

A Photochemical Di- π -methane Rearrangement leading to Methyl Chrysanthemate

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Irradiation of (2*E*)-methyl 4,4,6-trimethylhepta-2,5-dienoate (1b) affords methyl chrysanthemate (3b) and the *Z*-diene (6).

THE monoterpene chrysanthemic acid [2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylic acid] (3a) occurs as insecticidally active esters in *Chrysanthemum cinerariaefolium*. A number of ingenious syntheses of

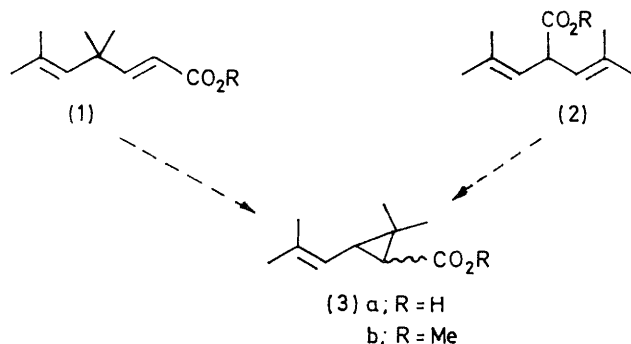
the acid have been described.¹ The presence of a vinyl-cyclopropane system suggested a new approach based on a photochemical 'di- π -methane' rearrangement of an appropriate 1,4-diene.² Either of the 1,4-dienes (1) and (2), *a priori*, can lead to the skeleton present in structure (3) by such a rearrangement. We report here a study of the rearrangement of the diene (1).

The diene ester (1b) was prepared from the alcohol (4), easily available *via* a Reformatsky reaction between

¹ For recent approaches see M. Julia and A. Guy-Rouault, *Bull. Soc. chim. France*, 1967, 1411; E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, 1967, **89**, 3912; B. P. 1 069 038; B.P. 1 178 880; J. Martel, C. Huynh, E. Toromanoff, and G. Nominé, *Bull. Soc. chim. France*, 1967, 982, 985; L. Velluz, J. Martel, and G. Nominé, *Compt. rend.*, 1969, **268C**, 2199; R. W. Mills, R. D. H. Murray, and R. A. Raphael, *J.C.S. Perkin I*, 1973, 133; *Ger. Offen.* 2 164 024.

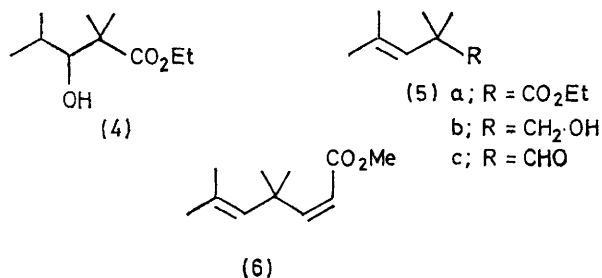
² See S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531 and references cited therein.

2-bromo-2-methylpropionate and 2-methylpropionaldehyde. Dehydration of the alcohol (4) with phosphoryl chloride-pyridine led first to the alkene (5a), which was



then reduced with lithium aluminium hydride. Oxidation of the resulting alcohol (5b) by the Moffatt procedure led to the aldehyde (5c), which in a Wadsworth-Emmons condensation with methyl di-*O*-ethylphosphonoacetate gave the *E*-diene (1b) exclusively.

Irradiation of the diene (1b) in hexane for 30 h with a medium-pressure mercury lamp resulted in three volatile products (*ca.* 66 : 20 : 14 in order of elution in g.l.c.); extended irradiations led to considerable decomposition. The photoproduct eluted second was separated by preparative g.l.c. and found to be identical in chromatographic behaviour and spectral data with authentic methyl chrysanthemate (3b). Inspection and comparison of the n.m.r. spectrum of the chrysanthemate photoproduct with those of authentic *cis*- and *trans*-methyl chrysanthemates³ showed that (3b) was produced as a *trans-cis* (*ca.* 2 : 1) mixture. It is not clear whether isomerisation occurs during the rearrangement

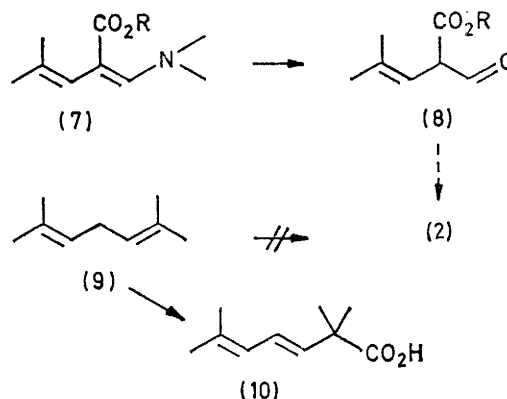


(1) \rightarrow (3), or subsequently as a result of photo-equilibration of the chrysanthemate photoproduct.⁴

The major photoproduct from (1b) was the *Z*-diene (6). Its structure and configuration followed from comparison of spectral data with those of (1b) (see Experimental section). Irradiation of (1b) in the presence of acetophenone as sensitizer gave the *Z*-diene (6) as the sole photoproduct; examination of the reaction

mixture at various times failed to reveal the presence of (3b). It appears therefore that the cyclopropane (3b) is derived from a singlet excited state of (1b), an observation in accord with similar observations² for other 'acyclic' di- π -methane chromophores.² Formation of (3) from a triplet excited state of (1) is prevented by preferred geometrical isomerisation.

We also briefly examined synthetic routes to the 1,4-diene (2). In one approach, the oxo-ester (8) was prepared by hydrolysis of the enamine (7) formed from ethyl propiolate and 2, *NN*-trimethylprop-1-enylamine.⁵ In spite of numerous attempts however, we were unable to effect the condensation of (8) with the ylide from 1-methylethylphosphonium iodide. In another approach,



carboxylation of the anion produced from the hydrocarbon (9) with *n*-butyl-lithium-*NNN'*-tetramethylethylenediamine was examined. Unfortunately only the isomeric diene acid (10) was obtained.

EXPERIMENTAL

For general experimental details, see preceding paper. G.l.c.-mass spectral data were obtained with a Varian CH5D instrument, through the courtesy of the Chemistry Department, University College, Cardiff (3% OV-1, 12 ft \times 2 mm column; 100 °C).

Ethyl 2,2,4-Trimethylpent-3-enoate (5a).—A Reformatsky reaction between ethyl 2-bromo-2-methylpropionate and 2-methylpropionaldehyde gave (73%) ethyl 3-hydroxy-2,2,4-trimethylpentanoate (4), b.p. 104–106° at 16 mmHg, n_D^{19} 1.4393 (lit.,⁶ b.p. 220–225°, v_{max} 3 510 and 1 730 cm⁻¹, τ (CCl₄) 5.91 (q, *J* 7.5 Hz, CH₂·CH₃), 6.68 (d, *J* 4 Hz, CHO), 6.79 (OH), 8.1–8.5 (m, Me₂CH), 8.74 (t, *J* 7.5 Hz, CH₂·CH₃), 8.8 (Me), 8.86 (Me), and 9.09 (d, *J* 6 Hz, CHMe). A solution of the alcohol (89 g) in dry pyridine (140 ml) was treated with phosphoryl chloride (70 ml) at such a rate that the temperature did not exceed 50 °C. The mixture was kept at 90–100 °C for 1 h, then cooled, poured onto ice, and extracted with ether. The extracts were washed successively with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water then dried and evaporated. Distillation gave the ester (48 g 60%), b.p. 80–85° at 20 mmHg, n_D^{15} 1.4350, v_{max} 1 732 and 861 cm⁻¹, τ (CCl₄)

³ A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, 1969, **25**, 1727.

⁴ Cf. M. J. Bullivant and G. Pattenden, *Pyrethrum Post*, 1971, **11**, 1; K. Ueda and M. Matsui, *Tetrahedron*, 1971, **27**, 2771.

⁵ K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, 1964, **29**, 818.

⁶ R. Shriner, *Org. Reactions*, 1942, **1**, 1.

4.91 (:CH), 5.95 (q, J 7.5 Hz, $\text{CH}_2\text{-CH}_3$), 8.33 (:CMe), 8.76 ($2 \times \text{Me}$), and 8.78 (t, J 7.5 Hz, $\text{CH}_2\text{-CH}_3$) (Found: M^+ , 170.1307. $\text{C}_{10}\text{H}_{18}\text{O}_2$ requires M , 170.1307).

2,2,4-Trimethylpent-3-enal (5c).—Reduction of the ester (5a) with lithium aluminium hydride, in the usual manner, gave (90%) 2,2,4-trimethylpent-3-en-1-ol (5b), n_{D}^{20} 1.4524 (lit.,⁷ n_{D}^{25} 1.4546), ν_{max} 3 340 and 1 048 cm^{-1} , τ (CCl_4) 4.99 (:CH), 6.73 (CH_2O), 7.45 (OH), 8.29 (:CMe), 8.32 (:CMe), and 8.94 ($2 \times \text{Me}$), M^+ 128 ($\text{C}_8\text{H}_{16}\text{O}$). Dry pyridine (9 ml) and then trifluoroacetic acid (9 ml) were added to a solution of the alcohol (27 g) and dicyclohexylcarbodiimide (137 g) in benzene (120 ml) and dimethyl sulphoxide (300 ml), and the resulting mixture was shaken and then kept at 25 °C for 16 h. The mixture was poured into ether (500 ml) and oxalic acid (80 g) was added. After dilution with water (400 ml), the mixture was filtered and the ether phase was separated. Distillation gave the aldehyde (16.4 g, 62%), b.p. 40–41° at 16 mmHg, n_{D}^{21} 1.4352 (lit.,⁸ b.p. 43–44° at 17 mmHg, n_{D}^{20} 1.4357), ν_{max} 2 720 and 1 729 cm^{-1} , τ (CCl_4) 0.71 (CHO), 4.97 (:CH), 8.27 (:CMe), 8.48 (:CMe), and 8.87 ($2 \times \text{Me}$), M^+ 126 ($\text{C}_8\text{H}_{14}\text{O}$).

(E)-Methyl 4,4,6-Trimethylhepta-2,5-dienoate (1b).—A solution of methyl di-*O*-ethylphosphonoacetate⁹ (13.9 g) in dry 1,2-dimethoxyethane (5 ml) was added dropwise to a stirred suspension of sodium hydride (1.9 g) in 1,2-dimethoxyethane (80 ml) under nitrogen, and the mixture was stirred at 25 °C for 1 h. The aldehyde (5c) (8 g) was introduced during 0.5 h, and the mixture was stirred at 25 °C for 2 h, then poured into water (50 ml) and extracted with ether. Evaporation of the dried extracts and chromatography of the residue (10.5 g) in petroleum (b.p. 60–80°) on silica gel gave the diene (5.3 g, 50%), b.p. ca. 120° at 12 mmHg (short-path distillation), λ_{max} 220 nm (ϵ 6 300), ν_{max} 1 727, 1 653, and 998 cm^{-1} , τ 3.08 (d, J 16 Hz, :CH·CO), 4.35 (d, J 16 Hz, ·CH:CH), 4.89 (:CH), 6.35 (OMe), 8.32 (:CMe), 8.42 (:CMe), and 8.8 ($2 \times \text{Me}$) (Found: C, 72.1; H, 10.1%; M^+ , 182.1303. $\text{C}_{11}\text{H}_{18}\text{O}_2$ requires C, 72.5; H, 9.9%; M , 182.1306).

Photolysis of the E-Ester (1b).—A solution of the ester (2.9 g) in hexane (1 000 ml) was irradiated in the usual manner for 30 h. Evaporation left a residue (2.85 g) which showed

four volatile products on g.l.c. analysis (41 : 12 : 9 : 38). Preparative g.l.c. (25% SE-30; 130 °C) gave (i) (*Z*)-methyl 4,4,6-trimethylhepta-2,5-dienoate (6) (eluted first) (ca. 41% total), ν_{max} 1 733, 1 638, and 825 cm^{-1} , τ 3.97 (d, J 12 Hz, :CH·CO), 4.48 (d, J 12 Hz, ·CH:CH), 4.77 (:CH), 6.43 (OMe), 8.39 (:CMe), 8.47 (:CMe), and 8.74 ($2 \times \text{Me}$) (Found: M^+ , 182.1314. $\text{C}_{11}\text{H}_{18}\text{O}_2$ requires M , 182.1307); (ii) methyl *cis-trans*-chrysanthemate (3b) (eluted second) (ca. 12% total), identical [g.l.c.–mass spectrometry: m/e 182 (25%), 167 (12), 151 (6), 139 (10), 123 (100), 107 (40), and 81 (73)] with an authentic sample;¹⁰ *cis:trans* ratio ca. 1 : 2 by integration of similar lines in the n.m.r. spectrum³ [particularly those due to the ester protons (τ 6.40 for *trans*-ester and τ 6.44 for *cis*-ester)]; (iii) starting *E*-diene ester (eluted last) (ca. 38% total), identical with an authentic sample.

A solution of the ester (1b) (0.04 g) and acetophenone (0.22 g) in hexane (200 ml) was irradiated through Pyrex for 23 h (g.l.c. monitoring); a photostationary 4 : 1 equilibrium mixture of (1b) and (6) was produced. Chromatography showed the absence of (3b) throughout the photolysis.

(E)-2,2,6-Trimethylhepta-3,5-dienoic Acid (10).—2,6-Dimethylhepta-2,5-diene¹¹ (2.9 g) was treated in the usual manner with 2.28M-*n*-butyl-lithium in hexane (12 ml) and *NNN'*-tetramethylethylenediamine (2.8 g). The solution was stirred for 1.5 h, and then added *via* a syringe to a slurry of solid carbon dioxide in ether. The mixture warmed to room temperature, and was then diluted with water. The aqueous phase was separated, then acidified with hydrochloric acid, and extracted with ether. Evaporation of the extract left the acid (2.7 g, 66%), λ_{max} 238 nm, ν_{max} 2 900 and 1 700 cm^{-1} , τ 3.7 (dd, J 16 and 10 Hz, :CH·CH:CH·), 4.3 (d, J 10 Hz, :CH·CH·), 4.4 (d, J 16 Hz, ·CH:CH·), 8.3 ($2 \times$:CMe), and 8.7 ($2 \times \text{Me}$), M^+ 168.

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⁷ C. F. Wilcox and D. L. Nearly, *J. Org. Chem.*, 1963, **28**, 3454.

⁸ R. H. Hasek, R. D. Clarke, and J. H. Chaudet, *J. Org. Chem.*, 1961, **26**, 3130; M. Julia and M. Baillarge, *Bull. Soc. chim. France*, 1966, 734.

⁹ J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, 1970, **35**, 3049.

¹⁰ G. Pattenden, L. Crombie, and P. Hemesley, *Org. Mass Spectrometry*, 1973, **7**, 719.

¹¹ S. M. Baba, H. H. Mathur, and S. C. Bhattacharyya, *Tetrahedron*, 1966, **22**, 903.