Kinetics of the Dienone–Phenol Rearrangement and Basicity Studies of Some Cyclohexa-2,5-dienones

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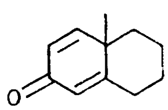
The basicities have been measured of 5,6,7,8-tetrahydro-4a-methylnaphthalen-2(4a*H*)-one, 5,6,7,8-tetrahydro-4a,8-dimethylnaphthalen-2(4a*H*)-one, androsta-1,4-diene-3,17-dione, 2,4,4-trimethylcyclohexa-2,5-dienone, and 2,4,4,6-tetramethylcyclohexa-2,5-dienone. The kinetics and products of the dienone–phenol rearrangements of these dienones in aqueous sulphuric and perchloric acids at 25 °C have been studied; limited kinetic studies have also been made in aqueous sulphuric acid at 40 °C. The effects of substitution pattern on the basicities and rates of rearrangement are discussed.

THE dienone–phenol rearrangement has found much application in the steroid series, and numerous studies have been made of the rearrangements of analogous bicyclic dienones (for reviews see refs. 1—4). Despite the many mechanistic discussions which have been published, we know of no studies of the kinetics of these reactions. We now report basicity measurements of the representative compounds, 5,6,7,8-tetrahydro-4a-methylnaphthalen-2(4a*H*)-one (1), its 4a,8-dimethyl analogue (2), and androsta-1,4-diene-3,17-dione (3), together with a study of the kinetics of their rearrangements in aqueous sulphuric and perchloric acids, and detailed product studies for (1) and (2). The products from (2) show that an unexpected phenol–phenol rearrangement takes place. We also report similar studies of the monocyclic compounds 2,4,4-trimethyl- and 2,4,4,6-tetramethyl-cyclohexa-2,5-dienone [(4) and (5)], and compare the results with those obtained for other monocyclic analogues.[5,6]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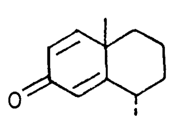
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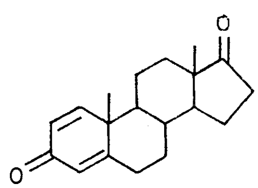
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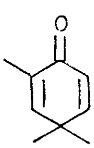
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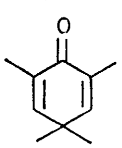
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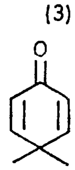
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EXPERIMENTAL

5,6,7,8-*Tetrahydro*-4a-*methylnaphthalen*-2(4aH)-*one* (1).—This was prepared by dehydrogenation with selenium dioxide[7] of 3,4,5,6,7,8-hexahydro-4a-methylnapththalen-2(4a*H*)-one,[8] and purified by chromatography on alumina followed by distillation (b.p. 102—104° at 0·6 mmHg; lit.,[9] 123—124° at 3 mmHg) to >99·9% purity (estimated by g.l.c.) (Found: C, 81·5; H, 8·8. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·7%), $\nu_{max.}$ (film) 1664, 1626, and 1605 cm^{-1}, $\lambda_{max.}$ (H_2O) 246 nm (log ε 4·187) [lit.,[9] 240 nm (log ε 4·1) in EtOH], τ (CCl_4) 4·05 (H-1), 3·94 (H-3), 3·37 (H-4), and 8·74 (Me-4), $J_{1,3}$ 1·7, $J_{3,4}$ 10 Hz; τ (C_6D_6) 3·87 (H-1), 3·86 (H-3), 3·77 (H-4), and 9·23 (Me-4), $J_{1,3}$ 1·6, $J_{3,4}$ 9·9 Hz.

5,6,7,8-*Tetrahydro*-trans-4a,8-*dimethylnaphthalen*-2(4aH)-*one* (2).—Prepared according to Bloom,[10] this had m.p. 58·5—59·5° [from petroleum (b.p. 40—60°)] (lit.,[10] 59·5—60·5°) (Found: C, 81·8; H, 8·9. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%), $\nu_{max.}$ (Nujol) 1656, 1618, and 1597 cm^{-1} (lit.,[10] 1658 and 1621 cm^{-1}), $\lambda_{max.}$ (H_2O) 246 nm (log ε 4·176), $\lambda_{max.}$ (EtOH) 241·5 nm (log ε 4·146) [lit.,[10] 243·5 nm (log ε 4·07)], τ (CCl_4) 4·05 (H-1), 3·93 (H-3), 3·37 (H-4), 8·74 (Me-4a), and 8·84 (d, *J* 6·4 Hz, Me-8), $J_{1,3}$ 1·6, $J_{3,4}$ 10 Hz; τ (C_6D_6) 3·79 and 3·80 (H-1, -3, and -4), 9·21 (Me-4a), and 9·21 (d, *J* 6·3 Hz, Me-8).

Androsta-1,4-*diene*-3,17-*dione* (3).—This was commercial material, recrystallised to m.p. 140—141·5° from hexane–acetone at −80 °C (lit.,[11] m.p. 140—141°; lit.,[12] 140—141·5°); $\lambda_{max.}$ (H_2O) 239 nm (log ε 4·210) [lit.,[12] 242·5 nm (log ε 4·18) in MeOH; lit.,[13] 244 nm (log ε 4·23) in EtOH], τ (CCl_4) 3·06 (H-1), 3·91 (H-2), and 4·06 (H-4), $J_{2,4}$ 1·7, $J_{1,2}$ 10·2 Hz.

2,4,4-*Trimethylcyclohexa*-2,5-*dienone* (4).—Prepared by K. L. Cook,[14] this was further purified by chromatography on alumina and molecular distillation to >99·8% purity (checked by g.l.c.) (Found: C, 79·1; H, 8·8. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·9%), $\lambda_{max.}$ (H_2O) 242·3 nm (log ε 4·190). Other spectroscopic data were as published.[14]

2-*Methylpent*-1-*en*-3-*one* (*Ethyl Isopropenyl Ketone*).—This was prepared from diethyl ketone and formaldehyde by the general method given in ref. 14, and had b.p. 109—111° (lit.,[15] 117—119°).

2,4,4,6-*Tetramethylcyclohex*-2-*enone*.—A mixture of 2-methylpent-1-en-3-one (24 ml), isobutyraldehyde (24 ml), water (24 ml), and methanol (30 ml) was added with stirring to potassium hydroxide (1·1 g) in methanol (7 ml) at 45 °C, during 1 h. The mixture was heated at 70—72 °C for 2 h, then water (5 ml) was added to cause separation of a pink oily layer which was extracted with ether (NaCl added).

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[2] A. J. Waring, *Adv. Alicyclic Chem.*, 1966, **1**, 129.
[3] A. J. Waring, *Österr. Chem.-Ztg.*, 1967, **68**, 232.
[4] B. Miller, in 'Mechanisms of Molecular Migration,' ed. B. S. Thyagarajan, Interscience, New York, 1968, p. 247.
[5] K. L. Cook and A. J. Waring, *J.C.S. Perkin II*, 1973, 84.
[6] K. L. Cook and A. J. Waring, *J.C.S. Perkin II*, 1973, 88.
[7] P. J. Kropp, *J. Amer. Chem. Soc.*, 1964, **86**, 4053, and references given in refs. 2 and 3.
[8] J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, 1964, **29**, 2501.
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[10] S. M. Bloom, *J. Amer. Chem. Soc.*, 1958, **80**, 6280.
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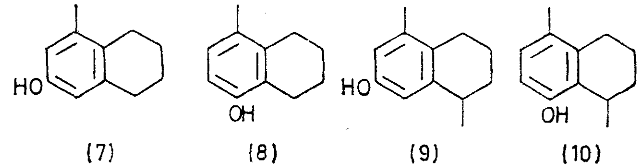
The extract was dried ($MgSO_4$) and evaporated. Distillation gave fractions (6·0 g), b.p. 93—98 °C at 12 mmHg, which contained the desired *cyclohexenone* as major product. A pure sample, from chromatography on alumina, had $\nu_{max.}$ (film) 1658 and 1644 cm^{-1}, $\lambda_{max.}$ (EtOH) 236·5 nm (log ε 4·059), τ (CCl_4) 3·77 (m, H-3), 7·56 (m, H-5 and -6), 8·32, 8·90, and 8·96 (Me-2, -4, and -4, respectively), and 8·87 (d, *J* 6 Hz, Me-6); τ (C_6D_6) 4·06 (H-3), 8·22, 9·17, and 9·23 (Me-2, -4, and -4, respectively), and 8·88 (d, *J* 6 Hz, Me-6) (Found: C, 79·0; H, 10·4. $C_{10}H_{16}O$ requires C, 78·8; H, 10·6%).

2,4,4,6-*Tetramethylcyclohexa*-2,5-*dienone* (5).—The foregoing tetramethylcyclohexenone (6·0 g; crude) was heated under reflux in dry benzene (250 ml) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (6·7 g) and a trace of toluene-*p*-sulphonic acid, under nitrogen for 2 days.* Filtration of the solution through Hyflo Supercel, and washing of the filter-bed with ether (600 ml), followed by drying ($MgSO_4$) and careful evaporation at 25 °C (vacuum) gave a brown residue. This was extracted with pentane (3 × 300 ml); the solution was dried and evaporated at 0°, and the residue was purified by chromatography on alumina (Activity I; 50 g) [eluant petroleum (b.p. 40—60°) and mixtures with ether]. The *dienone* (98% purity) was further purified by crystallisation from n-hexane (−80 °C), then molecular distillation to give material (900 mg) of >99·5% purity, m.p. 43—45° (Found: C, 80·1; H, 9·3. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%), $\nu_{max.}$ (melted film) 1673, 1667, 1643, 1633, and 1605 cm^{-1}, $\lambda_{max.}$ (H_2O) 248·5 nm (log ε 4·165), $\lambda_{max.}$ (EtOH) 243 nm (log ε 4·127), τ (CCl_4) 3·54 (H-3 and -5), 8·18 (Me-2 and -6), and 8·83 (Me-4); τ (C_6D_6) 3·88 (H-3 and -5), 8·08 (Me-2 and -6), and 9·21 (Me-4); τ (cation in 78% H_2SO_4 at −5 °C) 2·06 (H-3 and -5), 7·81 (Me-2 and -6), and 8·61 (Me-4).

Basicity and Kinetic Measurements.—The studies were performed on solutions in aqueous sulphuric or perchloric acid, by the u.v. and acidity function methods, as before.[5,6] Values of H_0 in sulphuric acid at 25° were taken from refs. 16*a* and *b*, values of H_A from refs. 17*a* and *b*, values of H_0 at 40° from ref. 18, and values of H_0 in perchloric acid at 25° from ref. 19. U.v. spectra were measured with a Cary 14 or Unicam SP 1800 spectrometer, with cell blocks thermostatted to within ±0·1 °C. Rate constants were calculated by Guggenheim's [20] or Swinbourne's [21] method, and plots of log (OD − OD_∞) against time, over 1—3 half lives; least squares parameters were calculated with a Hewlett–Packard 9100A calculator. For compound (3), which rearranges very slowly and develops slight colour after *ca.* 5 days, an iterative computer program was used to calculate the OD_∞ values and optimise the linearity of the logarithmic plot: use of the same program on data for other compounds gave results agreeing well with those obtained directly. We thank Mr. J. W. Pilkington for this program. Beer's Law checks for the dienones in water gave excellent constancy of ε values over a tenfold range of concentration. I.r. spectra were measured with a Unicam SP 200G grating instrument, and n.m.r. spectra with a Perkin-Elmer 100 MHz instrument ($SiMe_4$ as internal standard).

Preparative Rearrangements and Determination of Product Ratios.—Product ratios were measured by g.l.c. with a Pye 104 instrument fitted with a flame ionisation detector; pure authentic samples or mixtures of known composition were used for quantitative calibrations.

Rearrangements of 5,6,7,8-*Tetrahydro*-4a-*methylnaphthalen*-2(4aH)-*one* (1).—The authentic phenol products (7) and (8) were made by rearrangement of (1) with acetic



(7) (8) (9) (10)

anhydride–sulphuric acid at room temperature, during 5 h, followed by hydrolysis of the mixture of acetates by ethanolic hydrochloric acid [9] [this gave (7) and (8) in an 18 : 82 ratio (g.l.c. on E30 at 150°)].† Rearrangement in 50% sulphuric acid at 100° for 30 min [24] gave (7) and (8) in an 85 : 15 ratio.‡

Accurately weighed samples of the dienone (1) (*ca.* 5 mg) were each kept in 5·0 ml of sulphuric acid (acid strengths 78·8, 82·1, and 84·2%; H_0 −7·17, −7·69, and −8·01, respectively) for 72 h at 25 °C. Water (50 ml) was added to each sample, and each was extracted with ether (3 × 10 ml). The dried extracts were carefully evaporated, and the residues were dissolved in hexane (2·0 ml) and examined by g.l.c. The ratios of 5,6,7,8-tetrahydro-4-methyl-2-naphthol (7) to the 1-naphthol (8) were, respectively, 3·50 ± 0·06, 3·80 ± 0·07, and 3·55 ± 0·12, with average 3·62 ± 0·13; unchanged dienone remained in each case. The combined products (after evaporation) were dissolved in 70% sulphuric acid; the solution was heated at 100 °C for 2 h and worked up as before, and the products were re-examined: the ratio of phenols was then 3·60 ± 0·12. It was therefore assumed that the previous result was achieved under kinetic control, which was not disturbed by longer reaction times. The total estimated yields of phenols (not allowing for losses in work-up) were 62, 55, 45, and 35% (all ±4%), consistent with overall losses being due to sulphonation. Similar studies in perchloric acid of strengths 65·3, 67·4, and 70·7% (H_0 −6·50, −7·04, and −7·95), reacting for 24 h at 25°, gave ratios of the 4-methyl-2-tetralol (7) to the 4-methyl-1-tetralol (8) of 5·1 ± 0·1, 5·4 ± 0·2, and 4·8 ± 0·2,

* The dienone is very volatile, and is easily swept out of the preparation by a stream of nitrogen; serious losses in yield can result. Use of selenium dioxide in t-butyl alcohol with pyridine as catalyst gave up to 30% conversion into dienone, but the yield of isolated product was poor.

† In ref. 22 this ratio is given as 20 : 80; in ref. 23 it is given as 16 : 84.

‡ Ref. 23 used 20·6N-sulphuric acid (65·1%) at 51 °C for 2 days, giving a ratio of 86 : 14.

16 (*a*) M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; (*b*) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

17 (*a*) K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957; (*b*) C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc.* (*B*), 1967, 1235.

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19 K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408.

20 E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

21 E. S. Swinbourne, *J. Chem. Soc.*, 1960, 2371.

22 W. H. Hopff and A. S. Dreiding, *Angew. Chem. Internat. Edn.*, 1965, **4**, 690.

23 H. J. Shine and C. E. Schoening, *J. Org. Chem.*, 1972, **37**, 2899.

24 A. S. Dreiding, W. J. Pummer, and A. J. Tomasewski, *J. Amer. Chem. Soc.*, 1953, **75**, 3159; A. S. Dreiding and W. J. Pummer, *ibid.*, p. 3162.

with average $5{\cdot}2 \pm 0{\cdot}3$ and estimated total recoveries of 82, 77, and 69% (all ± 5%).

Rearrangements of 5,6,7,8-*Tetrahydro*-4a,8-*dimethylnaphthalen*-2(4aH)-*one* (2).—The authentic rearrangement products (9) and (10) were made by treating (2) in acetic anhydride–sulphuric acid for 6 or 8 h at room temperature,[10] followed by hydrolysis with ethanolic hydrochloric acid,[9] and by rearrangement in 50% sulphuric acid at 100 °C for 30 min [giving (10) and (9) in a $2{\cdot}2 \pm 0{\cdot}2 : 1$ ratio, measured by g.l.c. on an NGS column at 190°, or on E30 at 150°] (lit.,[25] 2·2 : 1 from isolation experiments), and in concentrated hydrochloric acid at 100 °C for 45 min [(10) : (9), $1{\cdot}7 \pm 0{\cdot}2 : 1$] (lit.,[25] 1·9 : 1 from isolation experiments). Separation by column chromatography on silica gave the major component (10), m.p. 93·5—94·5° [from petroleum (b.p. 40—60°)] (lit.,[10] m.p. 93—94·5°; lit.,[25] 95—96°) (Found: C, 81·8; H, 9·2. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%), τ (CCl_4) 3·27 (H-3), 3·64 (H-2), 7·93 (Me-4), and 8·80 (d, J 7·0 Hz, Me-8), $J_{2,3}$ 8 Hz. The minor component (9), m.p. 94·8—95·2° (from hexane) (lit.,[25] 95·5—96·0°), was slightly coloured and although pure by g.l.c. was not microanalysed; it had τ (CCl_4) 3·58 (H-1 and -3), 7·90 (Me-4), and 8·81 (d, J 7·1 Hz, Me-8) [lit.,[25] τ ($CDCl_3$) 3·42 (H-1 and -3), 7·82, and 8·76]. Product studies were conducted as before, using sulphuric acid of strengths 78·8, 82·1, and 84·2% at 25°,* but samples were taken at reaction times of 4, 7, 16, 24, 31, 41, 48, and 56 h. In each case, the ratio of (10) to (9) started below 1·0, rose to above 1·0 at 7—16 h, increased to 1·31, 1·12, and 1·08 for the three acid strengths, then decreased to 1·23, 0·82, and 0·57, respectively. Extrapolation to zero time gave an initial ratio of (10) to (9) of $0{\cdot}70 \pm 0{\cdot}09$ in each case. To determine the reason for changing product ratios, samples of the pure phenols in 82·1% sulphuric acid were kept at room temperature for 7 days. The usual work-up and g.l.c. showed that the 1-tetralol (10) was not converted into the 2-tetralol (9), although there was overall loss of material (presumably due to sulphonation), but that the 2-tetralol (9) was *ca.* 50% converted into (10), again with loss of material. In 50% sulphuric acid the 2-tetralol (9) was *ca.* 10% converted into (10) in 24 h at room temperature, and *ca.* 30% converted in 4 h at 100°: separation of these combined product mixtures by column chromatography on silica gave 22% of a compound whose spectroscopic properties agree with those of (10); the n.m.r. spectrum was slightly different [τ (CCl_4) 3·32 (H-3), 3·69 (H-2), 7·92 (Me-4), and 8·79 (d, J 7·2 Hz, Me-8), $J_{2,3}$ 7—8 Hz] from that of pure (10), but this may represent a concentration effect, or slight instrument calibration error.

Studies of the rearrangement of the dienone (2) in 65·3 and 70·7% perchloric acid at 25° gave ratios of 1-tetralol (10) to 2-tetralol (9) of $2{\cdot}75 \pm 0{\cdot}15$ in both cases after 3 h reaction, and $6{\cdot}6 \pm 0{\cdot}2$ in both cases after 24 h. Loss of phenolic material is less serious than in sulphuric acid (recovery 76% from 65·2% acid, and 55% from 70·6% acid, after 24 h). The variation of product ratio with reaction time in the 70·6% acid (H_0 −7·95) was studied (times of 1, 2, 4, 6, 10, 15, 20, and 30 h); † the ratio (10) : (9) started at *ca.* 1·65 (at 1 h), rising to 6·75 (at 20 h), then falling slightly. The estimated initial ratio was $1{\cdot}10 \pm 0{\cdot}15$; again the results are consistent with (9) being converted into (10).

Rearrangements of Androsta-1,4-*diene*-3,17-*dione*.—Rearrangement of (3) in 83% sulphuric acid, during 10 days at 25°, and separation by chromatography on silica, gave two products in essentially equal yields. The same products, obtained in the ratio *ca.* 4 : 1, were given by rearrangement in concentrated hydrochloric acid: they have been shown[24] to have structures analogous to (9) and (10), respectively (lit.,[24] ratio *ca.* 5·5 : 1).

Rearrangements of 2,4,4-*Trimethylcyclohexa*-2,5-*dienone* (4).—Authentic samples of 2,3,4- and 2,4,5-trimethylphenol were available from other work. Samples of the dienone (4) were treated wth sulphuric acid (strengths 33·8, 49·4, and 57·7%; H_0 −1·98, −3·32, and −4·20) at 25° for various times, and the products were worked up and examined by calibrated g.l.c. (E30 column at 130°) as before. The initial ratio of 2,4,5- to 2,3,4-trimethylphenol in each case was $2{\cdot}3 \pm 0{\cdot}13 : 1$, with total mass balance 93 ± 5%. After reaction for 24 h in 49·4% acid,‡ or 5 h in 57·7%,† the ratio had risen to $2{\cdot}6 \pm 0{\cdot}2$, with mass balances 97 ± 5 and 88 ± 4%, respectively. An equimolar mixture of the two phenols was treated similarly in 57·7 and 70·0% sulphuric acid for 30 h at 25 °C: the ratio changed slightly in the former case, and was increased to *ca.* 1·5 in the latter. These changes in ratio were shown not to be caused by isomerisation of 2,3,4- to 2,4,5-trimethylphenol, and are assumed to reflect faster loss by sulphonation of the former isomer. Rearrangements of the dienone (4) in 36·0, 47·0, and 52·2% perchloric acid (H_0 −2·05, −3·10, and −3·80) gave an initial ratio of 2,4,5- to 2,3,4-trimethylphenol of $3{\cdot}43 \pm \pm 0{\cdot}05 : 1$; this rose slowly to $3{\cdot}9 \pm 0{\cdot}4$, with the total mass balance remaining at 94 ± 5 to 87 ± 4%.

Rearrangements of 2,4,4,6-*Tetramethylcyclohexa*-2,5-*dienone* (5).—Authentic samples of 2,3,4,6- and other tetramethylphenols were available from other work. The dienone (5) was kept in 58% sulphuric acid for 6 h at 25 °C. Work-up was performed as before, and g.l.c. on a QF1 column at 180° showed complete conversion into a single compound (76%), identical (retention times and i.r. spectrum) with 2,3,4,6-tetramethylphenol. Similar rearrangements in perchloric acid (46·0 and 54·8%; H_0 −2·97 and −4·22) for periods of 10—360 min gave only the same phenol, with total mass balance falling from an initial value of 92 ± 4 to 81 ± 4%.

Test of Intramolecularity of Rearrangement: Mixed Rearrangement of 2,4,4,6-*Tetramethyl- and* 4-*Ethyl*-4-*methylcyclohexa*-2,5-*dienones*.—The 4-ethyl-4-methyl dienone[26] was supplied by Mr. J. W. Pilkington. The two dienones were mixed and kept in 53·1% sulphuric acid (H_0 −3·59) at 25 °C: their rearrangement rates are in the ratio *ca.* 1 : 4. Samples withdrawn after 1·0 and 4·0 h were worked up and analysed on an E30 column at 150°. The only product peaks had retention times identical with the products of the separate rearrangements; 0·5% of other products would have been detectable.

N.m.r. Spectrum of the Cation of 2,4,4,6-*Tetramethylcyclohexa*-2,5-*dienone*.—The cation in 78·4% sulphuric acid

* Under these conditions the half-lives of the dienone are 33·8, 24·5, and 21·3 h, respectively. Recoveries of both phenols in the work-up procedure were 80%.

† The half-life of the dienone under these conditions is *ca.* 6·5 h.

‡ Under these conditions the dienone has half-lives *ca.* 1·85 and 0·57 h, respectively. K. L. Cook (unpublished work) has shown that reaction for 24 h in 70·7% sulphuric acid gave a product ratio of $5{\cdot}3 \pm 0{\cdot}2 : 1$.

25 P. J. Kropp, *J. Amer. Chem. Soc.*, 1963, **85**, 3280.
26 J. W. Pilkington and A. J. Waring, *Tetrahedron Letters*, 1973, 4345.

at -5 °C (Me_4N^+ internal standard) has τ 7·81 (Me-2 and -6), 8·61 (Me-4), and 2·06 (H-3 and -5). These values are close to those reported [27] for numerous analogous cations of type (11). Because the cation rearranges rapidly during the n.m.r. measurement we cannot say that (11) is the only cation formed, although there is no evidence of significant peaks due to other possible cations.

DISCUSSION

Basicity Measurements.—Knowledge of the basicity of the dienones is necessary for interpreting the kinetics of their rearrangements, in that one needs to know both the observed rate of rearrangement in a given acid [given by $k_{obs.}$ in equation (1)] and the rate of rearrangement of the chemically reactive dienone

$$\underset{[B]}{\text{Dienone}} \underset{K_A}{\overset{H^+ \text{ fast}}{\rightleftharpoons}} \underset{[BH^+]}{\text{Cation}} \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} \text{Products}$$

$$d[\text{stoicheiometric dienone}]/dt = -k_{obs.}[\text{stoicheiometric dienone}] \quad (1)$$

$$d[BH^+]/dt = -k_{obs.}[BH^+] \qquad d[B]/dt = -k_{obs.}[B]$$

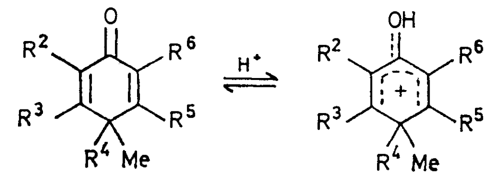
$$\text{Rate} = -d[B + BH^+]/dt = d[\text{Product}]/dt = k_1[BH^+] \quad (2)$$

$$k_1 = k_{obs.}(1 + [B]/[BH^+]) \quad (3)$$

$$\log I = m_A[(H_A)_{\frac{1}{2}} - H_A] \quad (4)$$

$$= m_0[(H_0)_{\frac{1}{2}} - H_0], \text{ where } I = [BH^+]/[B] = (\varepsilon - \varepsilon_B)/(\varepsilon_{BH^+} - \varepsilon) \quad (5)$$

cation * [given by k_1 in equations (2) and (3)]. The proportion of the stoicheiometric dienone which exists in the cationic form is given by the pK (or $H_{\frac{1}{2}}$) and slope parameters (m) in equations (4) and (5). The appropriate parameters are given in Table 1. The bicyclic dienone (1) follows the amide acidity function H_A much more closely than the Hammett H_0 function, but does not fit it perfectly: the estimate of the thermodynamic pK ($-1·93 \pm 0·10$) is a 'corrected' value (see ref. 5 for the correction procedure).† The analogue (2) seems to follow H_0, with pK $-1·95 \pm 0·12$: the steroid (3) falls between H_0 and H_A behaviour, with a 'corrected' pK of $-2·1 \pm 0·2$. Within experimental error these three pK values are approximately equal, and close to those of the analogously substituted 3,4,4-trimethyl- and 3-ethyl-4,4-dimethylcyclohexa-2,5-dienones studied earlier.[5] The variation of acidity function behaviour between H_A and H_0 has been noted



(11)

before,[5] and presumably results from differing solvation properties of the various cations relative to the dienones. The 2,4,4-trimethyl dienone (4) also falls between H_A and H_0 behaviour, with a 'corrected' pK value of $-2·7 \pm 0·2$; the 2,4,4,6-tetramethyl dienone appears to follow H_0 closely, with pK $-4·2 \pm 0·1$. Irrespective of the estimates of thermodynamic pK values it would be valuable to be able to predict the concentration of acid which is required to half-protonate each dienone. We have shown previously [5] that published additive substituent effects on the pK values of a number of cyclohex-2-enones,[28] which are also their $(H_A)_{\frac{1}{2}}$ values,[28] can also be applied to some alkylcyclohexa-2,5-dienones. The $(H_A)_{\frac{1}{2}}$ predictions for the dienones (1)—(5), derived as previously [5] are compared with the observed values in Table 2. The agreement for (1), (3), and (4) is good, for (2) it is poorer, and for (5) it is bad. A different type of correlation of dienone basicity with structure is given in the Appendix, and the surprisingly low basicity of the 2,4,4,6-tetramethyl dienone (5) is discussed there.

Kinetic Measurements.—Values of the observed first-order rate constants for rearrangement ($k_{obs.}$) and the derived values of k_1 are given in Tables 3—7. We found previously [6] that log k_1 was linearly related to H_0

TABLE 1

Basicity measurements

Compd.	Wavelengths [a]	$(H_A)_{\frac{1}{2}}$ [b]	m_A [c]	$(H_0)_{\frac{1}{2}}$ [d]	m_0 [e]	$\%H_2SO_4$ [f]	pK [g]	Range of acids [h]
(1)	245,* 265, 305 †	$-1·82 \pm 0·07$	$1·14 \pm 0·07$	$-2·14 \pm 0·06$	$0·77 \pm 0·04$	$36·2 \pm 1·0$	$-1·93 \pm 0·10$	20·1—51·3
(2)	245,* 265, 305 †	$-1·68 \pm 0·08$	$1·50 \pm 0·20$	$-1·95 \pm 0·12$	$1·02 \pm 0·04$	$33·5 \pm 1·4$	$-1·95 \pm 0·12$	20·1—47·5
(3)	250, 300 *	$-1·92 \pm 0·08$	$1·30 \pm 0·05$	$-2·31 \pm 0·18$	$0·82 \pm 0·07$	$38·6 \pm 2·0$	$-2·1 \pm 0·2$	27·9—51·1
(4)	240,* 245,* 266	$-2·45 \pm 0·07$	$1·30 \pm 0·08$	$-3·27 \pm 0·12$	$0·69 \pm 0·03$	$49·4 \pm 1·1$	$-2·7 \pm 0·2$	34·6—59·2
(5)	250	$-2·93 \pm 0·05$	$1·86 \pm 0·14$	$-4·20 \pm 0·07$	$1·01 \pm 0·03$	$57·6 \pm 0·8$	$-4·2 \pm 0·1$	45·5—63·8

[a] Wavelengths, in nm, used for the measurements. [b] Half-protonation acidity on amide acidity function H_A, using scales of refs. 17. [c] See equation (4). [d] Half-protonation acidity on Hammett's acidity function H_0, using scales of refs. 16 at 25 °C and ref. 18 at 40 °C. [e] See equation (5). [f] Half-protonation acidity; weight %. [g] Best estimates of thermodynamic pK values, based on the treatment detailed in ref. 5. [h] Equations (4) and (5) are obeyed with the tabulated parameters over this range of acidity; weight %.

* Moderately strong medium effect at this wavelength. † Strong medium effect.

* We have shown by n.m.r. that each of the dienones (1)—(4) and (6) gives an *O*-protonated cation (hydroxybenzenium ion) of type (11):[27] for evidence on the cation of (5), see Experimental section.

† By pK we mean the best estimate, assuming the discussion in ref. 5 to apply.

[27] K. L. Cook, M. J. Hughes, and A. J. Waring, *J.C.S. Perkin II*, 1972, 1506.

[28] R. I. Zalewski and G. E. Dunn, *Canad. J. Chem.*, (*a*) 1969, **47**, 2263; (*b*) 1970, **48**, 2538.

and H_A [equations (6) and (7)] for a series of dienone–phenol rearrangements. The same was found for all

TABLE 2

Predicted and observed values of $(H_A)_{\frac{1}{2}}$

Compd.	Experimental pK	Experimental $(H_A)_{\frac{1}{2}}$	Calculated pK = $(H_A)_{\frac{1}{2}}$
(1) [a]	-1.93 ± 0.10	-1.82 ± 0.07	-2.04 ± 0.13
(2) [a]	-1.95 ± 0.12	-1.68 ± 0.08	-2.04 ± 0.13
(3) [a]	-2.1 ± 0.2	-1.92 ± 0.08	-2.04 ± 0.13
(4) [b]	-2.7 ± 0.2	-2.45 ± 0.07	-2.57 ± 0.16
(5) [b]	-4.2 ± 0.1	-2.93 ± 0.05	-2.30 ± 0.19

[a] Models used:[28a] 3,4,5,6,7,8-hexahydro-3-methylnaphthalen-2(4aH)-one, pK -2.82 ± 0.03: 3,4,5,6,7,8-hexahydro-1-methylnaphthalen-2(4aH)-one, pK -2.47 ± 0.03, subtract 0·30 due to 1-methyl group, giving -2.77 ± 0.03; mean -2.80 ± 0.05. Value from Table III of ref. 28*a*, -2.82 ± 0.05. [b] Models used:[28a] cyclohex-2-enone, pK -3.60 ± 0.04, and the other compounds discussed in ref. 28*a*. Value from Table III of ref. 28*a* is -3.57 ± 0.05. The incremental correction for a 2- or 6-methyl group in the cyclohex-2-enone system is given as 0·30 in ref. 28*a*, and 0·25 in ref. 28*b*; we take 0.27 ± 0.03.

TABLE 3

Kinetics for compound (1) in aqueous sulphuric acid or perchloric acid (*) at 25 °C; u.v. at 265 nm

Acid, wt. %	$-H_A$	$-H_0$	$-\log k_1$/s^{-1} [a]
74·8	4·13	6·54	5·72
77·4	4·37	6·94	5·67
80·1	4·57	7·36	5·60
82·2	4·75	7·68	5·57
85·0	5·01	8·13	5·53
65·3 *	3·97	6·50	5·13
71·0 *	4·60	8·06	4·89

[a] $\log k_1 = \log k_{obs.}$; standard deviations 0·013—0·023.

TABLE 4

Kinetics for compound (2) in aqueous sulphuric acid at 25 °C, or at 40° (†), or in perchloric acid (*) at 25 °C; u.v. at 265 nm

Acid. wt. %	$-H_A$	$-H_0$	$-\log k_1$/s^{-1} [a]
68·1	3·61	5·52	5·65
71·5	3·87	6·04	5·54
75·2	4·17	6·60	5·43
77·0	4·33	6·87	5·29
78·8	4·45	7·16	5·25
80·1	4·57	7·35	5·21
81·2	4·67	7·54	5·16
82·6	4·78	7·75	5·10
67·6 †		5·18	4·78
65·3 *	3·97	6·50	4·94
70·9 *	4·58	8·04	4·50
71·0 *	4·60	8·06	4·49

[a] $\log k_1 = \log k_{obs.}$; standard deviation 0·008—0·025.

the rearrangements studied here, which follow equations (6) and (7) with the parameters given in Table 8. This

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

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

$$\log k_1 = \phi(H_0 + \log[H_2SO_{4\ stoich.}]) + \log k_1^0 \quad (8)$$

is particularly significant for the compounds (1)—(4). For some of the compounds studied before and for (5), which rearrange rapidly when extensively protonated, many of the kinetic measurements have been made in acids which give incomplete protonation. The factor which gives k_1 from $k_{obs.}$ [see equation (3)] can then

TABLE 5

Kinetics for compound (3) in aqueous sulphuric acid at 25 °C; u.v. at 260 nm

Acid. wt. %	$-H_A$	$-H_0$	$-\log k_1$/s^{-1} [a]
75·2	4·17	6·60	6·30
76·9	4·31	6·86	6·16
81·4	4·67	7·57	5·95
82·6	4·79	7·76	5·81
84·8	4·99	8·10	5·71

[a] $\log k_1 = \log k_{obs.}$; standard deviation 0·005—0·020.

TABLE 6

Kinetics for compound (4) in aqueous sulphuric acid at 25 °C, or at 40° (†), or in perchloric acid (*) at 25 °C; u.v. at 245, 250, 260, or 266 nm

Acid, wt. %	$-H_A$	$-H_0$	$-\log k_{obs.}$/s^{-1} [a]	$-\log k_1$/s^{-1} [a]
41·1	2·03	2·49	4·55	3·93
47·1	2·34	3·06	4·14	3·77
49·9	2·49	3·36	3·99	3·71
55·0	2·78	3·91	3·64	3·48
59·1	3·02	4·37	3·51	3·44
62·8	3·26	4·81	3·32	*b*
65·0	3·41	5·08	3·23	*b*
70·1	3·75	5·81	3·06	*b*
70·5	3·78	5·87	3·04	*b*
73·3	4·01	6·31	2·95	*b*
76·9	4·31	6·86	2·85	*b*
81·6	4·71	7·60	2·58	*b*
51·7 †		3·32	3·055	
58·9 †		4·07	2·68	
63·9 †		4·64	2·48	
42·0 *	2·14	2·57	4·03	
47·9 *	2·54	3·20	3·58	

[a] Standard deviation 0·006—0·014. [b] As $\log k_{obs.}$

TABLE 7

Kinetics for compound (5) in aqueous sulphuric acid at 25 °C, or at 40° (†), or in perchloric acid (*) at 25 °C; u.v. at 250 nm

Acid, wt. %	$-H_A$	$-H_0$	$-\log k_{obs.}$/s^{-1} [a]	$-\log k_1$/s^{-1} [b]
35·0	1·74	2·06	5·15	3·07
42·1	2·09	2·57	4·45	2·89
45·2	2·23	2·86	4·16	2·93
48·3	2·39	3·19	3·84	2·81
51·2	2·55	3·50	3·58	2·87
53·9	2·72	3·80	3·33	2·82
57·0	2·90	4·13	3·09	2·73
58·1	2·96	4·24	3·02	2·77
61·2	3·16	4·61	2·84	2·68
63·5	3·31	4·89	2·71	2·66
67·3	3·55	5·40	2·54	2·52
69·2	3·69	5·68	2·45	2·44
72·1	3·91	6·10	2·43	2·42
73·1	4·00	6·28	2·41	*c*
78·1	4·43	7·04	2·30	*c*
56·7 †		3·81	2·39	
61·3 †		4·32	2·09	
46·0 *	2·40	2·97	3·60	
54·8 *	3·10	4·22	2·56	

[a] Standard deviation 0·003—0·010. [b] Standard deviation 0·007—0·019. [c] As $\log k_{obs.}$

incorporate errors consequent on small errors in the measured values of $[BH^+]/[B]$. It could then be suggested that the linearity expressed by equations (6) and

(7) may be more apparent than real over the range of acidity which gives low degrees of protonation. However, all the kinetic measurements on compounds (1)—(3) refer to essentially completely protonated species, and for (4) the few measurements which are not on the cation have a $k_1/k_{obs.}$ factor less than 4, which can be determined with good accuracy. The linearity in every case is good (see Table 8). The conclusions

TABLE 8

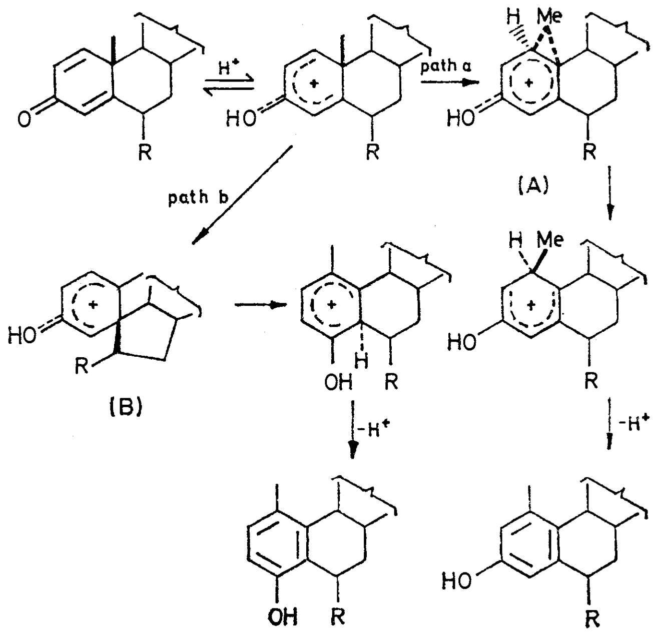
Kinetic relationships for rearrangements in aqueous H_2SO_4 at 25 °C

Compd.	$-a$ [a]	$-b$ [a]	$-c$ [b]	$-d$ [b]	$-\phi$ [c]	$-\log k_1^0/s^{-1}$
(1)	0·22	6·63 ± 0·12	0·12	6·51 ± 0·12	0·12 (5)	6·39
(2)	0·48	7·39 ± 0·12	0·25	7·06 ± 0·12	0·27 (5)	6·91
(3)	0·68	9·12 ± 0·23	0·37	8·73 ± 0·20	0·39	8·42
(4)	0·48	4·87 ± 0·05	0·25	4·53 ± 0·05	0·27	4·36
(5)	0·29	3·57 ± 0·06	0·15	3·35 ± 0·06	0·16	3·25

[a] Values in equation (6). [b] Values in equation (7). [c] Values in equation (8); log k_1^0 errors as in quantities b and d; all correlation coefficients 0·981—0·993.

drawn previously,[6] which relate changes in the activity coefficient ratio $f_{\ddagger}:f_{BH^+}$ to changing acidity, should also apply to compounds (1)—(5).

Qualitative Discussion of the Kinetics in Aqueous Sulphuric Acid.—The bicyclic compounds (1) and (2) and the steroid (3) are assumed to undergo methyl migration as shown in Scheme 1, by a direct 1,2-cationic shift (path a) through the transition state (A); the rearrangements of the monocyclic dienones (4)—(6) are similar. The alternative path, leading from (1) and (2) to products (8) and (10) has been shown to follow path b, *via* a spiran intermediate (B); this is referred to as the ' spiran migration ' path. For evidence on the existence of these paths, see refs. 1—4. For the reasons given earlier, the relative rates of rearrangement of a pair of dienones depend both on the proportions in the reactive cationic forms (11) [given by equations (4) and (5)], and on the cations' propensities for rearrangement. A measure of former factor is available from the basicity data; we will discuss the latter factor, given by k_1. Comparisons of k_1 data for various dienones depend to some extent on the acidity at which the comparison is made, because the change of k_1 with acidity [a and c in equations (6) and (7)] is not the same for all (see Table 8). The plots of log k_1 *vs.* H_A or H_0 for compounds (2)—(6) are roughly parallel over the acidities studied, but compound (1) has a different gradient. At the ' standard ' acidity taken before,[6] H_0 −5·80 in sulphuric acid, the total values of k_1 are $(1·53 \pm 0·17)10^{-6}$, $(2·47 \pm 0·17)10^{-6}$, $(2·7 \pm 1·0)10^{-7}$, $(8·6 \pm 0·25)10^{-4}$, $(3·4 \pm 0·1)10^{-3}$, and $(2·88 \pm 0·17)10^{-4}$ s^{-1} for compounds (1)—(6), respectively.* Dissected values of k_1 at the same acidity, assuming the product ratios measured at other acidities still apply are: in (1), methyl migration $(1·20 \pm 0·13)10^{-6}$, spiran migration $(3·3 \pm 0·4)10^{-7}$ s^{-1}; in (2), methyl migration $(1·45 \pm 0·2)10^{-6}$, spiran



SCHEME 1

migration $(1·02 \pm 0·15)10^{-6}$ s^{-1}; in (3), methyl and spiran migration *ca.* $(1·3 \pm 0·5)10^{-7}$ s^{-1} each; in (4), migration of methyl to C-5 $(6·0 \pm 0·2)10^{-4}$, and to C-3 $(2·55 \pm 0·2)10^{-4}$ s^{-1}; in (5) for methyl migration to C-3 or C-5 $(1·67 \pm 0·05)10^{-3}$ s^{-1} each; in (6), for methyl migration to C-3 or C-5 $(1·44 \pm 0·09)10^{-4}$ s^{-1} each.*

It is clear that the 2,4,4,6-tetramethyl dienone (5) rearranges ten or more times faster than the 4,4-dimethyl dienone (6); in a later paper we will give arguments for believing this to be the result of electronic effects. Similarly, in the 2,4,4-trimethyl dienone (4) migration to C-3 is about twice as fast as migration in one direction in (6), and migration to C-5 is faster by a further factor of about 2½. Previous reports on compound (4) state that its rearrangement in acetic anhydride–sulphuric acid is much more difficult than that of the 4,4-dimethyl dienone (6),[30] and that rearrangement under these conditions or by warming in dilute sulphuric acid[31] gives 2,4,5-trimethylphenol; the low m.p.s reported for the initially isolated products[30,31] and our own results suggest appreciable

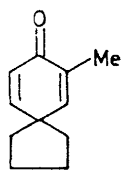
* The values quoted are for rearrangements of the cations, all in the same medium. However there is no reason to suppose that all the cations will be similarly solvated. To overcome this difficulty one may compare the values of k_1 extrapolated to infinite dilution in water [given by k_1^0 in the Bunnett and Olsen[29] equation (8)] which are tabulated in Table 8. The order of reactivities of the various compounds changes little, and the same qualitative conclusions apply.

[29] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

[30] M. Yanagita and S. Inayama, *J. Org. Chem.*, 1954, **19**, 1724; M. Yanagita, *Pharmazie*, 1955, **10**, 524.

[31] M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *J. Org. Chem.*, 1958, **23**, 690.

contamination by 2,3,4-trimethylphenol. Other reports on 2-methylcyclohexa-2,5-dienones have been confusing. Hemetsberger[32] found that rearrangement of the 2-methyl dienone (12) in methanolic 80% sulphuric acid at low acidities had $k_{obs.}$ about 1·6 times greater than did that of (13) at the same acidities, and that only one product (14) was produced. Our own results agree roughly, in that compound (4) has $k_{obs.}$ about 3 times greater than does (6) at a given acidity, but suggest that some of the alternative product (15) should also be formed. Rearrangement of a 2-methyl-substituted steroidal 1,4-dien-3-one was found to be faster than that of analogues which lack the 2-methyl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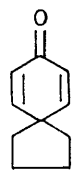
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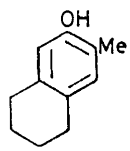
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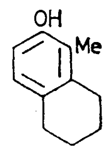
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group,[33] a result ascribed to the methyl group's base-strengthening effect. Our data show that this effect is at best small, although in the correct direction [compare (4), $(H_A)_{\frac{1}{2}}$ $-2·45 \pm 0·06$, with (6), $(H_A)_{\frac{1}{2}}$ $-2·38 \pm 0·03$; and 2,4,4,5-tetramethylcyclohexa-2,5-dienone,[5] $(H_A)_{\frac{1}{2}}$ $-1·86 \pm 0·04$, with the 3,4,4-trimethyl dienone,[5] $(H_A)_{\frac{1}{2}}$ $-2·01 \pm 0·03$]; it would be important only if the dienones were incompletely converted into their cations under the conditions used. In the rearrangement of 5,6,7,8-tetrahydro-3,4a-dimethylnaphthalen-2(4a*H*)-one[34] the poor yield (*i.e.* slow formation) of 3,4-dimethyl-2-tetralol, compared with that of (7) from (1), was attributed to the additional destabilising (buttressing) steric effects which would result from the proximity of the two methyl groups in the product.[34] However, our earlier work[6] showed that the analogously substituted 2,4,4,5-tetramethylcyclohexa-2,5-dienone rearranges to 2,3,4,5-tetramethylphenol slightly faster than the 3,4,4-trimethyl dienone rearranges to 3,4,5-trimethylphenol. Our present results can be reconciled with the earlier ones[6,34] if it is accepted that a 2-methyl group on the cyclohexa-2,5-dienone system inherently accelerates rearrangement (electronically), but that methyl migration to C-3 is slowed down by buttressing steric effects for dienones which have substituents at C-2, -4, -4, and -5 (or, presumably, at C-2, -4, -5, and -6).

* These three acids are considered because their acidity function behaviours have been most studied. Kropp[25] showed that ring opening of (2) occurs to the extent of about 16% within 45 min at 100° in concentrated hydrochloric acid, so we did not use this acid in kinetic studies.

† *Note added in proof:* Values of H_A for perchloric acid solutions at 25 °C have now been published,[35] and are quoted in Tables 3, 4, 6, and 7. Equal H_A values are not, in general, found for solutions of sulphuric and perchloric acid which have the same H_0 value. Comparison of rates in acids of equal H_A values shows the rearrangement in perchloric acid to be faster than that in sulphuric acid by the following factors: for (1), $4·7 \pm 0·5$; for (2), $4·2 \pm 0·7$; for (4), $2·3 \pm 0·2$; and for (5), $1·9 \pm 0·2$. For (1) and (2) the factor seems to increase with increasing acid strength.

It is noteworthy that methyl migration from C-4a to C-4 in the bicyclic dienones (1) and (2), and from C-10 to C-1 in the steroid (3) is much slower than that from C-4 to C-5 in 3,4,4-trimethylcyclohexa-2,5-dienone, or in the 3-ethyl-4,4-dimethyl dienone:[6] the rate reduction is to about 1/10th for (1) and (2), and to about 1/100th for (3). We suggest that the transition states (A), like the rearranged cations which lead to the products (7) and (9) (see Scheme 1) will be more strained than the dienone cations, and that the rearrangement will thus be slowed down: estimates of the size of this effect will be given in a later paper.

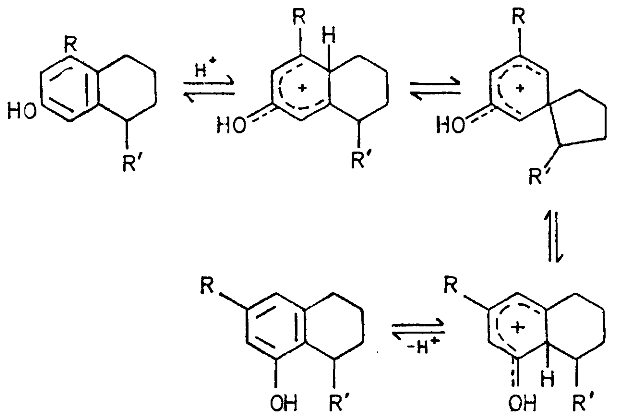
Studies in Perchloric Acid.—Limited studies were made of the rearrangement kinetics of compounds (1), (2), (4), and (5) in aqueous perchloric acid. This acid has an advantage over sulphuric acid in that it cannot sulphonate the phenolic rearrangement products and, unlike hydrochloric acid, should not cause ring opening of the saturated ring of the bicyclic dienone (2).* Values of H_A more negative than $-3·3$ are not recorded for perchloric acid, so we compare the rates in perchloric acid with those in sulphuric acid of the same H_0 value. In each case, reaction was faster in perchloric acid: for (1), methyl migration was accelerated by $4·5 \pm 0·3$ times, and spiran migration by $3·2 \pm 0·4$; for (2) the corresponding acceleration factors were $2·7 \pm 0·5$ and $4·3 \pm 1·0$. The reversal in behaviour of the two reaction paths for these two compounds does not, at present, permit discussion of the effects of the perchlorate or sulphate ion on the transition states, but the overall acceleration of both paths agrees with our previous findings for dienone–phenol rearrangements and the earlier discussion[6] should apply here. For compound (4), the overall acceleration factor was $2·8 \pm 0·2$, with migration to C-5 affected slightly more than migration to C-3; for (5) the acceleration factor was $2·9 \pm 0·3$. The kinetic measurements on (4) and (5) were performed at acidities which gave incomplete protonation; in each case the degree of protonation was close to that at the same H_0 or H_A value in sulphuric acid, suggesting that their pK values are not significantly dependent on the acid.†

Phenol–Phenol Rearrangement of 5,6,7,8-*Tetrahydro*-4,8-*dimethyl*-2-*naphthol* (9) *into* 5,6,7,8-*Tetrahydro*-4,8-*dimethyl*-1-*naphthol* (10).—The available evidence suggests that rearrangement of the bicyclic dienone (2) in aqueous sulphuric or perchloric acid gives a mixture of the phenolic products (9) and (10), and that (9) is itself isomerised to (10). The isomerisation is relatively slow at 25 °C, but about 30% complete within 4 h at 100 °C; it probably explains the findings that rearrangement of (2) in sulphuric acid at 25 °C gives an initial ratio of (9) to (10) of 59 : 41, but rearrangement for 30 min at 100° gives the ratio 31 : 69. Experiments

[32] M. Hemetsberger, *Monatsh.*, 1968, **99**, 1225, 1724.
[33] D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 1959, 788.
[34] P. J. Kropp, *Tetrahedron Letters*, 1963, 1671.
[35] K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418.

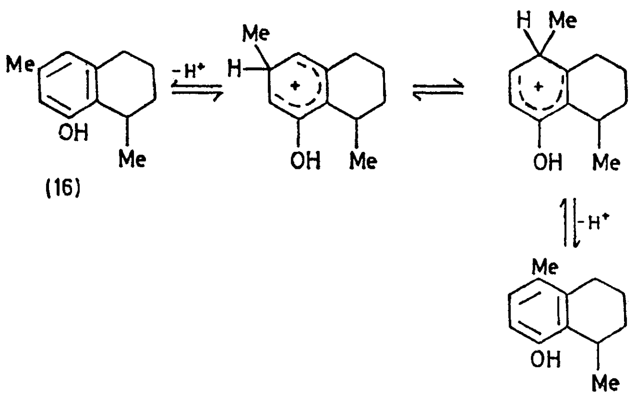
on the pure phenols suggest that (10) is not appreciably isomerised to (9), but overall loss of material under the acidic conditions employed may obscure the detection of a very slow reaction.

A phenol–phenol rearrangement of (7) to the isomeric 3-methyl-1-tetralol was reported by Hopff and Dreiding,[22] who also found 5,6,7,8-tetrahydro-1-naphthol and -2-naphthol to be interconverted in 70% $HClO_4$. The mechanism suggested is shown in Scheme 2, with R′ = H. The same sequence would not completely



SCHEME 2

explain the reaction (9) ⟶ (10), which also requires a methyl migration step. One possible mechanism is that (9) is protonated and follows path a of Scheme 1 in the reverse direction, giving the original dienone cation, which then reacts *via* path b to give (10). An alternative route could follow Scheme 2 (with R = R′ = Me), giving (16) which may then isomerise to (10). We have no strong evidence favouring one route over the other, but are loath to accept the first suggestion, which should lead to a drift from first-order kinetics as the reaction proceeds: this was not observed.



(16) (10)

We are investigating the occurrence of similar rearrangements which may give further information.

* Comparison of rates in acid of one *concentration* (wt. %) for (2), which is completely protonated at the acidity employed, changes the higher value to 27 ± 1 kcal mol^{-1} (113 ± 4 kJ mol^{-1}).

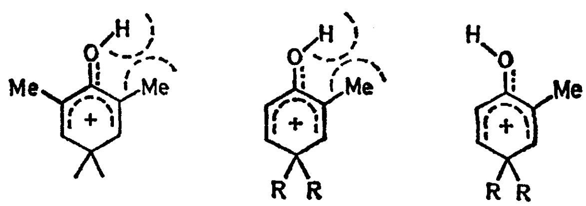
Activation Parameters.—Approximate values of the Arrhenius activation energies for the rearrangements of the bicyclic dienone (2) and the two monocyclic compounds (4) and (5) were obtained from kinetics in sulphuric acids of equal H_0 values at 25 and 40 °C. In each case the Arrhenius E_A value * was between 25·4 ± 0·6 and 28 ± 1 kcal mol^{-1} (106 ± 3 and 117 ± 4 kJ mol^{-1}). This may be compared with the isomerisation of hexamethylcyclohexa-2,4-dienone to hexamethylcyclohexa-2,5-dienone in 85 and 95% sulphuric acid,[36] which should be more exothermic than our reactions, and has $\Delta G^\ddagger$ 24·1 kcal mol^{-1} (100 kJ mol^{-1}); and the dienone–phenol rearrangement of 4,4-dimethylcyclohexa-2,5-dienone in 97·24% sulphuric acid, which has [37] $\Delta H^\ddagger$ 21·9 ± 0·4 kcal mol^{-1} (91 ± 2 kJ mol^{-1}). The entropies of activation are all positive (*ca.* 10 cal mol^{-1} deg^{-1}; 42J mol^{-1} K^{-1}), which may be due to the 'shedding' of water of solvation which has been shown to occur during the rearrangements.[6,37]

APPENDIX

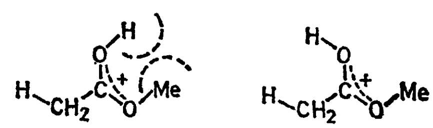
The pK values of the dienones studied here [apart from (5)], the alkylated analogues reported earlier,[5] and some other analogues,[26,38] (12 compounds; pK range 2·6 units) are correlated (r = 0·98) by a Hammett–Brown equation [equation (9)], using σ_m^+ for 2- and

$$-\mathrm{p}K = 2{\cdot}66 \pm 0{\cdot}12 + 2{\cdot}32\Sigma\sigma^+ \qquad (9)$$

6-substituents and σ_o^+ for 3- and 5-substituents. Values of σ_o^+ are available in ref. 39. This equation should



(17) (18) R = Me (21) R = H (19) R = Me (20) R = H



(23) (22)

apply equally to 4-methyl-, -ethyl-, or -n-propyl-cyclohexa-2,5-dienones, which we have shown to have equal pK values.[26,38] The measured pK of dienones which have one large group at C-2 or C-6 should be 0·3 unit lower than predicted by equation (9) because of a

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[37] V. P. Vitullo and N. Grossman, *J. Amer. Chem. Soc.*, 1972, **94**, 3844.
[38] J. W. Pilkington and A. J. Waring, unpublished work.
[39] C. W. McGary, jun., Y. Okamoto, and H. C. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037; H. V. Ansell, J. LeGuen, and R. Taylor, *Tetrahedron Letters*, 1973, 13.

statistical factor explained later. We attribute the low basicity of (5) to steric inhibition of protonation of the carbonyl group by the combined effect of the 2- and 6-methyl groups. The steric interaction shown in (17) and (18), relative to that in (19), is estimated using the cation of 2-methylphenol as a model. This was shown by n.m.r. to have structure (20), with none of (21) being observed.[40] A similar effect is seen in the cation of methyl acetate in HF–BF_3, which was shown [41] to be solely (22), and not (23). If the detection limit were 4% the energy difference between the cation conformers would be $\geqslant 1{\cdot}6$ kcal mol^{-1} (6·7 kJ mol^{-1}). Equation (10) for an equilibrium is equivalent to equation (11) at 25 °C, and the unavoidable methyl–hydrogen interaction shown in (17) will cause the basicity of dienone (5) to be reduced by at least 1·2 pK unit. Dienones which have only one 2- or 6-substituent of significant size will lack the cation conformation of type (18) and should be made less basic by $\log_{10} 2$, *i.e.* 0·3 pK unit thereby.

$$\Delta\Delta G = -RT\Delta(\ln K) \tag{10}$$

$$\Delta\Delta G_{\text{protonation}} = -1{\cdot}36\Delta \mathrm{p}K, \text{ in kcal mol}^{-1} = -5{\cdot}69\Delta \mathrm{p}K, \text{ in kJ mol}^{-1} \tag{11}$$

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[3/588 *Received*, 20*th March*, 1973]

[40] G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 1973, **38**, 353.
[41] H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 816.