured over *syn* elimination. The same structure assignments were obtained using Cram's rule. In NMR-spectra of mixtures of C_1 and C_2 the methyl group of C_2 appears at 0.18 ppm lower field. The proximity of the methyl group of C_2 to the deshielding region of the benzene ring is assumed to yield proton resonance at lower field than the methyl protons of C_1 .



Scheme 1.

The equilibrium constants for interconversion of the substrates were determined in an experiment using pyridine as catalyst. Pyridine was used because its catalytic efficiency in the 1,3-proton transfer reactions is much larger than the rate with which it effects elimination. Only trace amounts of elimination products were obtained. The equilibrium constants were $[B]_{\text{eq}}/[A_1]_{\text{eq}} \approx 22$, $[B]_{\text{eq}}/[A_2]_{\text{eq}} \approx 26$, and $[A_1]_{\text{eq}}/[A_2]_{\text{eq}} \approx 1.2$.

As shown in Table 1 the olefin C₁ is the predominant product in the reactions with all substrates. The same product compositions were obtained with KOMe and NaOMe as bases. Our analytical method did not allow accurate determinations of the absolute second order rate constants because the reactions were too fast ($k_{A_1} \approx 0.07 \text{ M}^{-1}\text{s}^{-1}$). However, it has been possible to measure relative rates of elimination reactions from the three substrates. Thus, mixtures of A₁ and A₂ or A₁ and B have been reacted in competition experiments with a deficiency of base. The ratios of elimination rates $k_{A_1}:k_{A_2}:k_B$ were found to be 1.5:2:1.6.

The results show that A₁ and A₂ exclusively give 1,2-elimination reactions and B exclusively 1,4-elimination reactions.

The studied reactions are expected to proceed by mechanisms in the E1cB-E2 part of the mechanistic spectrum. The results give indications of the operation of irreversible carb-

anion mechanisms, but they do not exclude concerted mechanisms. Carbanion mechanisms are supported by the fact that the elimination reactions from the three substrates converge towards olefin C₁. If the reactions are non-concerted, they all could have a common carbanion as intermediate. Rotation around the C_α-C_β bond interconverts different conformations of the carbanion. Thus, the substrates either could give fixed compositions of carbanion conformers, or the intermediate(s) formed have time to interconvert. The experimental results clearly show that an equilibrium mixture of the carbanion conformers is not formed.

The absence of competing epimerization and 1,3-proton transfer reactions is evidence against pre-equilibrium E1cB-mechanisms. In a similar reaction system Ahlberg and Bengtsson^{1,2} have found that ion-pairs are intermediates in elimination reactions from 1-(2-acetoxy-2-propyl)indene and 3-(2-acetoxy-2-propyl)indene in methanol with tertiary amines as bases.

The stereochemistry of elimination reactions near the borderline E1cB-E2 has been studied by Cristol and Pappas,³ who have reported stereoconvergent elimination reactions from *erythro*- and *threo*-2-*p*-toluenesulfonyl-1,2-diphenyl-1-chloroethane in NaOH/EtOH and explained the convergence with a duality of mechanism (E2/E1cB). Cram, Greene and

Depuy⁴ have made an extensive study of elimination reactions from diastereomeric substrates. 1,2-Diphenyl-1-propyl-X (X=Br, Cl or NMe₃⁺) was reacted in primary, secondary, and tertiary alkoxide/alcohol media. Furthermore the chloride was studied in potassium 2-octyloxyde/benzene. All the elimination reactions were *anti* eliminations with one exception, the *erythro* isomer with NMe₃⁺ as leaving group gave in *t*-BuOK/BuOH *syn* elimination. Later studies⁵ have shown that no exchange is involved, *i.e.* a pre-equilibrium E1cB-mechanism is excluded. Alunni and Baciocchi⁶ have also examined the stereochemistry of elimination reactions. They found that 1-phenyl-2-X-propanes (X=halogen) in EtONa/EtOH eliminate with a *trans/cis* ratio ranging from about 25 for the bromo and chloro compounds to 112 for the fluoro compound. Sufficient activation of a substrate destroys the stereospecificity and presumably changes the mechanism from E2 to E1cB.⁵

Examples of 1,4-elimination reactions, promoted by base are not common in the literature. Cristol and coworkers^{7,8} have studied 1,4-elimination reactions from *cis*- and *trans*-9,10-dihydroanthracene derivatives (X=halogen, OH, OAc, and OCOPh) with sodium hydroxide in ethanolic dioxane. *syn*-1,4-Elimination was found to be preferred. The diols react presumably with carbanion mechanisms, but the mechanisms of the other reactions are not settled. Naphthalene tetrachlorides with sodium methoxide in methanol/acetone gave 1,2- and 1,4-elimination reactions.⁹ Other substrates which have been found to give 1,4-elimination reactions are 1-chloro-2-alkylperfluorocyclobutene and -pentene in KOH/EtOH or MeOH. Contrary to other studies of 1,4-eliminations these two substrates have free rotation around the C_γ-C_δ bond. Mixtures of *cis*- and *trans*-olefins were obtained as products.¹⁰

Ahlberg and Bengtsson^{1,2} have recently reported the first true 1,4-elimination reactions, *i.e.* it was demonstrated that the reactions were not mixtures of 1,3-proton transfer and 1,2-elimination. The substrate, 3-(2-acetoxy-2-propyl) indene, was reacted with tertiary amines as bases in methanol.

The mechanisms of the above reported elimination reactions are under further study in these laboratories.

Experimental. The substrates were prepared by addition of acetaldehyde to indenylmagnesium bromide.^{11,12} Chromatographic separation of the alcohols formed followed by zinc dichloride catalysed esterification with acetic anhydride gave diastereomerically pure *threo*- and *erythro*-1-(1-acetoxyethyl)indenenes. Rearrangement of the diastereomeric acetate mixture in pyridine produced 3-(1-acetoxyethyl)indene.

Stock solutions of NaOMe and KOMe were prepared by dissolving pure-cut pieces of the metals in methanol (Fluka spectrograde quality dried over molecular sieves) under nitrogen

atmosphere. The reactions were carried out in a V-formed flask; 5 ml substrate solution was placed in one of the shanks and 5 ml base solution in the other. The flask was placed in a thermostat at a temperature of 29.96 ± 0.07 °C. After 10 min in the thermostat the reaction was started by shaking the flask. 90 min later the reaction mixture was quenched according to a method previously described by Ahlberg,¹ who has also reported the procedure for determining the equilibrium constants. The analysis were made with NMR-technique.

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