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## 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  $\sigma$ -bond.<sup>1</sup> Although these include 1,5-sigmatropic shifts of hydrogen,<sup>1b</sup> attempts to observe accelerated 1,5-shifts of alkyl groups failed.<sup>1b</sup> 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*- $\beta$ , $\gamma$ -enones (3a) (76%; ratio 1.23:1) and one stereoisomer of the  $\alpha$ , $\beta$ -enone (4a) (24%). For (4a), m.p. 122—124 °C, the chemical shift of the 5-methyl [ $\delta$ (CDCl<sub>3</sub>) 1.90] and the methine proton [ $\delta$ (CDCl<sub>3</sub>) 4.58] are in fair



Scheme 2

agreement with those [ $\delta$ (CCl<sub>4</sub>) 1.78 and 4.45] erroneously assigned<sup>2</sup> to 4-methyl-2,3,4,5-tetraphenylcyclopent-2-enone. In agreement with the constitution (**4a**) assigned here, treatment of the  $\alpha$ , $\beta$ -enone with KH–HMPA and quenching with acetic acid gave the same mixture as that formed by rearrangement of (**1a**).<sup>†</sup> Since uncatalysed rearrangement of pentaphenylcyclopentadienol requires<sup>3</sup> heating at 173 °C, and the migratory aptitude of methyl is generally considerably less than that of phenyl,<sup>4</sup> the rearrangement of (**1a**) to (**2a**) at 20 °C represents an acceleration of similar magnitude to that





(10)

associated with alkoxide substitution in other pericyclic processes.<sup>1</sup>

To test the stereochemistry of the rearrangement, *cis*- and *trans*-2-methoxycyclopropyl-lithium<sup>5</sup> 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. <sup>1</sup>H N.m.r. spectra showed that the *cis*-(**1b**) and *trans*-(**1c**) alkoxides gave distinct products; (**1b**) gave the four expected  $\beta$ ,  $\gamma$ -enones retaining a *cis*-geometry at the cyclopropane ring and no detectable  $\alpha$ ,  $\beta$ -enones, whilst (**1c**) gave four  $\beta$ ,  $\gamma$ -enones and two  $\alpha$ ,  $\beta$ -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  $\beta$ , $\gamma$ -enones in which the C-2 protons appear at  $\delta$  4.60 and 4.65, respectively. Since the Z- and E-lithiums (5) are interconverted rapidly above 0 °C,<sup>6</sup> 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.<sup>7</sup>

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.<sup>8</sup> m.p. 138—139 °C). The product (9) which would have been formed via a 1,3-shift or a dissociation-recombination process<sup>9</sup> 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

<sup>&</sup>lt;sup>†</sup> On similar treatment and as befits a 4,4-disubstituted cyclopent-2enone, the compound previously allocated the 5-methyl-2,3,4,5tetraphenylcyclopent-2-enone structure merely underwent *trans-cis* isomerisation.

<sup>&</sup>lt;sup>‡</sup> The cyclopropyl proton α to oxygen in the *cis*-cyclopropanes appears in the range  $\delta$  3.2—3.4 as a td, *J* 6.2 and 3.2 Hz whereas in the *trans*-cyclopropanes it appears at  $\delta$  2.65—3.7 as a dt, *J* 6.4 and 3.2 Hz.

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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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