Alkene Formation *via* Aluminium Trichloride-induced Elimination from Benzyl Alkoxides

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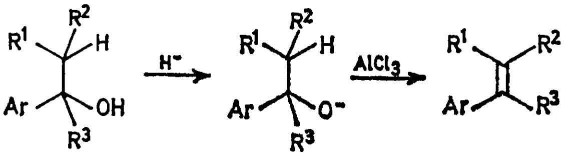
Summary Alkenes have been prepared by elimination from benzyl alkoxides, leading to anti-Saytzeff products; the mechanism is discussed on the basis of the products formed and of an observed hydrogen–deuterium isotope effect.

The formation of alkenes by β-eliminations has been extensively studied over many years.[1] We now report the aluminium trichloride induced elimination from benzyl alkoxides leading to the formation of the anti-Saytzeff alkenes [equation (1)].

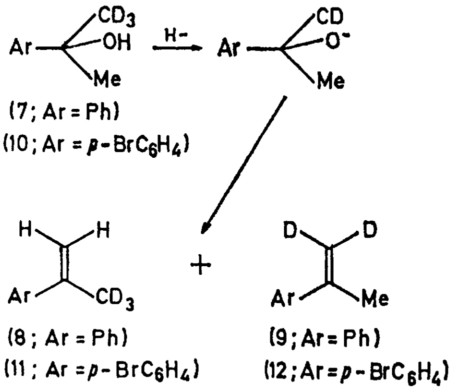


(1)

(1; $R^1=R^2=R^3=Me$; $Ar=Ph$)
(2; $R^1=R^2=H$; $R^3=Pr^i$; $Ar=Ph$)
(3; $R^1=R^2=H$; $R^3=Me$; $Ar=Ph$)
(4; $R^1=R^2=H$; $R^3=Me$; $Ar=Ph$)
(5; $R^1=R^2=H$; $R^3=Me$; $Ar=p\text{-}BrC_6H_4$)
(6; $R^1=R^2=H$; $R^3=Me$; $Ar=p\text{-}BrC_6H_4$)

In a typical experiment a solution of the butanol (**1**) (1·64 g) in anhydrous ether was added dropwise to a stirred slurry of $LiAlH_4$ (95 mg) in anhydrous ether. When formation of the alkoxide was complete, a solution of $AlCl_3$ (1·33 g) in anhydrous ether was added dropwise. The mixture was heated under reflux for 30 min, cooled to 0°, and hydrolysed with 10% aqueous NaOH. The organic layer was dried ($MgSO_4$) and ether removed to give the organic products (1·41 g). Analysis of this mixture by v.p.c. showed one major component (90%), which was identified by spectrometric methods as the butene (**2**). The same product was also obtained using sodium hydride to generate the alkoxide, but with otherwise identical procedure. In corresponding reactions the propanols (**3**) and (**5**) gave the propenes (**4**) (96%) and (**6**) (94%). Reaction of (**3**) with $AlCl_3$ but without alkoxide formation gave a reduced yield of olefin, with polymeric material as the major product.

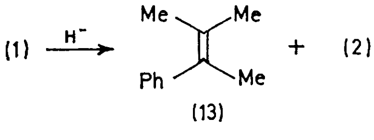
The reactions of the deuteriated alcohols (**7**) and (**10**) [equation (2)] were of particular interest since the positional equivalence of the methyl group allowed the possibility of observing direct competition between H and D loss. Analysis of the products (obtained as described above) by ^1H n.m.r. spectroscopy showed that olefins (**8**) and (**9**) were produced in 76 ± 1% and 24 ± 1% yield, and (**11**) and (**12**) in 72 ± 1% and 28 ± 1% yield. This showed that a hydrogen–deuterium isotope effect was operating [$k_H/k_D = 3{\cdot}2 \pm 0{\cdot}1$ for (**7**); $k_H/k_D = 2{\cdot}6 \pm 0{\cdot}1$ for (**10**)]. The low-eV mass spectra of the product mixtures gave similar values for k_H/k_D. As expected, dehydration of (**7**) under similar conditions but with acid catalysis showed no isotope effect. Thus an *E*1 mechanism involving a carbonium ion intermediate may be ruled out. The nature of the product (**2**) from alcohol (**1**) also argues against an ionic mechanism. In the latter case the more substituted Saytzeff product (**13**) (the thermodynamic product) would be expected as the major component. This is confirmed by the observation that with acid catalysis (**1**) gave (**2**) (43%) and (**13**) (57%) [equation (3)] under the same conditions as reaction (1).



(7; Ar = Ph)
(10; Ar = $p\text{-}BrC_6H_4$)
(8; Ar = Ph)
(11; Ar = $p\text{-}BrC_6H_4$)
(9; Ar = Ph)
(12; Ar = $p\text{-}BrC_6H_4$)

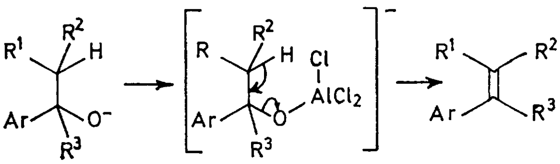
(2)

A simple *E*2 type mechanism, using the alkoxide ion as base, can also be ruled out, since this would also involve production of free alcohol, and so would give polymeric products. However, t.l.c. indicates that polymeric material is not formed in significant amounts during the reaction.



(13)

(3)



(4)

We propose a mechanism involving initial complexation of the alkoxide with the $AlCl_3$, followed by a concerted intramolecular *cis*-elimination [equation (4)]. The product obtained is determined by the formation of the more energetically favoured transition state conformation. The conformation which leads to the Saytzeff product from (**1**) is destabilised by van der Waals interaction between the 3-methyl group and an *ortho*-hydrogen atom on the phenyl ring. Thermal dehydration of (**1**) has also been found to give the anti-Saytzeff product,[2] and a mechanism has been suggested[3] on kinetic grounds, involving a *cis*-elimination leading to (**2**) because of energy differences in the transition states of conformers.

The magnitude of the primary hydrogen–deuterium isotope effect found for reaction of alcohols (**7**) and (**10**) is in reasonable agreement with a non-linear activated complex for the transition state of the reaction.[4]

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