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THE BEHAVIOUR IN ACID OF SOME ALKYLCYCLOHEXA-2, 5-DIENONES

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We report basicity measurements, and kinetics of dienone-phenol rearrangements of 3, 4, 4-trimethylcyclohexa-2, 5-dienone (I), and the analogous 3-ethyl-4, 4-dimethyl-(II), and 3, 4, 4, 5-tetramethyldienone (III).[1]

Dienone (I) rearranges in aqueous sulphuric or perchloric acid, with pseudo first-order kinetics, giving pure 3, 4, 5-trimethylphenol (93%) and no detectable 2, 3, 4-trimethylphenol. Dienone (II) rearranges similarly to 3-ethyl-4, 5-dimethylphenol (98% pure) and ca 1% each of two other products.

Kinetics and basicity data were obtained from u.v. spectra of the dienones in acid solution, using the equations given previously,[2] the kinetics being confirmed by n.m.r. spectra. The protonation of all three dienones (Table), like the 4, 4-dimethyl analogue (IV),[2] follows the amide acidity function[3] H_A. This is shown by "m" values (Eqn. 1) close to 1.0; the pK values are the closest estimates of thermodynamic values.[4] Introduction of a 3-methyl group into 4, 4-dimethylcyclohexa-2, 5-dienone increases its basicity by a factor of ca 2.3, a 3-ethyl by ca 2.8, and 3- and 5-methyl groups by ca 10 times.

Rate constants for rearrangement of (I) and (II) in aq. H_2SO_4 at 25.3° were converted to k_1 values, which are rate constants for rearrangement of the pure cations. Plots of $\log_{10}k_1$ against H_A or H_0 are straight lines (Eqns. 2 and 3). In a given medium the cation of (II) rearranges ca 2.0 times faster than that of (I). The earlier treatment[2] shows $\log f_{\ddagger}/f_{BH^+}$ to change with the medium just one third as fast as does H_A. Bunnett and Olsen plots[5] of the rate data give ϕ values −0.20 for (I) and −0.18 for (II).

Since migration from C4 *via* C3 to C2 is not observed for (I) and (II), dienone (III) should rearrange with difficulty. In fact (III) is <0.3% reacted after 14 days in 78% H_2SO_4 at 25.3°C; the half-lives of (I), (II) and (IV) under these conditions are *ca* 450, 250 and 20 minutes. Reasons for this stability, and mechanistic comparisons with further monocyclic and other cyclohexadienones will be discussed in our full paper.

Table. Protonation of cyclohexa-2,5-dienones[a]

Substituents	pK^b	"m" value[b]
3,4,4-Trimethyl-(I)	-2.01 ± 0.05	1.09 ± 0.04
3-Ethyl-4,4-dimethyl-(II)	-1.92 ± 0.06	1.12 ± 0.06
3,4,4,5-Tetramethyl-(III)	-1.38 ± 0.02	1.05 ± 0.05

[a] Obtained at 240, 260 and 305 or 320 nm. [b] See Eqn. 1.

Eqn. 1 $\log_{10}[B]/[BH^+] = m(H_A - pK)$

Eqn. 2, for (I) $-\log_{10}k_1 = (3.04 \pm 0.02) + (H_A + 4.00)(0.34 \pm 0.03)$

$= (3.07 \pm 0.01) + (H_0 + 6.00)(0.18 \pm 0.01)$ [min.$^{-1}$ units]

Eqn. 3, for (II) $-\log_{10}k_1 = (2.70 \pm 0.01) + (H_A + 4.00)(0.33 \pm 0.02)$

$= (2.74 \pm 0.01) + (H_0 + 6.00)(0.17 \pm 0.01)$

References

[1] New compounds have satisfactory spectra and analytical data.

[2] K. L. Cook and A. J. Waring, Tetrahedron Letters, 1971, 1675.

[3] K. Yates, J. B. Stevens and A. R. Katritzky, Canad. J. Chem., 42, 1957 (1964).

[4] The adherence to the H_A scale is not general: we have other dienones with similar pK values which do not follow this scale.

[5] J. F. Bunnett and F. P. Olsen, Canad. J. Chem., 44, 1917 (1966).