Kinetics of the Dienone–Phenol Rearrangement of Some 4,4-Dimethylcyclohexa-2,5-dienones

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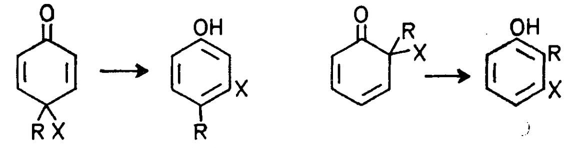
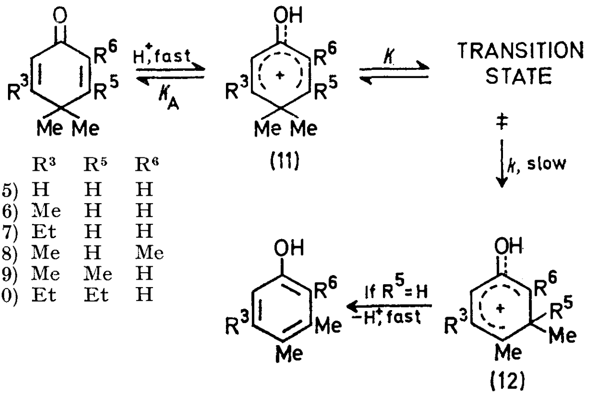
The kinetics of the dienone–phenol rearrangements of 4,4-dimethyl-, 3,4,4-trimethyl-, 3-ethyl-4,4-dimethyl-, 2,4,4,5- and 3,4,4,5-tetramethyl-, and 3,5-diethyl-4,4-dimethylcyclohexa-2,5-dienones have been measured in sulphuric and perchloric acid solutions at 25 °C, and the products identified. The reaction is interpreted in terms of an *A* 1 mechanism, and allows the transition state acidity function behaviour to be determined. The effects of substitution on the rates of rearrangement are discussed.

Dienone–phenol rearrangements, in which cyclohexa-2,5- or -2,4-dienones of types (1) and (2) are treated with acidic reagents to give phenolic products (3) and (4), or their *O*-acyl derivatives have been extensively studied.[1] However, with few exceptions,† mechanistic conclusions have been based solely on product studies. We now report kinetic studies of the rearrangements of a series of alkyl substituted monocyclic cyclohexa-2,5-dienones (5)—(10) in which methyl groups migrate.‡ Later reports will relate to more complex substrates, including compounds with different migrating groups.



(1) (2) (3) (4)



	R³	R⁵	R⁶
(5)	H	H	H
(6)	Me	H	H
(7)	Et	H	H
(8)	Me	H	Me
(9)	Me	Me	H
(10)	Et	Et	H

(11) (12)

Scheme 1

It is generally assumed,[1] and our results help to prove the assumption, that the rearrangement of a dienone such as (5) to the phenol occurs by a unimolecular alkyl migration from C(4) to C(5) in the dienone monocation. The cation has been shown to have the carbonyl oxygen protonated structure of type (11) for all the compounds reported here, and others.[8] The kinetic scheme for such an *A* 1 reaction is shown in Scheme 1, which assumes that deprotonation of the rearranged cation (12) to phenol is rapid if $R^5 = H$.

The observed rate of rearrangement in a given acid depends on (i) the concentration of cation (11) and (ii) its propensity to rearrange. Data on factor (i) are available from the p*K* studies reported in the preceding paper.[9] Factor (ii) depends on both the inherent reactivity of the cation, controlled by its substitution pattern, and on the medium. To disentangle these, kinetic measurements for each compound were made in aqueous sulphuric acids of various concentrations ranging as far as possible from those in which the dienone is unprotonated to those in which it is completely protonated. The limits are set by kinetics which are either too slow or too fast to measure accurately. Less extensive measurements were also made in perchloric acids. Product studies allow dissection of the rate constants for substrates which can rearrange to more than one product.

EXPERIMENTAL

The samples and instruments were those reported in the preceding paper.[9] U.v. spectra of solutions of known concentration were recorded at known times and the optical densities D at selected wavelengths were determined. The spectroscopic rate constant k_{obs} [see equation (1)] and optical density D_0 at the time of mixing were obtained using equation (2) and graphical and least-squares treatment of the data. The D_0 values were used in the basicity determinations of ref. 9. Values of D_∞ were normally determined experimentally after many half-lives. In the most concentrated acids where the optical density sometimes did not reach a constant low value (because of slow further reactions of the product phenols) an iterative technique

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† For studies of spiro[4,5]deca-6,9-dien-8-one and its 6-methoxy-, 6-methyl-, and 7-methyl-derivatives in a series of dilute sulphuric acids in 80% methanol, see ref. 2; for spiro-[5,5]undeca-1,4-dien-3-one, see ref. 3. Since our studies on (5) similar work in sulphuric [4,5] and perchloric acid [5b,6] has been reported.

‡ For preliminary communications of parts of this work, see ref. 7.

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was used to give D_∞. The kinetics were always cleanly pseudo-first-order over at least three half-lives.

Applying transition-state theory to Scheme 1 gives equation (3), where [‡] and [BH$^+$] are the molar concentrations of transition-state and cation (11), respectively. Thus k_1 is the first-order rate constant for conversion of cation

$$\frac{\mathrm{d}}{\mathrm{d}t}\,[\text{Stoicheiometric dienone}] = -k_{\text{obs}}\,[\text{Stoicheiometric dienone}];$$

$$\frac{\mathrm{d}[\mathrm{BH}^+]}{\mathrm{d}t} = -k_{\text{obs}}\,[\mathrm{BH}^+];\ \ \mathrm{d}[\mathrm{B}] = -k_{\text{obs}}\,[\mathrm{B}] \qquad (1)$$

$$\log\,(D_t - D_\infty) = \log\,(D_0 - D_\infty) - \frac{k_{\text{obs}}\,t}{2{\cdot}30} \qquad (2)$$

(11) into (12). The Brönsted equation gives equation (4); combination of equations (1) and (3) gives equation (5).

$$\text{Rate} = \frac{-\mathrm{d}}{\mathrm{d}t}\,[\mathrm{B} + \mathrm{BH}^+] = \frac{\mathrm{d}}{\mathrm{d}t}\,[\text{Product}] = k[\ddagger] = k_1\,[\mathrm{BH}^+]. \qquad (3)$$

$$\log k_1 = \log k_0 + \log\frac{f_{\mathrm{BH}^+}}{f_\ddagger},\ \text{where } f \text{ are activity coefficients} \qquad (4)$$

$$k_1 = k_{\text{obs}}\left(1 + \frac{[\mathrm{B}]}{[\mathrm{BH}^+]}\right) \qquad (5)$$

Values of k_{obs} and k_1 obtained using equation (5) and the raw (rather than smoothed) values of [B]/[BH$^+$] used in the preceding paper [9] are in Tables 1 to 5. The tetramethyldienone (9) rearranges so slowly that considerably less than 1% change could be detected in 20 days at 25 °C and the maximum value for $k_{\text{obs}} = k_1$ in Table 5 is calculated on this basis; the analogue (10) was measured only in one acid.

TABLE 1

Kinetics for (5) in aqueous sulphuric acid or perchloric acid * at 25 °C; u.v. at 240 and 260 nm; k in s^{-1}

Acid, wt. %	$-H_0$	$-H_A$	$-\log k_{\text{obs}}$ [a]	$-\log k_1$ [b]
43·5	2·71	2·16	4·836	4·414
48·3	3·16	2·39	4·638	4·331
50·4	3·42	2·52	4·415	4·188
51·7	3·57	2·60	4·387	4·173
53·5	3·75	2·70	4·258	4·098
56·0	4·07	2·86	4·095	3·978
57·2	4·17	2·91	4·057	3·948
60·0	4·49	3·09	3·976	3·920
64·5	5·02	3·37	3·771	3·749
66·9	5·35	3·54	3·662	*d*
68·4	5·55	3·63	3·564	*d*
71·1	5·96	3·82	3·430 [c]	*d*
71·2	6·00	3·84	3·475 [c]	*d*
75·1	6·58	4·15	3·348 [c]	*d*
77·7	7·06	4·44	3·258 [c]	*d*
50·7 *	3·60	2·82	3·865	3·701
55·4 *	4·35	3·14	3·513	3·427
62·8 *	5·80	*ca.* 3·65	2·976	*d*

[a] Standard deviation 0·002 to 0·008. [b] Standard deviation 0·004 to 0·01. [c] Standard deviation 0·01. [d] As $-\log k_{\text{obs}}$.

Rearrangement of 4,4-*Dimethylcyclohexa*-2,5-*dienone* (5).—*In* H_2SO_4. The dienone (118 mg) in 53·5% H_2SO_4 (5 ml) at 25 °C for 48 h deposited white needles. Dilution with water (10 ml), repeated ether extraction, drying ($MgSO_4$), and evaporation of the ether extracts gave 3,4-dimethylphenol (69 ± 5% by quantitative g.l.c.). Sublimation gave pure 3,4-dimethylphenol and a little brown hygroscopic residue. No trace of other volatile products could be detected by g.l.c. on N.G.S. or silicone E30 columns; in particular, 2,3-, 2,4-, and 3,5-dimethylphenols were absent. Separate experiments on mixtures of the 3,4- and 2,4-dimethylphenols under the above conditions showed that neither was significantly consumed, and that both were extracted with 70% efficiency using the standardised procedure. Thus the yield of 3,4-dimethylphenol is essentially quantitative.

TABLE 2

Kinetics for (6) in aqueous sulphuric acid or perchloric acid * at 25 °C; u.v. at 240, 260, and 305 nm; k in s^{-1}

Acid, wt. %	$-H_0$	$-H_A$	$-\log k_{\text{obs}}$ [a]	$-\log k_1$ [a]
60·7	4·56	3·13	5·136	5·104
65·7	5·16	3·45	5·026	5·014
68·5	5·57	3·64	4·921	*b*
70·7	5·90	3·80	4·878	*b*
73·6	6·35	4·09	4·846	*b*
78·9	7·18	4·50	4·596	*b*
82·2	7·70	4·76	4·561	*b*
83·8	7·95	4·89	4·533	*b*
60·8 *	5·35	*ca.* 3·50	4·486	*b*

[a] Standard deviation 0·006 to 0·016. [b] As $-\log k_{\text{obs}}$.

TABLE 3

Kinetics for (7) in aqueous sulphuric acid or perchloric acid * at 25 °C; u.v. at 240, 260, and 305 nm; k in s^{-1}

Acid, wt. %	$-H_0$	$-H_A$	$-\log k_{\text{obs}}$ [a]	$-\log k_1$ [a]
62·7	4·80	3·26	4·721	4·716
68·3	5·53	3·62	4·608	4·607
71·2	5·98	3·84	4·522	*b*
74·7	6·52	4·13	4·433	*b*
78·1	7·05	4·42	4·335	*b*
60·8 *	5·35	*ca.* 3·50	4·484	4·478

TABLE 4

Kinetics for (8) in aqueous sulphuric acid at 25 °C; u.v. at 245, 265, and 315 nm; k in s^{-1}

Acid, wt. %	$-H_0$	$-H_A$	$-\log k_1$ [a,b]
62·7	4·80	3·26	5·014
68·3	5·53	3·62	4·930
71·2	5·98	3·84	4·853
74·7	6·52	4·13	4·762
78·1	7·05	4·42	4·684

[a] Standard deviation 0·006 to 0·016. [b] As $-\log k_{\text{obs}}$.

TABLE 5

Kinetics for (9) and (10) in aqueous sulphuric acid at 25 °C

For (9) $k_{\text{obs}} = k_1 \leqslant 8 \times 10^{-9}$ s^{-1} in 68·3—78·1% acid.
For (10) $k_{\text{obs}} = k_1 = (1{\cdot}67 \pm 0{\cdot}03) \times 10^{-7}$ s^{-1} in 70·7% acid.

In $HClO_4$. A similar experiment in 50·7% $HClO_4$ gave (67 ± 2)% of 3,4-dimethylphenol (quantitative g.l.c.) and no evidence of other products. Sublimation at 50 °C and 20 mmHg gave 3,4-dimethylphenol, m.p. 64·5—65°, mixed m.p. 65—65·5° and i.r. spectrum identical to authentic material (Hopkin and Williams), m.p. 65—65·5°.

Rearrangement of 3,4,4-*Trimethylcyclohexa*-2,5-*dienone* (6).—Treatment of the dienone in 70·7% H_2SO_4 for 9 days at room temperature and work-up as above gave 3,4,5-trimethylphenol (93 ± 2% by quantitative g.l.c.) and no detectable (<0·3%) 2,3,4-trimethylphenol. Isolation gave material m.p. 105—105·8° (from hexane) with i.r. spectrum identical to authentic 3,4,5-trimethylphenol,[10] m.p. 105—106°, mixed m.p. 105—106°.

Rearrangement of 4,4-*Dimethyl*-3-*ethylcyclohexa*-2,5-*dienone* (7).—The dienone and 70·7% H_2SO_4 at room temperature and work-up as before gave a little unchanged dienone, a major (*ca.* 98%) and two minor products (*ca.* 1% each from g.l.c.). The product is slightly impure 3,4-dimethyl-5-ethylphenol, m.p. 76—79° (lit.,[11] 78°); i.r. (CCl_4) 3610 cm^{-1}, M^+ 150 (calc. 150), base peak 135. The n.m.r. (CCl_4) has τ 8·84 (t) and 7·41 (q, J 7·4 Hz, 5-ethyl), 7·90 (4-Me), 7·79 (3-Me), and 3·58 (2- and 6-H); the pattern and chemical shift values [12] indicate a 5-alkyl-3,4-dimethylphenol. Rearrangement for one half-life and work-up as before gave a mixture of the dienone and 3,4-dimethyl-5-ethylphenol. Careful n.m.r. analysis showed no evidence of 3,4-dimethyl-4-ethylcyclohexa-2,5-dienone or of the aromatic AB pattern expected for 3,4-dimethyl-2-ethylphenol.

Rearrangement of 2,4,4,5-*Tetramethylcyclohexa*-2,5-*dienone* (8).—The dienone in 70·7% H_2SO_4 for 7 days at room temperature deposited crystals. Work-up as before gave mainly 2,3,4,5-tetramethylphenol and small amounts of 2,3,4- and 2,4,5-trimethylphenols (identified by g.l.c.). Under the same conditions authentic 2,3,4,5-tetramethylphenol [13] shows some instability towards demethylation.

Rearrangement of 3,4,4,5-*Tetramethylcyclohexa*-2,5-*dienone* (9).—The dienone in 75% H_2SO_4 was heated at 70 °C for 51 h. Dilution and steam distillation gave a mixture of phenols identified by g.l.c. as mainly the 2,3,4,6- and/or 2,3,5,6-tetramethylphenols, *ca.* 10% each of 2,3,4,5-tetramethyl- and 2,4,5-trimethylphenols, and *ca.* 20% of pentamethylphenol. The expected product, 2,3,4,5-tetramethylphenol undergoes demethylation and methylation under the rearrangement conditions to give a similar mixture of phenols. We cannot say whether the products from the dienone all arise from 2,3,4,5-tetramethylphenol or whether demethylation of the dienone also occurs with methylation of the phenol products.

DISCUSSION

Over the range of acidity studied, increasing acidity always leads to increasing values of k_{obs} and k_1. Various kinetic criteria have been used in investigating the nature of the transition states for the rearrangements. Equation (4) shows that a graph of log k_1 against some measure of the acidity of the medium will show the variation of log $f_{BH^+}/f_\ddagger$. Since, within experimental uncertainty, all the dienones studied here follow the amide acidity function [9] H_A, we plot log k_1 against H_A. Such plots are straight lines with equation (6) and the

$$\log k_1 = aH_A + b \qquad (6)$$

$$\log k_1 = cH_0 + d \qquad (7)$$

parameters given in Table 6. Since H_A varies linearly with the Hammett acidity function H_0 over the acidity range studied plots of log k_1 against H_0 are also linear with equation (7) and the parameters in Table 6. These plots show that log $f_{BH^+}/f_\ddagger$ varies linearly with H_A and H_0. A treatment given by Hammett [14] can be modified to allow examination of the acidity function followed by the transition state. For the pseudo-equilibrium between dienone B and the transition state ‡, and for the equilibrium with cation BH$^+$ acidity function definitions give equations (8) and (9), and thence equation (10).

TABLE 6

Kinetic relationships for rearrangements

Compd.	$-a$ [a]	$-b$ [a]	$-c$ [b]	$-d$ [b]	$-\phi$ [c]	$-\log k_1^\circ$ [c]
(5)	0·534	5·55	0·277	5·15	0·30	4·97
(6)	0·337	6·17	0·176	5·92	0·19	5·80
(7)	0·330	5·80	0·170	5·54	0·18	5·41
(8)	0·286	5·95	0·147	5·73	0·159	5·63

[a] Values in equation (6). [b] Values in equation (7). [c] Values in equation (13). All k in s^{-1}; all correlation coefficients 0·991 to 0·999.

$$h_\ddagger = a_{H^+}f_B/f_\ddagger \qquad (8)$$

$$h_A = a_{H^+}f_B/f_{BH^+} \qquad (9)$$

$$\therefore \log f_{BH^+}/f_\ddagger = H_A - H_\ddagger \qquad (10)$$

$$\log f_{BH^+}/f_\ddagger = aH_A + b - \log k_0 \qquad (11)$$

$$\therefore H_\ddagger = H_A(1 - a) + \log k_0 - b \qquad (12)$$

A graph of log $f_{BH^+}/f_\ddagger$ against H_A is shown by our experimental findings to have equation (11) [see equations (4) and (6)], which leads to equation (12). Thus the acidity function followed by the transition state varies with the medium just $(1 - a)$ times as fast as does H_A, and the values of $H_\ddagger$ for each dienone may in theory be calculated.

The empirical treatment of Bunnett and Olsen [15] uses plots of log k_1 against (H_0 + log [H^+]), which for sulphuric acid of the concentrations we are using is the same as (H_0 + log [H_2SO_4, stoicheiometric]).[15,16] The plots are normally linear according to equation (13). The ϕ value is used to classify reactions as: $\phi < 0$,

$$\log k_1 = \phi\,(H_0 + \log [H_2SO_4, \text{stoich.}]) + \log k_1^\circ \qquad (13)$$

water not involved as a nucleophile in the rate-limiting step; ϕ + 0·22 to +0·56, water involved as a nucleophile in this step; $\phi > +0·58$, water involved as a proton-transfer agent in this step.[15] The dienones fall into the first class (see Table 6), again supporting the $A1$ mechanism. An estimate of the increase of hydration number on passing from protonated substrate to transition state is given by multiplying ϕ by 4·5.[15] This assumes that the activity coefficient variation in f_{BH^+} and $f_\ddagger$ is due

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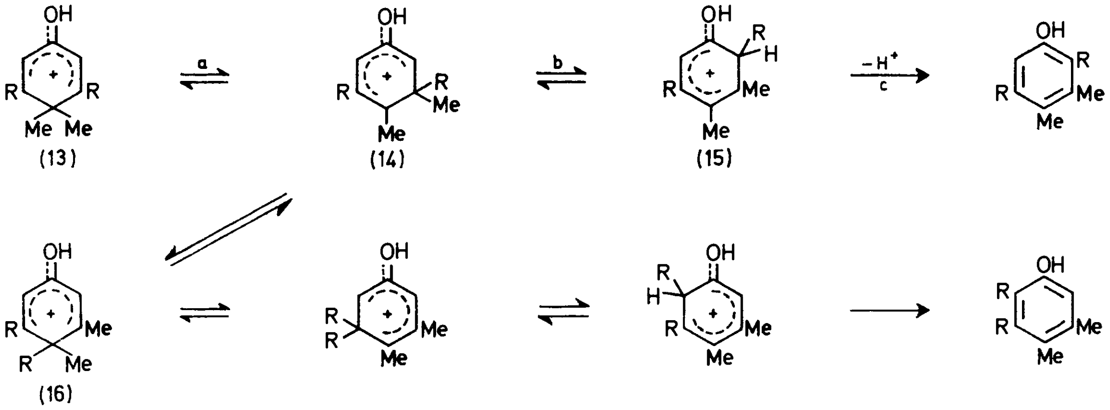
solely to hydration changes, and is an extreme view:[15,17,18] however, if this limitation is accepted, the transition state might appear to be desolvated by about 1 mole of water. Yates and his co-workers have used an alternative treatment based on that devised by Swain and Rosenberg,[19] which makes the same assumptions. This uses plots of log k_1 against log (water activity). Such plots are often linear with a gradient which is claimed to represent the hydration number of the transition state relative to the protonated substrate.[20] The treatment assumes that the ratio $f_{\mathrm{BH}^+}/f_\ddagger$ is essentially independent of the medium, which is not the case for our compounds. We obtain curved plots,* all of which have negative gradients and suggest merely that the transition state is less hydrated than the dienone cation.

The correspondence of our results with those expected for an $A1$ mechanism is supported by kinetics in acids other than sulphuric. Bunton and his co-workers[21] have provided evidence that carbonium ion-like transition states in $A1$ or A–S_E2 reactions are stabilised by low charge density anions such as perchlorate, and that the catalytic order in such reactions is $HClO_4 > HCl \sim H_2SO_4$. For $A2$ hydrolyses, which involve a transition state with strong bonding to water, the catalytic order is $H_2SO_4 > HCl \sim HBr > HClO_4$. Kresge and his co-workers[22] have shown that some reactions with rate-determining protonation and general acid catalysis are faster in polybasic acids such as sulphuric than in monobasic acids such as perchloric. Our limited kinetic studies in perchloric acid show the reactions to be significantly faster than in sulphuric acid of the same H_A value (that is, at the same degree of protonation) (see Tables 1—3), thus supporting this mechanistic criterion.

A number of qualitative deductions may be made from the kinetic data. For (6), (7) and (8) the rates of rearrangement of the cations in sulphuric acid increase roughly equally with acidity, whereas that of (5) increases almost twice as rapidly. Thus any quantitative rate comparisons involving (5) will depend on the acidity considered. The most meaningful comparisons probably correspond to infinitely dilute aqueous conditions, given by the intercept log k_1° of the Bunnett and Olsen plots (see Table 6). A weakness of this treatment for our data is that it requires quite long extrapolations with attendant loss in accuracy. Statistically, (5) might be expected to rearrange twice as fast as (6), (7), and (8), but under the standard conditions the relative rates of (5), (6), (7) and (8) are *ca.* 1·0 : 0·15 : 0·36 : 0·22. Another useful comparison is obtained from the relative rates in 70% sulphuric acid; the corresponding values are *ca.* 1 : 0·04 : 0·09 : 0·04. The correlation of rate constants with the substitution pattern of the dienones is discussed in more detail in a future report.



SCHEME 2

The rearrangements of (9) and (10), which require migration of a 4-methyl group to C(3) and then to C(2) to produce phenols, are very slow indeed. The slowness could be associated with steps (a), (b), or (c) of Scheme 2. We reject the idea of a rapid pre-equilibrium of (13) $\rightleftharpoons$ (14) $\rightleftharpoons$ (15) followed by a rate-limiting deprotonation (c) which would have to be very slow for (9) and (10), though much faster for (5)—(8). The slowness would presumably be due to the high buttressing steric interactions in the tetra-alkylphenol product. However we will show[23] that 2,4,4,6-tetramethylcyclohexa-2,5-dienone rearranges faster than any compound reported here, giving 2,3,4,6-tetramethylphenol which has very similar

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* A plot of log k_1 against log $a_{\mathrm{H_2O}}$ is given for (5) in ref. 4. This should have the axes changed to 5 + log k', with labelling 1 and 2 instead of 1 and 10, and −log $a_{\mathrm{H_2O}}$: k' is the same as our k_1.

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buttressing interactions. The remaining possibilities are that step (a) is slow, that step (a) may have a normal rate and be followed by a slow step (b), or that both (a) and (b) are slow. Some of these have been studied. If step (a) is completely rate limiting the introduction of faster steps (b) cannot affect the overall rate. The dienone (10), which was made to test this point,* does rearrange faster than (9), although still very slowly. It allows the rate of step (a) to be estimated. Since step (b) is not fast, (13) and (14) are in equilibrium. The equilibrium lies strongly on the side of (13) since the n.m.r. of the cation of the tetramethyldienone (9) in 70% H_2SO_4 or D_2SO_4 shows none (<3% noise level) of the peaks expected for (14) or (15).† The first rearranged ion (14) should revert to dienone by migration of R = Et from C(5) to C(4) to give the new cation (16) which will have an n.m.r. signal due to the allylic methyl group. Slow n.m.r. changes consistent with this alkyl interchange process do occur: an allylic methyl signal appears at the correct position, τ 7·55, together with a non-overlapping triplet due to the methyl part of a 4-ethyl group at τ 9·58 (*J* 7 Hz). The former peak increases with a net rate constant *ca.* 3×10^{-7} s^{-1}, and the rate constant for step (a) will be a little higher than this. The low overall reaction rates of (9) and (10) presumably reflect the slow formation of ion (14) and its low equilibrium concentration, combined with faster reversion to (13) and (16) than forward reaction to (15). This last assumption is consistent with the fact that the cation of hexamethylcyclohexa-2,4-dienone [analogous to (15)] isomerises to that of the 2,5-dienone [analogous to (13) or (16)].[25]

The finding that migration beyond an alkyl substituted centre is very slow is supported by the results for the 3-methyl- and 3-ethyl-dienones (6) and (7). No migration to C(2) was detected [less than 0·3% for (6) and less than *ca.* 1% for (7)] although the 3,4,5-substituted phenols were formed in high yield.

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* This assumes that R = Et will migrate much faster than methyl in step b. Evidence that ethyl migrates about 25 times faster than methyl in another dienone–phenol rearrangement will be reported later.[24]

† No peaks additional to those expected for the cation (13; R = Me) [8] can be seen. The allylic R group in (14; R = Me) should give a peak near τ 8·0 and the two vinyl proton signals should be clearly distinguishable; cation (15; R = Me) would have a *gem*-dimethyl doublet and at least two distinguishable allylic methyl peaks.

[24] J. W. Pilkington and A. J. Waring, to be published.

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