Thermal Acid-catalysed Rearrangements of Natural Chrysanthemic Acids

By **Dismas A. Otieno, Gerald Pattenden,*** and **Christopher R. Popplestone,** Department of Chemistry, The University, Nottingham NG7 2RD

Treatment of *trans*-chrysanthemic acid (1) with pyridine hydrochloride at 210 °C leads to (E)-2-isopropylidene-5-methylhex-3-enoic acid (3) (22%) and to a mixture of neutral products (55%) containing (E)-2,6-dimethylhepta-2,4-diene (4), three butanolides [(5), (6), and (8)], and a pentenolide (7). The conversions (1) ⟶ (3) and (1) ⟶ (4) proceed with cleavage of the cyclopropane 2,3-bond *via* a thermal homodienyl 1,5 H-shift, leading to a dienoic acid intermediate (11), followed by decarboxylation [to (4)] and isomerisation [to (3)] ; the dienoic acid (3) is converted further into the butanolide (6). The butanolide (8) and the pentenolide (7) result from cleavage of the cyclopropane 1,2-bond. Separate treatment of the butanolide (8) with pyridine hydrochloride leads to a mixture of isomeric pentenolides (7) and (13). Cleavage of the cylcopropane 1,3-bond in (1) accounts for the formation of the butanolide (5).

The principal neutral products from the thermal decomposition of chrysanthemumdicarboxylic acid (2) are shown to be a cyclohexadienone (19), 2,6-dimethylphenol (21), a pentenolide (20), and a butanolide (22). The conversion (2) ⟶ (19) takes place *via* acid-catalysed cyclodehydration of an intermediate (Z)-dienoic acid (16), whereas the formation fo the phenol (21) is envisaged as proceeding *via* demethylation of the methyl ether product (25) of [1,3]-sigmatropic rearrangement of the cyclohexadienone (19).

THE cyclopropane monoterpenoid chrysanthemic acids (1) and (2) occur naturally as insecticidal esters in pyrethrum, *Chrysanthemum cinerariaefolium*.[1] The carbon framew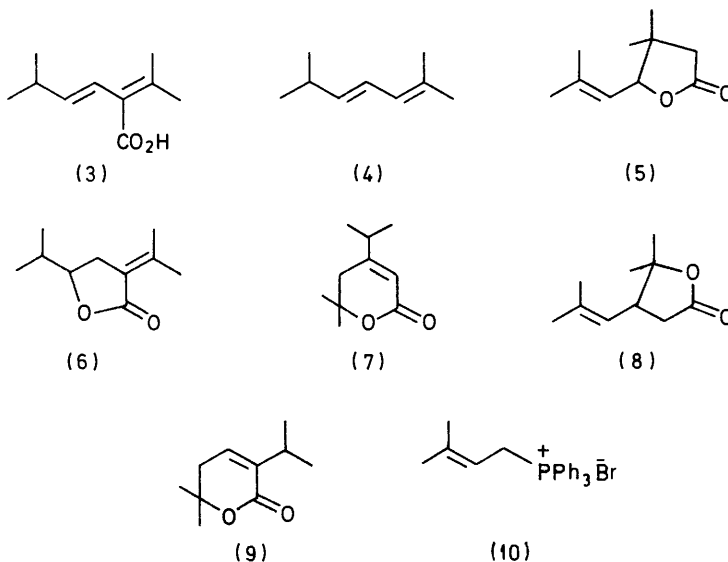orks in the acids illustrate an unusual ('tail-to-middle') union of isopentane units which more recently has also been found in 'presqualene' and

---

[1] See 'Pyrethrum, the Natural Insecticide,' ed. J. E. Casida, Academic Press, New York and London, 1973.

'prephytoene,' the biogenetic precursors of squalene and phytoene, respectively.[2] Our studies of the biosynthesis of the chrysanthemic acids required the development of degradative procedures for the isolation of specific atoms in the two acids.[3] The cyclopropane ring systems in (1) and (2), and their derivatives, are known to be susceptible to cleavage by both thermal and photolytic processes, and under carbocation initiation, and a range of structurally diverse rearrangement and breakdown products has been encountered.[4] In this paper, we show that the thermal acid-catalysed rearrangement of the monoacid (1) follows a much more complex pathway than hitherto imagined, leading to isomeric products formally resulting from cleavage of all three cyclopropane ring bonds. We also report the structures for several novel neutral products resulting from thermal decomposition of the diacid (2).

(1)   (2)
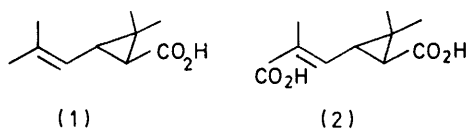
Treatment of chrysanthemic acid (1) with pyridine hydrochloride at 210 °C for 3 h produced a mixture of acidic and neutral products in *ca.* 77% total yield.

disubstituted double bond ($\nu_{max.}$ 970 cm^{-1}). Its ^{1}H n.m.r. spectrum revealed the presence of an isopropyl group attached directly to the *trans*(E)-disubstituted double bond (J_{vic} 16 Hz), and also two non-equivalent vinylic methyl groups (τ 8.06 and 8.16). These data led to the formula (3) for the acid. Oxidative cleavage with osmium tetraoxide–sodium periodate led to a mixture of acetone and isobutyraldehyde, isolated as their crystalline 2,4-dinitrophenylhydrazones.

G.l.c. analysis of the neutral product (*ca.* 55% total recovery) indicated the presence of five components, in the approximate proportions 15 : 9 : 32 : 12 : 32. The four major components (eluted first, third, fourth, and fifth) were isolated by liquid chromatography and identified as the hydrocarbon (4), the butanolides (5) and (6), and the pentenolide (7). The minor neutral component (eluted second) was not obtained chromatographically homogeneous but by comparison was shown to be the known butanolide 'pyrocin' (8).[5]

The volatile hydrocarbon eluted first was shown to be (E)-2,6-dimethylhepta-2,4-diene (4) by comparison with an authentic sample (containing *ca.* 10% Z-isomer) prepared by Wittig condensation between the 3-methylbut-2-enylphosphonium salt (10) and isobutyraldehyde. The hydrocarbons displayed closely similar i.r. ($\nu_{max.}$ 960 cm^{-1}) and n.m.r. [J_{vic} 15 Hz (olefinic protons)]

(3)   (4)   (5)

(6)   (7)   (8)

(9)   (10)

The acidic product (*ca.* 22% yield) was homogeneous according to both t.l.c. and g.l.c., and the mass spectrum showed that it was isomeric with the starting acid. Absorption data indicated the presence of an unsaturated carboxylic acid ($\nu_{max.}$ 1 695 cm^{-1}) and a conjugated system ($\lambda_{max.}$ 235 nm) containing a *trans*(E)-

spectra, and the major isomer in the synthetic sample did not separate in mixed g.l.c. from the product obtained from chrysanthemic acid (1).

^{1}H N.m.r. data of the product ($C_{10}H_{16}O_{2}$) eluted third in g.l.c. indicated the presence of a methylene group [AB quartet (J 12 Hz) centred at τ 7.52 and 7.76] and two vinylic (τ 8.20 and 8.25) and two saturated (τ 8.84 and 8.98) methyl groups; an olefinic proton resonance at

[2] For bibliography see. R. V. M. Campbell, L. Crombie, D. A. R. Findley, R. W. King, G. Pattenden, and D. A. Whiting, *J.C.S. Perkin I*, 1975, 897; see also (a) G. Popjak, H. Nigan, and W. Agnew, *Bioorg. Chem.*, 1975, **4**, 279; (b) E. J. Corey and R. P. Volante, *J. Amer. Chem. Soc.*, 1976, **98**, 1291.

[3] (a) G. Pattenden and R. Storer, *Tetrahedron Letters*, 1973, 3473; (b) S. A. Abou-Donia, C. F. Doherty, and G. Pattenden, *ibid.*, p. 3477; (c) G. Pattenden, C. R. Popplestone, and R. Storer, *J.C.S. Chem. Comm.*, 1975, 290.

[4] (a) L. Crombie, C. F. Doherty, G. Pattenden, and D. K. Woods, *J. Chem. Soc.* (*C*), 1971, 2739, and references cited therein; (b) L. Crombie, P. A. Firth, R. P. Houghton, D. A. Whiting, and D. K. Woods, *J.C.S. Perkin I*, 1972, 642.

[5] L. Crombie, S. H. Harper, and R. A. Thompson, *J. Sci. Food. Agric.*, 1951, **2**, 421.

τ 4.8 showed spin-coupling (J 9 Hz) to CH·O (τ 5.2). The i.r. spectrum showed the presence of a saturated γ-lactone ($\nu_{max.}$ 1 770 cm^{-1}). Taken together, these data established the butanolide structure (5). Absorption data on the isomeric butanolide eluted fourth in g.l.c. showed the presence of an exocyclic α-unsaturated butanolide group ($\nu_{max.}$ 1 750 cm^{-1}) and a conjugated system [$\lambda_{max.}$ 229 nm (ε 10 800)]. The ^{1}H n.m.r. spectrum indicated two vinylic methyl groups, one of which (τ 7.75) was considerably deshielded (cf. τ 8.13), and an isopropyl grouping (overlapping methyl doublets

did not provide an unambiguous distinction. We ultimately resolved the problem by X-ray measurements,* which established the constitution (7). The symmetry inherent in structure (7) is reflected in the apparent equivalence of the geminal methyl groups α to the ring oxygen atom. The tertiary olefinic carbon (C-3) signal was not visible in the ^{13}C n.m.r. spectrum.

Formation of the rearrangement products (3) and (6) and of the hydrocarbon (4) from chrysanthemic acid is best rationalised in terms of an initial thermal homodienyl 1,5 H-shift to produce the (Z)-dienoic acid (11)
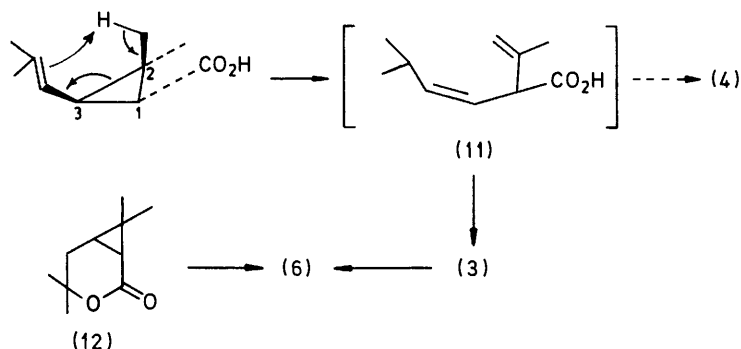
SCHEME 1
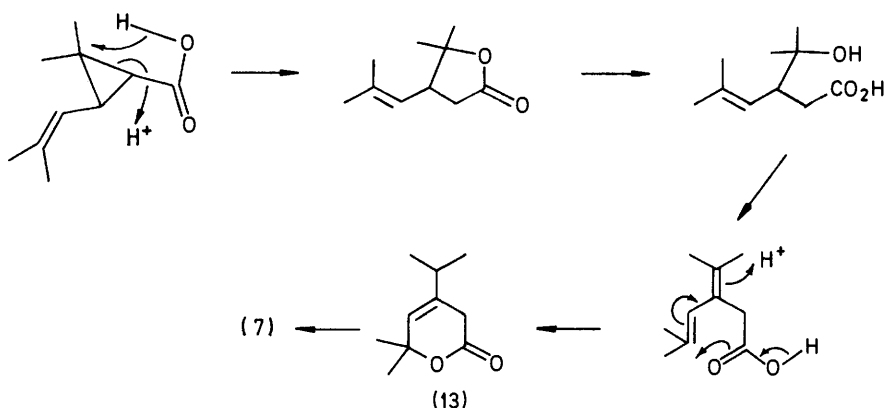
SCHEME 2

between τ 8.9 and 9.12) adjacent to a chiral centre. The data supported structure (6).

The principal neutral product obtained from (1), eluted last in g.l.c., separated as a solid. The i.r. spectrum showed the presence of an unsaturated δ-lactone group ($\nu_{max.}$ 1 720 and 1 640 cm^{-1}) and the compound displayed weak u.v. absorption [$\lambda_{max.}$ 219 nm (ε 10 500)]. The ^{1}H n.m.r. spectrum was deceptively simple, revealing just three singlet resonances at τ 4.23, 7.67, and 8.59 (ratio 1 : 2 : 6) and an isopropyl doublet (J 7 Hz) at τ 8.9. ^{13}C N.m.r. data distinguished only seven of the ten carbon atoms present in the molecule: two sp^3 quartets (δ 19.4 and 26.9), one sp^3 triplet (δ 36.8), an sp^3 doublet (δ 33.8) and singlet (δ 77.3), an sp^2 doublet (δ 110.5), and the carbonyl signal (δ 220). The foregoing data supported either structure (7) or (9), but
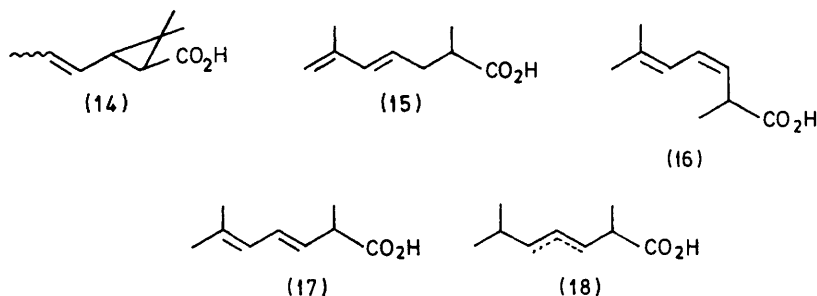
(Scheme 1). Acid-catalysed isomerisation of (11) then leads to (3) which is converted into the isomeric butanolide (6). Loss of carbon dioxide from (11), which can involve either of the proximate βγ-double bonds, followed by isomerisation, leads to the hydrocarbon (4). The purely thermal rearrangement of chrysanthemic acid to (11), in vacuo at 300 °C, has been reported by Ohloff,[6] and the hydrocarbon (4) has been observed earlier amongst the thermal degradation products of the insecticidal ester, ' allethrin,' which is derived from (1).[7] The compounds (3), (4), and (6), which together make up ca. 50% of the total products, are therefore derived via cleavage of the 2,3-bond in the cyclopropane ring of (1). The butanolide (6) was also obtained as the major rearrangement product from

[6] G. Ohloff, Tetrahedron Letters, 1965, 3795.
[7] Cf. Y. Nakada, Y. Yura, and K. Murayama, J. Agric. Chem. Soc. Japan, 1970, 44, 1724.

treatment of the pentanolide (12) with pyridine hydrochloride. The rearrangement of chrysanthemic acid *via* 1,2-cyclopropane bond cleavage leading to pyrocin (8) has been known for a long time.[5] It seemed likely that pyrocin (8) was the precursor of the pentenolide (7) (see Scheme 2); indeed treatment of authentic pyrocin with pyridine hydrochloride at 210 °C led to (7) and its isomer (13) in high yield. After completion of our work, Matsui and his co-workers [8] reported the rearrangement of pyrocin to a single pentenolide, assigned the constitution (7), in hot concentrated hydrochloric acid. The butanolide (5) which results from cleavage of the 1,3-cyclopropane bond in (1) has previously been obtained by the photolysis of chrysanthemic acid.[9]

We have previously [4a] described the composition of the acidic products [*viz.* (14)—(18)] from the thermal decomposition of chrysanthemumdicarboxylic acid (2); these studies produced results pertinent to certain

four were separated by a combination of preparative layer and gas-liquid chromatography and identified as the cyclohexadienone (19), the pentenolide (20), the phenol (21), and the butanolide (22).

The major neutral component eluted first in g.l.c. separated initially as a viscous oil which solidified overnight to give crystals. Elemental analysis and mass spectral data agreed with the molecular formula $C_{18}H_{24}O_2$. The base peak in the mass spectrum (*m/e* 136) suggested a dimer of $C_9H_{12}O$. Spectral data recorded immediately on freshly separated oily material were different from those recorded for the crystalline material (see Experimental section). These data led to the supposition that the crystalline material was the Diels–Alder dimer (23) of the cyclohexadienone (19). An authentic specimen of the dimer (23) was prepared by methylation of sodium 2,6-dimethylphenolate,[10] and was identical (m.p. and spectral data) with the crystalline

conclusions arrived at before, regarding the biosynthesis of the diacid carbon skeleton in *C. cinerariaefolium*. The acidic decomposition products (14)—(18) were
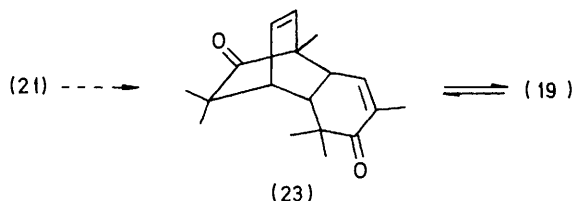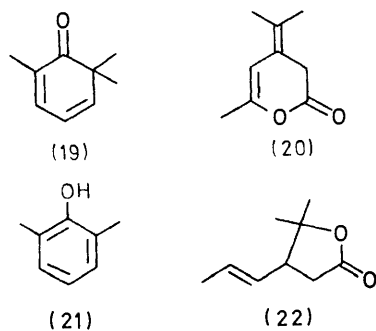
accompanied by neutral products (*ca.* 20%) which possessed collectively a characteristic aroma. We have now examined the constitutions of the major components in this neutral mixture. G.l.c. analysis showed the presence of at least fifteen components, four of which made up *ca.* 80% of the total fraction. These

material separated by g.l.c. Furthermore, retro-Diels–Alder reaction of authentic (23) led to authentic dienone (19), which displayed spectral data (i.r. and n.m.r.) identical with those recorded for the neutral oil eluted first in g.l.c.

The [1]H n.m.r. spectrum of the neutral component ($C_9H_{12}O_2$) eluted second in g.l.c. showed a low-field olefinic proton quartet (J 1.5 Hz) at τ 3.05 which by double irradiation experiments was found to be spin-coupled to a vinylic methyl group (τ 8.25); two other vinylic methyl groups resonated as singlets at τ 7.75 and 8.14, and a broad absorption at τ 7.05 was ascribed to a methylene group. The corresponding [13]C n.m.r. spectrum revealed three sp^3 quartets at δ 10.9, 19.6, and 24, an sp^3 triplet at δ 32.3, one olefinic carbon doublet at δ 147.5, and three olefinic carbon singlets at δ 128.9, 144.6, and 146.1 in addition to a carbonyl resonance at δ 197.1. The electronic absorption spectrum suggested the presence of a conjugated system [$\lambda_{max.}$ 254 nm (ε 9 500)] and the compound displayed i.r. data ($\nu_{max.}$ 1 755, 1 688, 1 650, and 1 632 cm^{-1}) indicative of a pentenolide containing extended conjugation. The foregoing data are best accommodated by structure (20) (see below).

The compound eluted third in g.l.c. ($C_8H_{10}O$) was

[8] H. Hirai, K. Ueda, and M. Matsui, *Agric. Biol. Chem.*, 1976, **40**, 153.

[9] (*a*) M. J. Bullivant and G. Pattenden, *Pyrethrum Post*, 1971, **11**, 1; (*b*) T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, 1970, **35**, 790.

[10] T. L. Brown, D. Y. Curtin, and R. R. Fraser, *J. Amer. Chem. Soc.*, 1958, **80**, 4339.

established as 2,6-dimethylphenol (21) by comparison (mixed g.l.c. and spectral data) with an authentic sample. Features of the [1]H n.m.r. and i.r. spectral data of the neutral component ($C_9H_{14}O_2$) eluted fourth in g.l.c. closely resembled those of the butanolide (8) (see Experimental section), and therefore suggested the butanolide structure (22). The compound was not isomerically homogeneous however, and inspection and comparison of data with those recorded for Z- and E-isomers of (14) indicated that the compound was contaminated with its Z-isomer.

The above data suggested a scheme from the diacid (2) to 2,6-dimethylphenol involving the dienoic acid (16) and the dienone (19) as intermediates. A homo-[1,5]-sigmatropic shift in (2) followed by loss of carbon dioxide from the (Z)-1,4-dienedioic acid intermediate (24) leads first to the dienoic acid (16), which then undergoes acid-catalysed cyclodehydration (presumably via an acylium ion intermediate) producing the cyclohexadienone (19). Acid-catalysed [1,3]-sigmatropic shift of one of the C-2-methyl groups in (19) (which may be a concerted process) [11] then leads to the methyl ether (25),
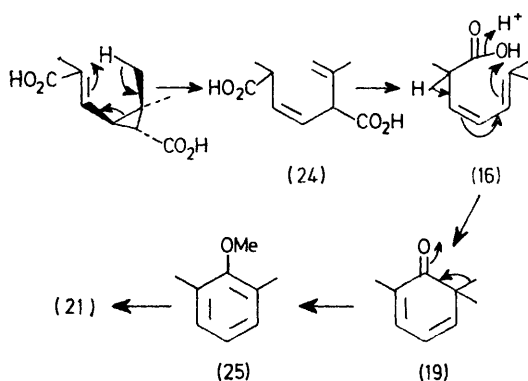
SCHEME 3

which is demethylated in situ giving rise to the phenol (21). The methyl ester of the (Z)-dienoic acid (16) has been prepared previously by photolysis of the dienone (19) in methanol.[12] To demonstrate that the phenol (21) was derived from (2) via the dienone (19) we heated the dimer (23) at 280 °C in the presence of a catalytic amount of hydrochloric acid. Isolation of the acidic products of this reaction led almost entirely to the phenol (21) (>90% by g.l.c.). In related studies we showed that when the dienone (19) was treated with
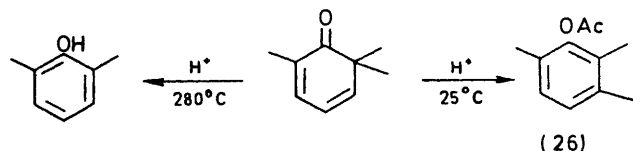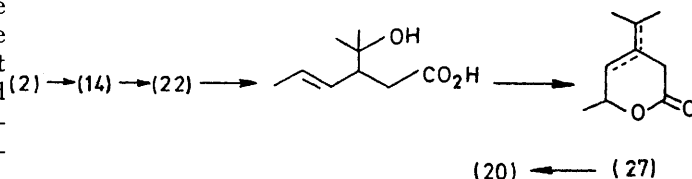

acetic anhydride containing sulphuric acid at 25 °C only the acetate (26) of the phenolic [1,2]-rearrangement product was produced.

[11] Cf. B. Miller, J. Amer. Chem. Soc., 1974, 96, 7155.
[12] P. M. Collins and H. Hart, J. Chem. Soc. (C), 1967, 1197.

The origin of the pentenolide (20) is not immediately clear, but the butenolide (22) is probably implicated as an intermediate by analogy with the conversion of (1) into (7) via (8). Isomerisation of (22) into an un-

saturated pentenolide [viz. (27)] followed by acid-catalysed disproportionation would then account for the formation of (20) from the diacid (2).

EXPERIMENTAL

For general experimental details see ref. 4a. [13]C N.m.r. spectra were recorded at 20 °C with a JEOL-PS-100 spectrometer operating at 25.15 MHz interfaced with a Nicolet 1085 20 K computer.

Rearrangement of (+)-trans-Chrysanthemic Acid (1).—A mixture of (+)-trans-chrysanthemic acid (4 g) and pyridine hydrochloride (40 g) was heated at 210 °C for 3 h, then cooled to 25 °C and treated with 25% hydrochloric acid (100 ml). The solution was filtered, and the filtrate was thoroughly extracted with ether and then washed with sodium hydrogen carbonate solution. The sodium hydrogen carbonate extract was acidified with hydrochloric acid, and then extracted with ether. Evaporation of the dried ether extract left a pale yellow liquid (ca. 0.85 g, 22%), homogeneous according to t.l.c. and g.l.c. (10% PEGA; 180 °C) and identified as (E)-2-isopropylidene-5-methylhex-3-enoic acid (3), n_D^{22} 1.4814, $\lambda_{max.}$ 235 nm (ϵ 14 300), $v_{max.}$ 1 695 and 970 cm^{-1}, τ 0.5 (OH), 3.85 (d, J 15 Hz, CH:CH·), 4.4 (dd, J 15 and 7 Hz, ·CH·CH:CH·), 7.7 (m, CHMe$_2$), 8.08 (:CMe), 8.16 (:CMe), and 8.98 (d, J 7 Hz, CHMe$_2$) (Found: m/e, 168.1131. $C_{10}H_{16}O_2$ requires M, 168.1131).

Evaporation of the dried ether solution remaining after the sodium hydrogen carbonate extraction left a neutral oil (ca. 2.2 g, 55%). G.l.c. (10% Apiezon L; 140 °C) showed that this contained five major components in the approximate proportions 15 : 9 : 32 : 12 : 32. The mixture was separated by column chromatography on silica gel [light petroleum (b.p. 40—60 °C)–ethyl acetate (4 : 1) as eluant], and pure samples of four of the components (eluted first, third, fourth, and fifth) were obtained. The component eluted second was not obtained pure.

(E)-2,6-Dimethylhepta-2,4-diene (4), eluted first [ca. 8% overall yield from (1)], showed n_D^{22} 1.4470, $\lambda_{max.}$ 230 nm, $v_{max.}$ (film) 980 cm^{-1}, τ 3.99 (dd, J 15 and 10 Hz, :CH·CH:CH), 4.13 (dm, J ca. 10 Hz, Me$_2$C:CH·CH), 4.59 (dd, J 15 and 7 Hz, ·CH·CH:CH·), 7.67 (m, Me$_2$CH·CH), 8.29 (:CMe$_2$), and 9.02 (d, J 7 Hz, Me$_2$CH), M^+ 124. An authentic sample (containing ca. 10% of the Z-isomer) was synthesised by Wittig condensation between 3-methylbut-2-enyltriphenylphosphonium bromide [13] and isobutyraldehyde in ether with n-butyl-lithium as base. The authentic sample showed spectral data closely similar to those recorded for the hydrocarbon obtained from (1) (cf. ref. 7).

3,3-Dimethyl-4-(2-methylpropenyl)butanolide (5), eluted third [ca. 17% overall yield from (1)], obtained as a viscous

[13] C. E. Griffin and M. Gordon, J. Organometallic Chem., 1965, 3, 417.

oil (lit.,[14] m.p. 49°), showed $\nu_{max.}$ 1 770 and 1 650 cm^{-1}, τ 4.8 (d, J 10 Hz, $\stackrel{..}{\cdot}$CH·CH), 5.24 (d, J 10 Hz, $\stackrel{..}{\cdot}$CH·CH), 7.60 (d, J 12 Hz, CHH), 7.68 (d, J 12 Hz, ·CHH), 8.2 ($\stackrel{..}{\cdot}$CMe), 8.26 ($\stackrel{..}{\cdot}$CMe), 8.84 (·CMe), and 8.98 (·CMe), M^+ 168.

4-Isopropyl-2-isopropylidenebutanolide (6), eluted fourth [*ca.* 6% overall yield from (1)], a viscous oil, showed n_D^{22} 1.4798, $\lambda_{max.}$ 229 (ε 10 800), $\nu_{max.}$ 1 750 and 1 670 cm^{-1}, τ 5.9 (m, ·CHO), 7.3 (m, CHMe$_2$), 7.75 ($\stackrel{..}{\cdot}$CMe), *ca.* 7.6 (obscured, 2 H), 8.13 ($\stackrel{..}{\cdot}$CMe), and 9.0 and 9.07 (overlapping d, J 7 Hz, ·CHMe_2) (Found: *m/e*, 168.115. C$_{10}$H$_{16}$O$_2$ requires M, 168.1131).

3-Isopropyl-5,5-dimethylpent-2-enolide (7), eluted fifth [*ca.* 17% overall yield from (1)], crystallised from ethanol as needles, m.p. 59—60°, $\lambda_{max.}$ 219 nm (ε 10 500), $\nu_{max.}$ 1 720 and 1 640 cm^{-1}, τ 4.23 (m, $\stackrel{..}{\cdot}$CH), 7.67 (CH$_2$), 8.59 (CMe$_2$), and 8.9 (d, J 7 Hz, CHMe_2), δ_C 220, 110.5, 77.3, 36.8, 33.8, 26.9, and 19.4 (Found: *m/e*, 168.1151).

Rearrangement of the Butanolide (8).—The butanolide (4 g) was treated with pyridine hydrochloride (40 g) as described above. G.l.c. analysis of the neutral products (*ca.* 60%) showed the presence of three components in the approximate proportions 14 : 58 : 28; the individual components were separated by chromatography on silica gel [light petroleum (b.p. 40—60°)–ethyl acetate (4 : 1) as eluant]. Unchanged butanolide (8), eluted first, and the pentenolide (7), eluted last, were identical with authentic samples. *3-Isopropyl-5,5-dimethylpent-3-enolide* (13), eluted second, the major product, an oil, showed $\lambda_{max.}$ 211 nm, $\nu_{max.}$ 1 745 cm^{-1}, τ 4.26 ($\stackrel{..}{\cdot}$CH), 7.6 (1 H, m), 7.84 (CH$_2$), 8.55 (CMe$_2$), and 9.0 (d, J 6 Hz, CHMe_2) (Found: *m/e*, 168.1150. C$_{10}$H$_{16}$O$_2$ requires M, 168.1150).

Rearrangement of the Pentanolide (12).—The pentanolide [5] (2 g) was treated with pyridine hydrochloride (20 g) as described above. G.l.c. analysis of the neutral products showed the presence of five components in the approximate proportions 7 : 9 : 25 : 44 : 15. The major component (*ca.* 44% of total), eluted fourth in g.l.c., was purified by chromatography and identified as the butanolide (6). The component eluted last in g.l.c. was identified as pentenolide (7) by mixed g.l.c. analysis and spectral comparison.

Thermal Decomposition of Chrysanthemumdicarboxylic Acid (2).—G.l.c. analysis (5% Carbowax 20M; 140 °C) of the neutral product (*ca.* 20%) obtained from the thermal decomposition of the diacid [4a] showed the presence of *ca.* fifteen compounds, four of which were major constituents. The mixture was first chromatographed in chloroform on preparative layer (40 × 40 in) plates (silica gel HF 254); fractions were then taken and the individual components separated and purified by preparative g.l.c. (10% Carbowax 20M; 180 °C). *2,6,6-Trimethylcyclohexa-2,4-dienone* (19), eluted first, showed $\nu_{max.}$ 1 665 and 1 645 cm^{-1}, τ 3.16 (m, 1 H), 3.6—3.95 (m, 2 H), 8.1 ($\stackrel{..}{\cdot}$CMe), and

8.8 (2 × ·CMe), M^+ 136. The oil slowly crystallised to give the corresponding Diels–Alder dimer (23), m.p. 106—108° (lit.,[10] 110—110.5°), $\lambda_{max.}$ 239 nm, $\nu_{max.}$ 1 720 and 1 680 cm^{-1}, τ 3.5—3.8 (2 H, m), 4.5 (1 H, dm, J *ca.* 7 Hz), 7.2—7.5 (3 H, m), 8.2 ($\stackrel{..}{\cdot}$CMe), 8.7 (Me), 8.85 (3 × Me), and 8.96 (Me) (Found: C, 79.1; H, 8.7%; *m/e*, 272. Calc. for C$_{18}$H$_{24}$O$_2$: C, 79.4; H, 8.9; M, 272). An authentic sample of the dimer (23), synthesised as outlined previously,[10] displayed identical spectral data (m.p. and mixed m.p. 108—109°). Pyrolysis of the dimer, as described previously,[10] gave the dienone (19) which exhibited spectral data (i.r. and ^{1}H n.m.r.) identical with those given above.

3-Isopropylidene-5-methylpent-4-enolide (20), eluted second, an oil, showed $\lambda_{max.}$ 254 nm (ε 9 500), $\nu_{max.}$ 1 755, 1 688, 1 650, and 1 632 cm^{-1}, τ 3.05 (q, J 1.5 Hz, $\stackrel{..}{\cdot}$CH), 7.0br (2 H), 7.75 ($\stackrel{..}{\cdot}$CMe), 8.14 ($\stackrel{..}{\cdot}$CMe), and 8.25 (d, J 1.5 Hz, CMe), δ_C 10.9 (Me), 19.6 (Me), 24.0 (Me), 32.3 (CH$_2$), 128.9 ($\stackrel{..}{\cdot}$C), 144.8 ($\stackrel{..}{\cdot}$C), 146.1 ($\stackrel{..}{\cdot}$C), 147.5 ($\stackrel{..}{\cdot}$CH), and 197 ($\stackrel{..}{\cdot}$CO) (Found: *m/e*, 152.0831. C$_9$H$_{12}$O$_2$ requires M, 152.0837).

2,6-Dimethylphenol (21), eluted third, had m.p. 44—47° (lit.,[15] 49°), $\nu_{max.}$ 3 300 cm^{-1}, τ 2.9—3.2 (3 H), 5.4 (OH), and 7.75 (2 × $\stackrel{..}{\cdot}$CMe), *m/e*, 122; these data are identical with those recorded for an authentic sample.

4,4-Dimethyl-3-[(ZE)-prop-2-enyl)butanolide (22), eluted fourth, showed $\nu_{max.}$ 1 778 and 1 655 cm^{-1}, τ 3.2—3.8 (*ca.* 2 H, m), 6.6—7.2 (m, $\stackrel{..}{\cdot}$CH·CH·CH$_2$), 7.4—7.65 (m, CH$_2$), 8.15—8.35 ($\stackrel{..}{\cdot}$CMe), 8.6 (Me), and 8.75 (Me), *m/e*, 154.

Rearrangement of the Cyclohexadienone (19).—(a) The dimer (23) (0.1 g) was heated at 280 °C in a sealed tube in the presence of concentrated hydrochloric acid (1 drop) for 2 h. The residue was dissolved in ether and the solution washed with aqueous sodium hydroxide. The aqueous layer was acidified (dil. HCl) and then extracted with ether. Evaporation of the dried ether extracts left a solid residue (25 mg) which by g.l.c. analysis and comparative ^{1}H n.m.r. data was shown to be the phenol (21) (>90% by g.l.c.).

(b) (with D. W. KNIGHT) A solution of the dienone (19) (0.5 g) in acetic anhydride (20 ml) containing concentrated sulphuric acid (5 drops) was stirred at 25 °C for 18 h, then poured onto ice–water and extracted with ether. Evaporation of the extract and chromatography of the residue in chloroform on silica gel gave the acetate (26) (0.3 g), an oil, $\nu_{max.}$ 1 760 cm^{-1}, τ 3.15 (2 H), 7.71 (3 H), 7.79 (3 H), 7.9 (3 H), and 7.96 (3 H), identical with a specimen prepared by acetylation of 2,3,6-trimethylphenol.

[14] F. Korte, D. Scharf, and K. H. Buechel, *Annalen*, 1963, **664**, 97.

[15] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.