β′,β-Carbanionic Elimination Reaction of a Carboxylic Ester

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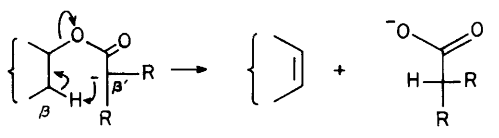
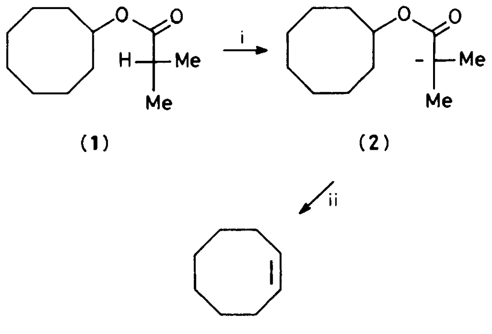
The β′,β-elimination reaction of the ester (**1**) gives *cis*-cyclo-octene in > 70% yield; the corresponding reactions of the stereoselectively deuterium labelled compounds (**1a**) and (**1b**) show that the elimination is *syn*.

The preparation of olefins from alcohols or esters has been rationalised in terms of carbocationic mechanisms: even in the pyrolysis of esters the formation of ion-pairs[1] and thus the risk of rearrangement cannot be completely ignored.[2] The pyrolytic *trans* elimination of alkoxytropones has been described recently and may be a solution to this problem.[3] These last experiments have prompted us to report our own results which provide another approach to exclude the risk of rearrangement. The well-known carbanions derived from carboxylic esters[4] can undergo elimination reactions *via* six-membered transition states, [reaction (1), which may be called a β′,β-elimination] and surprisingly, this reaction seems not to have been investigated.[5]

We report here our preliminary results which constitute the

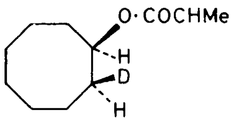


(1)

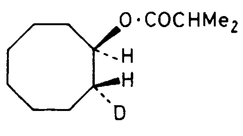


Scheme 1. i, Pr^i_2NMgBr, Et_2O, −40 °C; ii, heat, C_6H_6.

first example of this reaction. Treatment of cyclo-octyl isobutyrate (**1**) (1.5×10^{-1} M) with magnesium di-isopropylamide (1.4 equiv.) [prepared from ethylmagnesium bromide (1 equiv.) and di-isopropylamine (1 equiv.)] in diethyl ether for 2 h at −40 °C gave the magnesium enolate (**2**).† It was found that heating at a moderate temperature of (**2**) in benzene for 2 h gave the *cis*-cyclo-octene in greater than 70% yield (Scheme 1).



(1a)



(1b)

Experiments with compounds (**1a**) and (**1b**) stereoselectively labelled with deuterium indicate a *syn* elimination. Compound (**1a**) ($D_0 = 4.7$, $D_1 = 74$, $D_2 = 15.3$, $D_3 = 6\%$) in which deuterium is *cis* to the leaving group, gave cyclo-octene in which the proportion of deuterium was appreciably diminished ($D_0 = 24.3$, $D_1 = 62$, $D_2 = 10.5$, $D_3 = 3.5\%$). Conversely, compound (**1b**) ($D_0 = 3.2$, $D_1 = 92.4$, $D_2 = 4.1$, $D_3 = 0.3\%$) in which the deuterium is *trans* to the leaving group gave cyclo-octene without loss of deuterium ($D_0 = 3.3$, $D_1 = 95.6$, $D_2 = 1.1\%$). ^2H N.m.r. spectra of the labelled olefins agree with the expected isotope distribution.

It is interesting to note that the primary ($k_H/k_D = 2.8$–3.0) and secondary ($k_H/k_D = 1.05$–1.1) isotope effects are much weaker in the reaction of (**1**) than those measured in the elimination reactions of sulphides and ethers proceeding *via* five-membered transition states.[6,7]

The elimination reaction reported here proceeds *via* a six-membered transition state (β′,β) and its synthetic applications are under investigation.

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† At −40 °C, after addition of methyl iodide the *C*-methylated product was isolated in 100% yield, showing that quantitative formation of the enolate occurs and is stable in diethyl ether at this temperature.