The Migratory Aptitude of the s-Butyl Group in a Cationic Rearrangement

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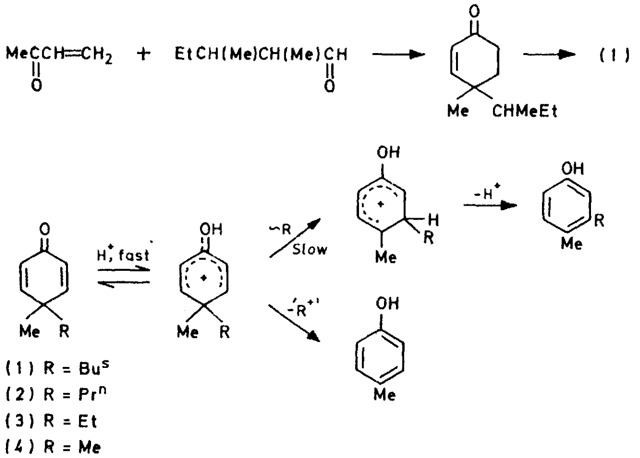
The acid-induced dienone–phenol rearrangement of 4-s-butyl-4-methylcyclohexa-2,5-dienone (1) gives 3-s-butyl-4-methylphenol, and 4-methylphenol by fragmentation. Kinetic measurements in aqueous and in methanolic aqueous sulphuric acid, and product studies in the latter, allow the migratory aptitude of the s-butyl group in this cationic rearrangement to be estimated at *ca.* 7 000 relative to methyl as unity and n-propyl as 50.

We have previously shown that the migratory aptitudes $(\text{m.a.})_R$ of groups R can be found from their rates of migration in dienone–phenol rearrangements of cyclohexadienones of type (1)—(4). These values of $(\text{m.a.})_R$ are free of ambiguity caused by conformational and other effects, and were reported for methyl (as the standard for comparison), ethyl, and n-propyl groups.[1] We now report the value for the s-butyl group, which is taken as a typical secondary alkyl group, and is of additional interest as a rough analogue of the C-9 atom which migrates in the dienone–phenol rearrangement of many steroidal 1,4-dien-3-ones.[2]

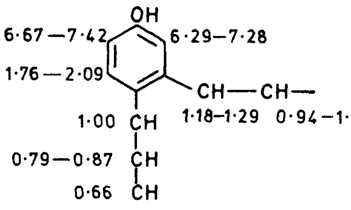


Scheme 1

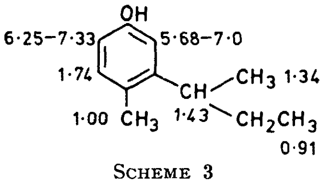
The necessary 4-s-butyl-4-methylcyclohexa-2,5-dienone (1) was prepared by dichlorodicyanobenzoquinone dehydrogenation of the corresponding cyclohex-2-enone, which was made by base-induced condensation of methyl vinyl ketone with 2,3-dimethylvaleraldehyde (Scheme 1).

Products of Rearrangement of (1).—Rearrangement of the dienone (1) in aqueous sulphuric acid and methanolic aqueous sulphuric acid of various concentrations showed the formation of only two products. Because the dienone and products were only very slightly soluble in aqueous acid our main studies used one volume of methanol and three volumes of aqueous sulphuric acid to effect solution. One product was shown by g.l.c., i.r., and n.m.r. spectroscopy, and by isolation, to be 4-methylphenol, produced by formal loss of an s-butyl cation from the protonated dienone (see later). The other product was an s-butyl(methyl)phenol, shown to be 3-s-butyl-4-methylphenol. The coupling pattern and coupling constants in its ^{1}H n.m.r. spectrum are consistent only with a 1,3,4-trisubstituted benzene structure. The chemical shifts of the aromatic protons are correct for a 3,4-dialkylphenol structure, and agree closely with those reported for analogous phenols.[1] To distinguish between the two possible isomers we used the lanthanide-induced ^{1}H n.m.r. shifts (LSIS) brought about by the addition of Eu(fod)_3, which we have shown to be valuable in determining the substitution pattern in alkylphenols. The protons on the aromatic ring and on the alkyl groups show larger downfield shifts as they become closer to the phenolic hydroxy function. In particular, if the proton on the carbon atom which is attached to C-4 of the aromatic ring is arbitrarily given an LSIS of unity, the scaled LSIS of the other protons[1] are as shown in Scheme 2. The LSIS pattern observed for the rearranged phenol is shown in Scheme 3, and is consistent only with the 3-s-butyl-4-methylphenol structure. In particular, the apparent sextet assigned to the tertiary hydrogen atom of the s-butyl group has an LSIS significantly greater than that of the aromatic-attached 4-methyl group's singlet n.m.r. peak. There was no ^{1}H n.m.r. evidence of tertiary butylphenols which might arise by re-butylation by a rearranged butyl cation of the 4-methylphenol.

Quantitative studies of reactions conducted in a range of strengths of aqueous methanolic sulphuric acids, for at least 11 half-lives, showed the rearrangement to give the 3-s-butyl-4-methylphenol and 4-methylphenol in the molar ratio (52 ± 6) : (48 ± 6). In another series of experiments the dienone was allowed to react for periods



Scheme 2



Scheme 3

from *ca.* 0.5 to 6.3 half-lives. The ratio of products was uniformly (41 ± 4) : (59 ± 4), showing that the product ratio did not vary with the extent of reaction and, particularly, that the 4-methylphenol does not arise by debutylation of the s-butyl(methyl)phenol. We believe the agreement between the two ratios is satisfactory, considering the experimental problems involved in measuring them accurately.

Kinetics.—Two series of kinetic measurements were made. In the first, reaction of the dienone in a range of aqueous sulphuric acids was followed by u.v. spectrophotometry. The observed rate constants, k_{obs}, for the clean first-order reaction were compared with those previously obtained [1] under the same conditions for the analogous 4-methyl-4-n-propyldienone (2). This allows a ' stepwise ' comparison to be made with the rate constants for the 4,4-dimethyldienone (4). However, for accurate migratory aptitudes to be derived one needs product ratios to be available under the same conditions so that the total rate can be dissected to yield the rate due to rearrangement rather than fragmentation. Because the product studies were more satisfactorily achieved using methanolic aqueous acid we also measured the rate constants, in methanolic aqueous sulphuric acids, for both the 4-s-butyl-4-methyldienone (1) and the 4,4-dimethyldienone (4) under identical conditions. This allows a direct, rather than ' stepwise ', comparison of rates. Rate data are given in Tables 1 and 2.

Kinetics in aqueous acid. A plot of $\log_{10} k_{\mathrm{obs}}$ against the amide activity function, H_{A}, for the butyl methyl dienone is linear according to equation (1). This acidity function is used because it is the appropriate one for

$$\text{For (1)} \log k_{\mathrm{obs}} = -H_{\mathrm{A}}(1.42 \pm 0.05) - 3.91 \pm 0.06 \quad (r\ 0.996) \qquad (1)$$

describing the protonation behaviour of other analogous cyclohexadienones which we have previously studied [1,3] [see equation (3)]. The kinetic scheme established previously is expressed by equations (4)—(8), which simplify to (9) when the dienone is not appreciably protonated. This predicts the linearity between $\log k_{\mathrm{obs}}$ and H_{A} which is found in equation (1). A similar plot for the 4-methyl-4-n-propyldienone (2), over the same range of acidity, is linear, according to equation (2).

$$\text{For (2)} \log k_{\mathrm{obs}} = -H_{\mathrm{A}}(1.37 \pm 0.04) - 6.66 \pm 0.05 \quad (r\ 0.998) \qquad (2)$$

The two lines are essentially parallel, with the butyldienone (1) reacting faster than the propyl analogue (2) by a uniform factor of (660 ± 30) in the acidity range common to both. Since the latter reacts faster than the dimethyl analogue (4) by a factor of (21.8 ± 0.8), the butyldienone is seen to react faster than the dimethyl analogue by a crude factor of (14 400 ± 1 200) in aqueous sulphuric acid.

TABLE 1

Kinetics for compounds (1) and (2) in aqueous sulphuric acid at 25.0 °C; u.v. at 246 or 245 nm

Acid (wt. %)	$-H_{\mathrm{A}}$ [a]	$-\log k_{\mathrm{obs}}/\mathrm{s}^{-1}$ for (1) [b]	$-\log k_{\mathrm{obs}}/\mathrm{s}^{-1}$ for (2) [c]
6.0	0.00	3.851 3.795	6.54
10.6	0.43	3.382	6.11
14.4	0.68		5.83
14.8	0.71	3.054	
21.6	1.06	2.319	
21.8	1.07	2.435	5.22
29.2	1.46	1.857	4.78
		1.869	
33.8	1.69	1.405	4.32
37.8	1.88	1.118	
		1.213	

[a] Values of H_{A} are taken from K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957. [b] ±0.006. [c] ±0.005 to ±0.001; further kinetics are reported in ref. 1.

TABLE 2

Kinetics for compounds (1) and (4) in methanolic aqueous sulphuric acid [a] at 25.0 °C; u.v. at 239 nm

Acid (wt. %)		$k_{\mathrm{obs}}/\mathrm{s}^{-1}$ for (1) [b]	$k_{\mathrm{obs}}/\mathrm{s}^{-1}$ for (4) [c]	Ratio (1) : (4)
A	B			
23.4	19.1	8.98×10^{-4}	1.00×10^{-7}	8.98×10^{3}
32.0	26.3	3.10×10^{-3}	3.70×10^{-7}	8.38×10^{3}
40.3	33.5	1.11×10^{-2}	1.36×10^{-6}	8.16×10^{3}

Mean ratio $(8.6 \pm 0.4) \times 10^{3}$

[a] One volume of methanol is mixed with three volumes of aqueous H_2SO_4 of strength A to give a final mixture of strength B. [b] $\pm 0.02 \times 10^{-3}$—0.01×10^{-2}. [c] $\pm 0.08 \times 10^{-7}$—0.02×10^{-6}.

Kinetics in methanolic acid. Direct comparison of dienones (1) and (4) gives a factor of $(8.6 \pm 0.4) \times 10^{3}$ in reactivity, in 1 : 3 methanol–aqueous sulphuric acid of known strength. As far as we are aware there has been no determination of either the Hammett acidity function, H_0, or of the amide acidity function, H_{A}, for methanolic sulphuric acids, and so no test of the regularity of kinetics according to equations such as (1) and (2) can be made. If (41 ± 4)% of the rate for the butyldienone is due to butyl migration, and 50% of the rate for the dimethyldienone is due to migration of a single methyl group, the ratio of rates for (1) and (4) must be multiplied by (0.82 ± 0.08) to give the migratory aptitude of s-butyl relative to methyl as (7 000 ± 1 000). If the proportion of the total rate of (1) which leads to s-butyl migration is taken to be the mean of the quoted values 0.52 and 0.41, *i.e.* 0.47, the migratory aptitude would assume the value (8 100 ± 1 300). It is clear that, irrespective of the exact value, the m.a. of the s-butyl group is very high, and is even higher than the lower limit quoted previously for the t-butyl group.[4]

The relatively rapid loss of the s-butyl group which is responsible for the formation of 4-methylphenol from the s-butyldienone (1) is not unexpected. In rearrangements of 4-ethoxycarbonyl-4-isopropylcyclohexa-2,5-dienone in trifluoroacetic acid the isopropyl group was always lost, and trapped as isopropyl trifluoroacetate.[5] Similarly, 4-benzyl-4-ethoxycarbonylcyclohexa-2,5-dienone underwent loss of the benzyl group, with 50% of recombination of the cleavage products to form 2-benzyl-4-ethoxycarbonylphenol.[5] We detected no analogous formation of butyl(methyl)phenols. Reaction of 4-methyl-4-isopropyl-2,6-di-t-butylcyclohexa-2,5-dienone in sulphuric acid–acetic acid gave fragmentation to

4-methyl-2,6-di-t-butylphenol,[6] and other analogous fragmentations with the formal loss of a secondary alkyl cation are known.[7] The group which is lost is trapped by nucleophiles, or is deprotonated to form an alkene.[7] Loss of the t-butyl group is facile when 4-t-butyl-substituted cyclohexa-2,5-dienones, and 6-t-butyl-substituted cyclohexa-2,4-dienones are treated with acid,[8] and this suggests that measurements of the migratory aptitudes of tertiary alkyl groups by the method reported here would be very difficult.

EXPERIMENTAL

4-s-Butyl-4-methylcyclohex-2-enone.—Aqueous 90% methyl vinyl ketone (17 cm^3, 15.3 g, 0.219 mol), and 2,3-dimethylvaleraldehyde (30 cm^3, 25 g, 0.219 mol), water (20 cm^3), and methanol (45 cm^3) were mixed to give a homogeneous solution. Potassium hydroxide (1.0 g) was dissolved in methanol (4.5 cm^3), warmed to 45 °C, and stirred whilst the above mixture was added dropwise over *ca.* 20 min. During the addition the mixture was warmed to 70 °C. After 60 min further heating on a boiling-water-bath the mixture had separated into two layers. Salt was added, and extraction with ether (2 × 100 cm^3) was followed by washing of the ether layers (H_2O), drying ($CaSO_4$), removal of solvent, and distillation at 124—128°, up to 132—139° at 12 mmHg. The fractions (7.8 g, 22%) were $\geqslant$95% pure. Distillation through a spinning-band column gave the product (7.50 g), b.p. 80—95° at 1.5 mmHg, also $\geqslant$95% pure. The fraction, b.p. 93—94° at 1.5 mmHg, was *4-s-butyl-4-methylcyclohex-2-enone*,* >99% pure (g.l.c. on a 10% SE 30 column at 150°), $\nu_{max.}$ (liquid film), 1 665sh, 1 673sh, 1 678, and 1 688 (st doublet) cm^{-1}, τ (CCl_4) 8.89 (s, 4-Me), 7.68 (2 H, m, 6-CH_2), 4.29 (1 H, d, *J* 10.0 Hz, 2-H), 3.44 (1 H, d, *J* 10.0 Hz, 3-H), 7.8—8.8 (5 H, m, 5-CH_2 and side chain $CHCH_2$), and 9.03—9.12 (6 H, m, side chain C*Me*CH_2*Me*) (Found: C, 79.3; H, 10.9. $C_{11}11_{18}O$ requires C, 79.5; H, 10.9%).

4-s-Butyl-4-methylcyclohexa-2,5-dienone.—The foregoing cyclohexenone (3.0 g, 0.018 mol) in dried benzene (70 cm^3) was heated at reflux with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (6.0 g, 0.026 mol) during 35 h. Analysis by g.l.c. (25% PEGA column at 180°) showed $\geqslant$94% conversion. The product was concentrated under vacuum and the residue extracted with light petroleum (b.p. 40—60°) (6 × 25 cm^3). The petroleum extract was washed with aqueous sodium sulphite, then water, dried ($MgSO_4$), and evaporated. A second preparation was combined and distilled to give the *dienone* (1.56 g, 23.7%), b.p. 121—122° at 15 mmHg, >99.5% pure by g.l.c., $\nu_{max.}$ (liquid film) 1 600w, 1 630m, 1 660, 1 670s, and 1 715w cm^{-1}, $\lambda_{max.}$ (95% EtOH) 240 nm (ε 14 900); $\lambda_{max.}$ (H_2O) 245.5 nm (ε 14 200); τ(CCl_4) † 8.77 (3 H, s, 4-Me), 3.89 (2 H, d, *J* 10 Hz, 2- and 6-H), 3.31 (2 H, d, *J* 10 Hz, 3- and 5-H), and 8.4—8.6 and 9.0—9.2 (9 H, m, Bu^s) (Found: C, 80.2; H, 9.6%; *m/e*, 164.117 ± 0.005. $C_{11}H_{16}O$ requires C, 80.4; H, 9.8%; *M*, 164.120).

Rearrangement of 4-s-Butyl-4-methylcyclohexa-2,5-dienone.—The dienone (50 mg) was treated with 21.8% sulphuric acid (19 cm^3) and methanol (6 cm^3) (to improve solubility) for 2 h at 23.5° C.‡ Iced water (20 cm^3) was added, and the mixture extracted with ether (4 × 25 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to give a mixture of two phenols in about equal amounts. Separation by preparative g.l.c. of a larger sample (25% PEGA column; 180°) gave the two products, identified as 4-methylphenol and 3-s-butyl-4-methylphenol. 4-Methylphenol had τ($CDCl_3$) 7.72 (3 H, s, 4-Me), 5.35 (1 H, s, OH), 3.27 (2 H, d, *J* 8.5 Hz, 2- and 6-H), and 2.85 (2 H, d, *J* 8.5 Hz, 3- and 5-H) and had i.r. and g.l.c. properties (on PEGA and 5% Versamid 930 columns) identical with those of resublimed commercial 4-methylphenol. The 3-s-butyl-4-methylphenol had τ($CDCl_3$) 9.13 (3 H, t, *J* 8 Hz, CCH_2*Me*), 8.83 (3 H, d, *J* 7 Hz, CH*Me*CH_2), 8.48 (2 H, quintet, *J* 8 Hz, CHMeC*H*$_2$Me), 7.77 (3 H, s, 4-Me), 7.17 (1 H, sextet, *J* 7 Hz, C*H*MeCH_2), 5.40 (1 H, s, OH), 3.46 (1 H, dd, *J* 8 and 3 Hz, 6-H), 3.32 (1 H, d, *J* 3 Hz, 2-H), and 3.00 (1 H, d, *J* 8 Hz, 5-H); $\nu_{max.}$ (CCl_4) 1 165, 1 190s, 1 260, 1 290s, 1 465, 1 508, 1 590, 1 613s, 2 880, 2 935, 2 970s, 3 030w, and 3 623s cm^{-1} (Found: *m/e*, 164.120 ± 0.005. $C_{11}H_{16}O$ requires *M*, 164.120). The pattern of the n.m.r. coupling is consistent only with a 1,3,4-trisubstituted benzene structure, and the chemical shifts agree well with those for other 3,4-dialkylphenols.[1]

Lanthanide-shift Studies on the s-Butyl(methyl)phenol.—To the phenol (5.0 mg) in $CDCl_3$ (1.0 cm^3) was added $Eu(fod)_3$ in small, weighed portions. The shifts of the individual n.m.r. peaks were followed. At an equimolar ratio of $Eu(fod)_3$ to the phenol the downfield shifts, and the relative shifts, taking that of the Ar*Me* peak as 1.0 (given in parentheses) were: 2-H, 1.31—1.61 p.p.m. (5.68—7.0); 4-Me, 0.23 p.p.m. (1.00); 5-H, 0.40 p.p.m. (1.74); 6-H, 1.44—1.69 p.p.m. (6.25—7.33); C*H*MeEt, 0.33 p.p.m. (1.43); CH*Me*Et, 0.31 p.p.m. (1.34); CHMeCH_2*Me*, 0.21 p.p.m. (0.91).

Quantitative Dienone–Phenol Rearrangements of 4-s-Butyl-4-methylcyclohexa-2,5-dienone.—Samples of the dienone (*ca.* 3.0 or 10.0 mg) were accurately weighed and treated with sulphuric acid (3.75 cm^3) of 6.1, 21.8, or 33.6% by weight, and methanol (1.25 cm^3) thermostatted at 23.5 °C. After the desired time the mixtures were quenched by adding to iced water (10 cm^3), extracted with dichloromethane (4 × 15 cm^3), and the extracts dried ($CaSO_4$) and concentrated to *ca.* 1 cm^3. This solution was diluted to 10.00 cm^3 with spectroscopic grade iso-octane. The mixtures were analysed by g.l.c., using a 5% Versamid 930 column at 180° to determine unchanged dienone and 4-methylphenol, and at 220° to determine the s-butyl(methyl)-phenol. The detector response to the individual compounds was calibrated using g.l.c.-pure specimens. Only unchanged dienone, 4-methylphenol, and 3-s-butyl-4-methylphenol could be detected. The butyl(methyl)phenol yield was (41.0 ± 4.0) mole % of the sum of butyl(methyl)-phenol and 4-methylphenol, at reaction times of 0.49—6.34 half-lives, in the experiments using 21.8% sulphuric acid. The total estimate of these phenols and recovered dienone ranged from 105 to 68% of the dienone used. These data are taken to show that the two phenolic products are both formed by reactions having the same kinetic order (*i.e.* first order). Reaction for at least 11 half-lives in the

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* Detailed analysis of the n.m.r. spectra in CCl_4 and C_6D_6 suggested this to be a mixture of diastereoisomers (in *ca.* 57 : 43 ratio), as a result of the chiral centres at C-4 and in the s-butyl group. There are two sets of signals for the 3-H signals, separated by 0.03 p.p.m. in CCl_4, each of which couples with *J* 10.0 Hz to 2-H, and with *J* 1.5 Hz to a 5-H.

† The olefinic protons give rise to an AA′BB′ system, whose cross-coupling constants were not examined in detail.

‡ Under these conditions the half-life was determined as 21.4 min.

6.1 and 33.6% acids gave (52 ± 6)% of the butyl(methyl)-phenol in the phenolic mixture, with *ca.*96% total recovery. We believe this ratio is not seriously at variance with the earlier one, and that there is no evidence for debutylation of the initially formed 3-s-butyl-4-methylphenol.

Kinetic Measurements.—U.v. spectroscopy was used to determine the kinetics of reaction of the dienone, using Pye–*Unicam SP 1800* and SP 8–100 spectrometers with cell holders and all solutions thermostatted at 25 ± 0.1 °C. Two techniques were used. For slow reactions a stock solution of the dienone in water was placed in a 25 cm^3 volumetric flask and made up to volume rapidly with sulphuric acid of known concentration. The final concentration of acid was calculated by equations similar to those given earlier.[9] After rapid mixing the solution was placed into the cells in the spectrometer. For rapid reactions the technique had to be modified. A small glass adapter was made, of inverted shape. The vertical part had tapered joints, that at the bottom mating with a tapered socket in the u.v. cell, and that at the top took a glass stopper. The inclined part of the adaptor was closed at the lower end, and had injected into it a known volume (usually 0.15 cm^3) of the stock solution, using a 250 μl Hamilton syringe. The u.v. cell had 3.00 cm^3 of acid placed in it, and the whole was thermostatted in the u.v. machine. The cell + adaptor was then tipped about six times to allow mixing and draining back into the cell, with the timer set at the moment of first mixing. Using this technique the u.v. absorbance could be monitored reliably within 9 s of mixing. The acid strengths were corrected for dilution by stock solution. Reproducible kinetic plots of log $(D - D_\infty)$ against time, free of curvature for the first six half-lives, were obtained for reactions with half-lives as low as 9 s. The results are shown in Tables 1 and 2; they were obtained from the plots of log $(D - D_\infty)$ against time, and from plots according to Swinbourne's method.[10]

APPENDIX

$$\underset{\text{B}}{\text{Dienone}} \underset{\text{fast}}{\overset{\text{H}^+}{\rightleftharpoons}} \underset{\text{BH}^+}{\text{Cation}} \longrightarrow \text{Transition state} \longrightarrow \text{Product}$$

SCHEME 4

For a reaction which follows Scheme 4 (*A*-1 mechanism) and whose protonation equilibrium follows equation (3), with acidity $(H_\text{A})_{\frac{1}{2}}$ at half-protonation, equations (4)—(6) apply.[1] We have found the linear equation (7) to relate log k_1, the rate constant for the slow step of the reaction, to H_A. At 'low' acidities, where the dienone is not much protonated, $[\text{B}]/[\text{BH}^+] \gg 1$, and equation (6) simplifies to (8), which combines with equation (3), to give (9) [*i.e.* equations (1) and (2)].

The parallelism of the straight line plots [equations (1) and (2)] for dienones (1) and (2) shows that their values of $(c - m_\text{A})$ are equal. The quantity c is a kinetic parameter, whereas m_A is a basicity parameter. We showed earlier[1] that dienones (2)—(4) have essentially identical values for m_A and $(H_\text{A})_{\frac{1}{2}}$, and we assume that this is true for (1) also, and that it is true in methanolic aqueous acid as well as for aqueous acid.* If this is so, the values of c are equal for (1) and (2), even though both are composites for the rearrangement and fragmentation of the dienone cations, which appear to change equally with acidity. An alternative possibility, that the cation reacts by a single, rate-determining (rearrangement) path, followed by partial debutylation, is ruled out by the product studies. The constant ratio of rates for dienones (1) and (4) in methanolic aqueous acid is taken to parallel that for (1) and (2) in aqueous acid and, with the previous assumptions regarding m_A, c, and $(H_\text{A})_{\frac{1}{2}}$, equals the ratio between the respective $k_1{}^0$ values, and thus the migratory aptitudes.

$$\log\,[\text{BH}^+]/[\text{B}] = m_\text{A}[(H_\text{A})_{\frac{1}{2}} - H_\text{A}] \qquad (3)$$

$$\text{d[stoicheiometric dienone]}/\text{d}t = -k_\text{obs}\text{[stoicheiometric dienone]} \qquad (4)$$

$$\therefore\ \text{d}[\text{B} + \text{BH}^+]/\text{d}t = -k_\text{obs}[\text{B} + \text{BH}^+] = -k_1[\text{BH}^+] \qquad (5)$$

$$\therefore\ k_1 = k_\text{obs}(1 + [\text{B}]/[\text{BH}^+]) \qquad (6)$$

$$\log k_1 = cH_\text{A} + \log k_1{}^0 \qquad (7)$$

$$\text{When } [\text{B}]/[\text{BH}^+] \gg 1,\ k_1 = k_\text{obs}[\text{B}]/[\text{BH}^+] \qquad (8)$$

$$\therefore\ \log k_\text{obs} = \log k_1{}^0 + m_\text{A}(H_\text{A})_{\frac{1}{2}} + H_\text{A}(c - m_\text{A}) \qquad (9)$$

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* Support for these assumptions is partly available from our work in ref. 9 and, more strongly, from studies of closely related cyclohexenones which are not complicated by rearrangements. In the latter, the p*K* values of 3-methylcyclohex-2-enone, 3,5-dimethylcyclohex-2-enone, 3-methyl-3,4,5,6,7,8-hexahydronaphthalen-2(4a*H*)-one, and four analogously constituted steroidal 4-en-3-ones were all essentially equal (2.76 ± 0.04—2.88 ± 0.03) in perchloric acid and in sulphuric acid (2.79—2.92), with values of m_A all in the range 0.97—1.03.[11] The structural changes in both series are more profound than in the dienone series (1)—(4), but are electronically similar, and are equidistant from the basic centre, the carbonyl group.

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