Alkoxide Accelerated 1,5-Sigmatropy of Alkyl, Vinyl, Aryl, and Cyclopropyl Groups

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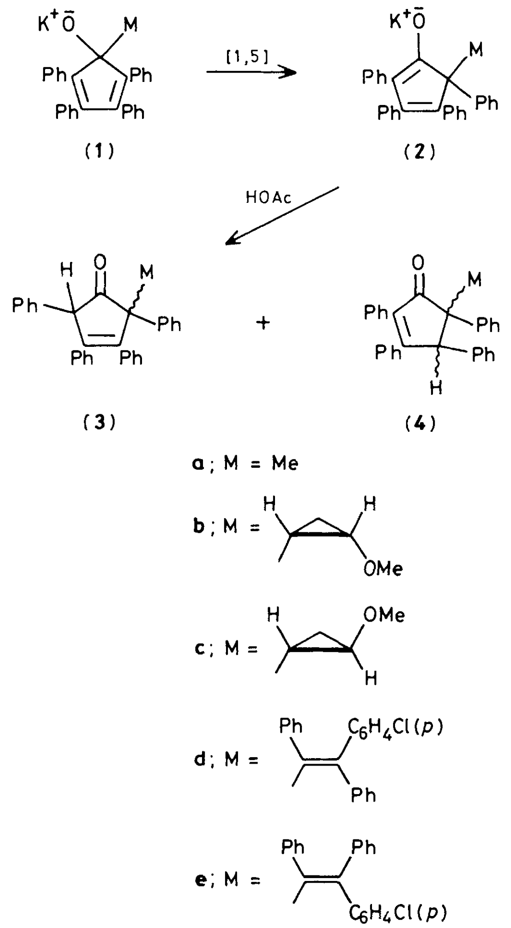
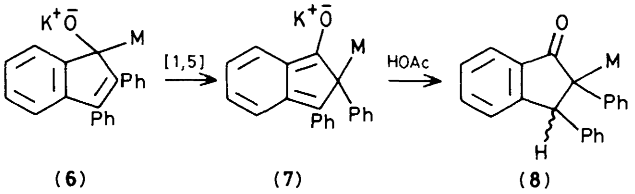
The alkoxides (**1a**—**e**) undergo accelerated 1,5-shifts in hexamethylphosphoric triamide (HMPA) at 20 °C, and the alkoxides (**6a**—**c**) rearrange similarly in HMPA at 80—95 °C; the stereospecificity of the rearrangements and the exclusive formation of 2,2-disubstituted indanones (**8**) from (**6**) testify to the concerted nature of these shifts.

Several pericyclic reactions are dramatically accelerated by placement of an alkoxide substituent at the terminus of a breaking σ-bond.[1] Although these include 1,5-sigmatropic shifts of hydrogen,[1b] attempts to observe accelerated 1,5-shifts of alkyl groups failed.[1b] We describe the observation of accelerated alkyl, vinyl, aryl, and cyclopropyl migration in cyclopentadiene systems together with evidence for the concerted nature of these processes.

The alkoxide (**1a**) (Scheme 1) prepared by reaction of the corresponding alcohol with potassium hydride in hexamethylphosphoric triamide (HMPA) rearranged at 20 °C (30 min) to the red enolate (**2a**) which with acetic acid gave a mixture of the *cis*- and *trans*-β,γ-enones (**3a**) (76%; ratio 1.23 : 1) and one stereoisomer of the α,β-enone (**4a**) (24%). For (**4a**), m.p. 122—124 °C, the chemical shift of the 5-methyl [$\delta(CDCl_3)$ 1.90] and the methine proton [$\delta(CDCl_3)$ 4.58] are in fair



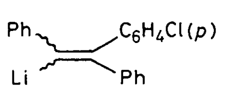
Scheme 1



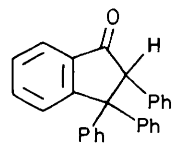
a; M = Ph
b; M = *trans*-propenyl
c; M = *cis*-propenyl

Scheme 2

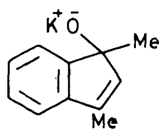
agreement with those [δ(CCl_4) 1.78 and 4.45] erroneously assigned[2] to 4-methyl-2,3,4,5-tetraphenylcyclopent-2-enone. In agreement with the constitution (**4a**) assigned here, treatment of the α,β-enone with KH–HMPA and quenching with acetic acid gave the same mixture as that formed by rearrangement of (**1a**).† Since uncatalysed rearrangement of pentaphenylcyclopentadienol requires[3] heating at 173 °C, and the migratory aptitude of methyl is generally considerably less than that of phenyl,[4] the rearrangement of (**1a**) to (**2a**) at 20 °C represents an acceleration of similar magnitude to that associated with alkoxide substitution in other pericyclic processes.[1]



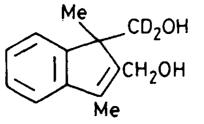
(**5**)



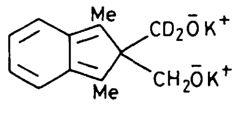
(**9**)



(**10**)



(**11**)



(**12**)

To test the stereochemistry of the rearrangement, *cis*- and *trans*-2-methoxycyclopropyl-lithium[5] were added to tetracyclone and the resulting alcohols (m.p. 198—200 °C and 109—111 °C, respectively) were converted into the alkoxides (**1b**) and (**1c**). In both cases rearrangement was complete in 30 min at 20 °C. ^{1}H N.m.r. spectra showed that the *cis*-(**1b**) and *trans*-(**1c**) alkoxides gave distinct products; (**1b**) gave the four expected β,γ-enones retaining a *cis*-geometry at the cyclopropane ring and no detectable α,β-enones, whilst (**1c**) gave four β,γ-enones and two α,β-enones all of which retained a *trans*-substituted cyclopropane ring.‡

Accelerated vinyl migration is likewise stereospecific. In 1,2-dimethoxyethane the alkoxides (**1d**) and (**1e**) rearranged rapidly (*ca.* 5 min) at 20 °C to distinct β,γ-enones in which the C-2 protons appear at δ 4.60 and 4.65, respectively. Since the *Z*- and *E*-lithiums (**5**) are interconverted rapidly above 0 °C,[6] stereospecific rearrangement of (**1d**) and (**1e**) is unlikely to involve potassium salts related to (**5**) which would be expected to be configurationally more labile. Rearrangement is also unlikely to involve a dissociation–recombination process involving configurationally unstable vinyl radicals.[7]

Rearrangement of the indenyl alkoxides (**6a—c**) (Scheme 2) requires more vigorous conditions (HMPA, 80—95 °C, 2 h) reflecting disruption of aromaticity in the transition states leading to the anions (**7**). Quenching the green enolate (**7a**) (HOAc) gave (**8a**), m.p. 139—141 °C (lit.[8] m.p. 138—139 °C). The product (**9**) which would have been formed *via* a 1,3-shift or a dissociation–recombination process[9] was not detected. Further evidence for concerted rearrangement was obtained by observing rearrangement of (**6b**) and (**6c**) with retention of double bond stereochemistry. In accordance with the lower migratory aptitude of alkyl groups compared with unsaturated groups, (**10**) fails to rearrange even under more vigorous conditions (135 °C, HMPA, 2 h).

The foregoing accelerated 1,5-shifts stand in contrast to the racemisation of (**11**) (KH, THF, 20 °C) which proceeds without positional exchange of CD_2OH and CH_2OH groups

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† On similar treatment and as befits a 4,4-disubstituted cyclopent-2-enone, the compound previously allocated the 5-methyl-2,3,4,5-tetraphenylcyclopent-2-enone structure merely underwent *trans–cis* isomerisation.

‡ The cyclopropyl proton α to oxygen in the *cis*-cyclopropanes appears in the range δ 3.2—3.4 as a td, *J* 6.2 and 3.2 Hz whereas in the *trans*-cyclopropanes it appears at δ 2.65—3.7 as a dt, *J* 6.4 and 3.2 Hz.

which should result from formation of the intermediate (**12**) by an accelerated 1,5-shift; a mechanism of the 'reverse Grignard' type involving an indenyl anion may be favoured in this case.

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