# A New Stereoselective Synthesis of *trans*-Chrysanthemic Acid [2,2-Dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylic Acid] [1,2]

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Base-catalysed interaction of 3-chloro-3-methylbut-1-yne and 3-methylbut-2-en-1-ol has been shown to produce 2,2-dimethyl-3-(2-methylprop-1-enylidene)cyclopropylmethanol (2). Selective reduction of this allene and subsequent oxidation gave racemic *trans*-chrysanthemic acid. The method represents a versatile route to many analogues.

THE pyrethrin family of insecticides, *e.g.* pyrethrin I (1), has attracted considerable attention.[3,4] The combination of insecticidal properties, knock-down effect, low mammalian toxicity, and ready biodegradability contrasts favourably with some of the more vilified methods of insect control. The recent observations [5] that simpler derivatives of (+)-*trans*-chrysanthemic acid (12) show even higher insecticidal activity than the natural esters have focused attention on new synthetic approaches to this acid. Recent ingenious routes include the addition of diphenylsulphonium isopropylide to δ-methylsorbic ester [6] and the base-catalysed interaction of β-methylcrotonic ester and isopentenyl aryl sulphones.[7] We now report a novel stereoselective synthesis of

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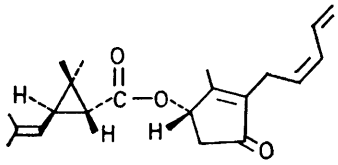
chrysanthemic acid which has the feature that both isoprenoid ' halves ' of the molecule are derived from the same readily available starting material, 2-methylbut-3-yn-2-ol.

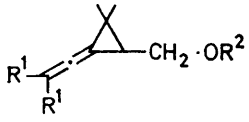
Conversion [8] of this alcohol into the corresponding chloride, followed by treatment with base has already been shown [9] to produce the allenyl carbene (6). The formation of this entity has been demonstrated [9] by trapping with various ethylenic hydrocarbons, whereby allene cyclopropanes are formed by electrophilic attack. We have found that when the carbene acceptor is provided by the double bond of 3-methylbut-2-en-1-ol (itself readily prepared [10] from 2-methylbut-3-yn-2-ol) there is produced in moderate yield an allene cyclopropane (2) possessing precisely the carbon skeleton of chrysanthemic acid.

Attempted reduction of the exocyclic double bond of structure (2) by hydride attack was unsuccessful, and catalytic hydrogenation of such a system is known [9] to proceed in a non-specific manner to produce complex mixtures. The requisite regioselective reduction of (2) was, however, readily achieved by treatment with sodium in liquid ammonia,[11] which gave a high yield of chrysanthemyl alcohol (7). Although a second chiral centre was thereby introduced, the two possible *cis*- and *trans*-diastereoisomers were not formed in equal amounts, the *trans*-alcohol comprising 75% of the product. A rationalisation for this selectivity involves intramolecular participation of the pendant hydroxy-group, which is conveniently placed to effect proton transfer to the carbanionic centre of an initially produced radical anion [12] (11). Such a process would lead necessarily to *trans* stereochemistry in the product. Some support for this directing role of the hydroxy-group was provided by carrying out the reduction on the tetrahydropyranyl ether (3) of the alcohol (2). Reduction was again regioselective but no longer stereoselective, hydrolysis of the product producing a 1 : 1 mixture of *cis*- and *trans*-chrysanthemyl alcohols.

Oxidation of chrysanthemyl alcohol at room temperature with chromium trioxide in dry pyridine gave the




(1)

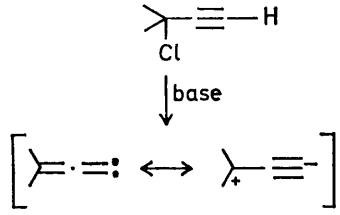



(2) $R^1$ = Me, $R^2$ = H

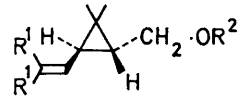
(3) $R^1$ = Me, $R^2$ = 

(4) $R^1R^1$ = $[CH_2]_5$, $R^2$ = H

(5) $R^1R^1$ = $[CH_2]_4$, $R^2$ = H




(6)

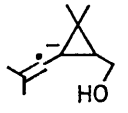



(7) $R^1$ = Me, $R^2$ = H

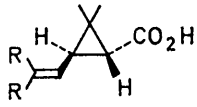
(8) $R^1$ = Me, $R^2$ = 

(9) $R^1R^1$ = $[CH_2]_5$, $R^2$ = H

(10) $R^1R^1$ = $[CH_2]_4$, $R^2$ = H



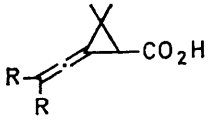

(11)




(12) R = Me

(13) RR = $[CH_2]_5$

(14) RR = $[CH_2]_4$




(15) R = Me

(16) RR = $[CH_2]_5$

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corresponding aldehyde. Addition of water then allowed the oxidation to proceed further, to the carboxylic acid. The (±)-*trans*-chrysanthemic acid (12) thus obtained was identical with an authentic sample. Similar oxidation of the allenic alcohol (2) gave the novel dehydrochrysanthemic acid (15). Attempts to by-pass the oxidation step by using the less nucleophilic double bond of 3-methylcrotonic acid as the carbene trap in the initial condensation were uniformly unsuccessful.

Structural variations in the starting chloroacetylene and allyl alcohol give analogues of chrysanthemic acid. The cyclohexylidene (13) and cyclopentylidene (14) analogues were prepared to demonstrate the scope of the reaction.

## EXPERIMENTAL

M.p.s were determined on a Reichert hot-stage apparatus. I.r. spectra were recorded for carbon tetrachloride solutions (0·1 mm cell) by Mrs. F. Lawrie (Perkin-Elmer 257 and Unicam SP 100 Mark II spectrophotometers). N.m.r. spectra were recorded by Mr. A. Haetzman (Varian T-60 spectrometer) for deuteriochloroform solutions with tetramethylsilane as internal standard. Mass spectra were recorded by Mr. A. Ritchie (A.E.I.–G.E.C. MS 12 spectrometer). Microanalyses were performed by Mr. J. M. L. Cameron and his staff. Kieselgel G (Merck) was used for analytical t.l.c. (0·25 mm) and Kieselgel $HF_{254}$ (Merck) for preparative t.l.c. (1 mm.). Analytical g.l.c. separations were performed on a Pye–Argon chromatograph (5% Carbowax column at 100°). Light petroleum refers to the fraction of b.p. 60—80°.

*Carbene Additions.*—(a) 2,2-*Dimethyl*-3-(2-*methylprop*-1-*enylidene*)*cyclopropylmethanol* (2). A flask containing 3-methylbut-2-en-1-ol (15 g, 0·175 mol) was flushed with dry nitrogen for 30 min and potassium t-butoxide (5·06 g, 0·045 mol) was added. The slurry was stirred and cooled to −10°. 3-Chloro-3-methylbut-1-yne (4·64 g, 0·045 mol) was added during 30 min with the temperature maintained at −10 to 0°. Stirring was continued for 3 h, during which time the mixture was allowed to warm slowly to room temperature. n-Pentane (50 ml) was added to the residue and the mixture was then filtered. The solid was washed with n-pentane (3 × 20 ml), and the solvent removed from the combined filtrates at 20 mmHg. Excess of 3-methylbut-2-en-1-ol was recovered at 30° and 0·1 mmHg. The allenic alcohol (2) was separated by column chromatography on silica (elution with light petroleum containing increasing amounts of ethyl acetate up to 15%). Alternatively, preparative t.l.c. was employed [ethyl acetate–light petroleum (20 : 80)]. The *allenic alcohol* (2) (3·1 g, 45%) was isolated as a mobile oil, b.p. 40° at 0·02 mmHg; $\nu_{max.}$ 3620, 3320, and 2000 (allene) $cm^{-1}$; *m/e* 152 ($M^+$, 33%), 121 ($M$ − $CH_2$·OH, 100), 91(64), and 79(53); τ 8·73 and 8·72 (each 3H, s, geminal tertiary Me), 8·25 (6H, s, vinyl Me), 8·15 (1H, t, *J* 7 Hz), and 6·24 (2H, dd, *J* 7 and 2 Hz, $CH_2$·OH); *p*-nitrobenzoate, m.p. 98—99° (from ether–light petroleum) (Found: C, 67·6; H, 6·2; N, 4·6. $C_{17}H_{19}NO_4$ requires C, 67·8; H, 6·4; N, 4·65%).

The foregoing reaction was carried out in the presence of various solvents and bases (1 : 1 ratio of reactants); the results are given in the Table.

(b) 3-*Cyclohexylidenemethylene*-2,2-*dimethylcyclopropylmethanol* (4). With the same reaction conditions, work-up, and isolation procedure given in (a), 3-methylbut-2-en-1-ol (10 g, 0·12 mol) was treated with potassium t-butoxide (3·38 g, 0·03 mol) and 1-ethynylcyclohexyl chloride [7] (4·32 g, 0·03 mol) to yield the *allenic alcohol* (4) (1·16 g, 20%), m.p.

Effect of variation of conditions on yield of allene (2)

| Base | Solvent | Yield of allene (%) |
|---|---|---|
| $KOBu^t$ | Pentane | 20 |
| $KOBu^t$ | Benzene | 20 |
| $KOBu^t$ | Tetrahydrofuran | 20 |
| $KOBu^t$ | Methanol | No reaction |
| KOH | 3-Methylbut-2-en-1-ol | 35 |
| KOH | Methanol | Trace |
| NaOH | 3-Methylbut-2-en-1-ol | 35 |
| $KO(CMe_2Et)$ | Benzene | 20 |
| NaOEt | Ethanol | Trace |
| NaOMe | Methanol | Trace |

45—46°; $\nu_{max.}$ 3620, 3320, and 2000 $cm^{-1}$; *m/e* 192 ($M^+$, 28%), 161(59), 105(60), and 91(100); τ 8·75 and 8·73 (each 3H, s), 8·28 (1H, t, *J* 7 Hz), 6·28 (2H, dd, *J* 7 and 2 Hz), 7·84br (4H, m), and 8·45br (6H, m); 3,5-*dinitrobenzoate*, m.p. 82—84° (needles from ether–light petroleum) (Found: C, 62·0; H, 5·95; N, 6·9. $C_{20}H_{22}N_2O_6$ requires C, 62·2; H, 5·7; N, 7·25%).

(c) 3-*Cyclopentylidenemethylene*-2,2-*dimethylcyclopropylmethanol* (5). 1-Ethynylcyclopentanol (25 g, 0·23 mol) was added to a solution of freshly prepared copper(I) chloride (4·5 g, 0·045 mol) in concentrated hydrochloric acid (100 ml). After 1 h of intermittent shaking, the upper layer was washed with concentrated hydrochloric acid (2 × 80 ml) and shaken with anhydrous potassium carbonate. The product was immediately distilled from fresh potassium carbonate to yield 1-ethynylcyclopentyl chloride (15 g, 55%) as an unstable mobile oil, b.p. 42—50° at 15 mmHg.

With the same conditions, work-up, and isolation procedure given in (a), 3-methylbut-2-en-1-ol (4·0 g, 0·05 mol) was treated with potassium t-butoxide (2·6 g, 0·023 mol) and 1-ethynylcyclopentyl chloride (3·0 g, 0·023 mol) to yield the *allenic alcohol* (5) (0·415 g, 10%) as a mobile oil; $\nu_{max.}$ 3630, 3320, and 2000 $cm^{-1}$; *m/e* 178 ($M^+$, 4%), 147(8), 83(30), 67(36), 55(98), and 41(100); τ 8·68 and 8·71 (each 3H, s), 8·2 (1H, m), 8·30br (4H, m), 7·65br (4H, m), and 6·25 (2H, m); 3,5-*dinitrobenzoate*, m.p. 151—152° (needles from ether–light petroleum) (Found: C, 61·1; H, 5·45; N, 7·5. $C_{19}H_{20}N_2O_6$ requires C, 61·3; H, 5·4; N, 7·5%).

*Regioselective Reduction of Vinylidenecyclopropanes.*—(a) (±)-*Chrysanthemyl alcohol* [2,2-*dimethyl*-3-(2-*methylprop*-1-*enyl*)*cyclopropylmethanol*] (7). (i) trans–cis, 3 : 1. A solution of the allenic alcohol (2) (300 mg, 2·0 mmol) in dry ether (3 ml) was added dropwise with stirring to a solution of sodium (100 mg, 4·3 mmol) in liquid ammonia (10 ml). After stirring for 1 h the excess of sodium was destroyed with ammonium chloride and the ammonia was distilled off by gentle heating. Water (2 ml) was added; extraction with ether then gave, after conventional work-up, almost pure (one spot on t.l.c.) racemic chrysanthemyl alcohol [4] (7) (270 mg, 90%; *trans–cis*, 3 : 1 by g.l.c.), identical (t.l.c., i.r., n.m.r., and mass spectra) with an authentic sample. Crystallisation of the derived 3,5-dinitrobenzoate (needles from ether–light petroleum) preferentially afforded the derivative, m.p. and mixed m.p. 97—105°, of the *trans*-isomer (Found: C, 58·6; H, 5·7; N, 8·1. Calc. for $C_{17}H_{20}N_2O_6$: C, 58·6; H, 5·8; N, 8·1%). The wide m.p. range includes a period of preliminary weeping and was characteristic of both samples.

(ii) trans–cis, 1 : 1. With the same reaction conditions and work-up procedure as in (i), the readily derived allenic tetrahydropyranyl ether (3) [$\nu_{max.}$ 2000 $cm^{-1}$; *m/e* 236 ($M^+$, 2%), 152(10), 121(40), and 55(100)] (127 mg, 0·55 mmol) in dry ether (4 ml) was added to a solution of sodium (40 mg, 1·7 mmol) in liquid ammonia (5 ml) to produce chrysanthemyl alcohol tetrahydropyranyl ether (8) (118 mg, 92%).

Hydrolysis of (8) (110 mg) with a catalytic amount of toluene-*p*-sulphonic acid in ethanol (4 ml) produced chrysanthemyl alcohol (7) (64 mg, 90%) in a *cis–trans* ratio of 1 : 1 (by n.m.r. and g.l.c.).

(b) 3-*Cyclohexylidenemethyl*-2,2-*dimethylcyclopropylmethanol* (9). With the same reaction conditions and work-up procedure as in (a), the allenic alcohol (4) (195 mg, 1·0 mmol) in dry ether (4 ml) was added to a solution of sodium (50 mg, 2·2 mmol) in liquid ammonia (10 ml) to produce, as a mobile oil, the *alcohol* (9) (177 mg, 90%; *trans–cis*, 3 : 1); $\nu_{max.}$ 3620 and 3330 $cm^{-1}$; *m/e* 194 ($M^+$, 16%), 163(100), 91(98), and 79(97); τ 8·96 and 8·89 (each 3H, s), 8·50br (6H, m), 7·92br (4H, m), 5·28br (1H, d, *J* 7 Hz; in the *cis*-isomer this signal appears at τ 5·16), 6·43 (2H, AB of ABX, $J_{AB}$ 12 Hz, $CH_2$·OH), *ca.* 8·8 (1H, m), and *ca.* 9·2 (1H, m). Crystallisation of the derived 3,5-*dinitrobenzoate* from ether–light petroleum preferentially afforded the *trans*-isomer as needles, m.p. 110—112° (Found: C, 61·8; H, 6·0; N, 7·0. $C_{20}H_{24}N_2O_6$ requires, C·61·9; H, 6·2; N, 7·2%). The relative proportions of *cis*- and *trans*-isomers in this series can conveniently be assessed by comparison of the intensity of the signals for the vinyl proton associated with each, that of the former appearing at slightly lower field.

(c) 3-*Cyclopentylidenemethyl*-2,2-*dimethylcyclopropylmethanol* (10). With the same reaction conditions and work-up procedure as in (a), the allenic alcohol (5) (240 mg, 1·35 mmol) in dry ether (4 ml) was added to a solution of sodium (70 mg, 3·0 mmol) in liquid ammonia (10 ml) to produce, as a mobile oil, the *alcohol* (10) (195 mg, 80%; *trans–cis*, 3 : 1); $\nu_{max.}$ 3630 and 3320 $cm^{-1}$; *m/e* 180 ($M^+$, 15%), 149(100), 93(57), and 79(50); τ 9·0 and 8·94 (each 3H, s), 8·4br (4H, m), 7·8br (4H, m), 5·10br (1H, d, *J* 7 Hz; in the *cis*-isomer this signal appears at τ 5·0), 6·45 (2H, AB of ABX, $J_{AB}$ 11 Hz, $CH_2$·OH), and *ca.* 9·0 (2H). Crystallisation of the derived 3,5-*dinitrobenzoate* from ether–light petroleum preferentially afforded the *trans*-isomer as prisms, m.p. 106—108° (Found: C, 61·0; H, 6·0; N, 7·4. $C_{19}H_{22}N_2O_6$ requires C, 60·95; H, 5·9; N, 7·5%).

*Oxidations.*—(a) *Chrysanthemic acid* [2,2-*dimethyl*-3-(2-*methylprop*-1-*enyl*)*cyclopropanecarboxylic acid*] (12). AnalaR chromium trioxide (1 g, 0·01 mol) was added carefully to dry pyridine (10 ml) at 0°. The alcohol (7) (380 mg, 2·5 mmol) in dry pyridine (3 ml) was added in one portion and the mixture stirred at room temperature for 24 h, after which the aldehyde had formed [τ 8·8 and 8·69 (each 3H, s, geminal tertiary Me), 8·28 (6H, s, vinyl Me), 5·05br (1H, d, *J* 7 Hz; a weak signal at τ 6·6 indicated the presence of the *cis*-isomer), and 0·58 (1H, d, *J* 6 Hz)]. Normally, the aldehyde was not isolated, but after the addition of 5 drops of water, the mixture was stirred for a further 4 days.

The mixture was then poured into water (25 ml) and ether was added (5 ml). Powdered sodium hydrogen sulphate was added until the pH reached 3—4 and the product was then extracted with ether (3 × 50 ml). The combined extracts were washed with brine, dried ($MgSO_4$), and warmed under reduced pressure to remove the solvent. The product (300 mg) was shown (t.l.c., i.r. and n.m.r. spectra) to comprise about 25% chrysanthemaldehyde and 75% chrysanthemic acid (12) (*trans–cis*, 3 : 1), the latter being obtained in a yield of 55% based on chrysanthemyl alcohol. Preparative t.l.c. (ethyl acetate–light petroleum, 2 : 3) followed by sublimation (60° and 0·01 mmHg) afforded racemic *trans*-chrysanthemic acid, identical with an authentic sample (i.r., n.m.r., and mass spectra, t.l.c.); m.p. and mixed m.p. 46—48°.

(b) 3-*Cyclohexylidenemethyl*-2,2-*dimethylcyclopropanecarboxylic acid* (13). The alcohol (9) (175 mg, 0·9 mmol) in dry pyridine (2 ml) was treated with chromium trioxide (370 mg, 3·7 mmol) in dry pyridine (5 ml) as in (a). Water (3 drops) was added after 24 h and the mixture was stirred for a further 4 days. After work-up as before the product (100 mg) was shown (t.l.c., i.r. and n.m.r. spectra) to comprise about 90% of the acid [7] (13) (*trans–cis*, 3 : 1) and 10% of the corresponding aldehyde, the yield of acid, purified by preparative t.l.c. (ethyl acetate–light petroleum, 2 : 3), being 50% based on (9). Although the acid (13) slowly solidified, preferential crystallisation of the *trans*-isomer could not be effected. The product showed *m/e* 208 ($M^+$, 25%), 163(56), 121(42), 111(56), 81(100), and 55(70); τ 8·82 and 8·70 (each 3H, s), 8·44br (6H, m), 7·9br (4H, m), and, for the *trans*-isomer 5·12br (1H, d, *J* 7 Hz), the corresponding signal for the *cis*-isomer appearing at τ 4·70.

(c) 3-*Cyclopentylidenemethyl*-2,2-*dimethylcyclopropanecarboxylic acid* (14). The alcohol (10) (495 mg, 2·9 mmol) in dry pyridine (5 ml) was treated with chromium trioxide (1 g, 0·01 mol) in dry pyridine (15 ml) as in (a). Water (5 drops) was added after 24 h and the mixture was stirred for a further 6 days. After work-up as before the product (336 mg) was shown (t.l.c., i.r. and n.m.r. spectra) to comprise about 70% of the acid [7] (14) (*trans–cis*, 3 : 1) and 20% of the corresponding aldehyde, the yield of acid, isolated as a viscous oil by preparative t.l.c. (ethyl acetate–light petroleum, 2 : 3), being 45%, based on (10). The product showed *m/e* 194 ($M^+$, 10%), 149(24), 111(31), 67(54), and 41(100); τ 8·84 and 8·68 (each 3H, s), 8·3br (4H, m), 7·7br (4H, m), and for the *trans*-isomer, 4·96br (1H, d, *J* 7 Hz), the corresponding signal for the *cis*-isomer appearing at τ 4·50.

(d) 2,2-*Dimethyl*-3-(2-*methylprop*-1-*enylidene*)*cyclopropanecarboxylic acid* (15). The allenic alcohol (2) (460 mg, 3·0 mmol) in dry pyridine (5 ml) was treated with chromium trioxide (1·1 g, 0·011 mol) in dry pyridine (15 ml) as in (a). Water (5 drops) was added after 24 h and the mixture was stirred for 14 days. After work-up as before the product (265 mg) was shown (t.l.c., n.m.r. spectrum) to comprise about 80% of the allenic acid (15) and 20% of the corresponding aldehyde, the yield of acid isolated as a viscous oil by preparative t.l.c. (ethyl acetate–light petroleum, 2 : 3) being 40% based on (2). The product showed *m/e* 166 ($M^+$, 8%), 151(12), 74(55), and 59(100); $\nu_{max.}$ 1715 and 2025 $cm^{-1}$; τ 8·66 and 8·50 (each 3H, s) and 8·20 (6H, s, vinyl Me).

(e) 3-*Cyclohexylidenemethylene*-2,2-*dimethylcyclopropanecarboxylic acid* (16). The allenic alcohol (4) (200 mg, 1·0 mmol) in dry pyridine (4 ml) was treated with chromium trioxide (570 mg, 5·7 mmol) in dry pyridine (6 ml) as in (a). Water (3 drops) was added after 24 h and the mixture was stirred for 14 days. After work-up as before, the product (75 mg) was shown (t.l.c., i.r. and n.m.r. spectra) to comprise about 75% of the *allenic acid* (16) and about 25% of the corresponding aldehyde. Preparative t.l.c. (ethyl acetate–light petroleum, 2 : 3) afforded the pure acid (56

mg, 25%), m.p. 138—139° (prisms from ether–light petroleum); $\nu_{max.}$ 1700 and 2015 $cm^{-1}$; *m/e* 206(72%), 191(59), 119(43), 105(62), and 91(100); $\tau$ 8·65 and 8·58 (each 3H, s), 8·44 (6H, m), and 7·84 (4H, m) (Found: C, 75·6; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

We thank Professor L. Crombie (Nottingham) for samples of (±)-*trans*-chrysanthemic acid and (±)-*cis*- and (±)-*trans*-chrysanthemyl alcohols. We also thank the S.R.C. for a studentship (to R. W. M.).

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