Synthesis of *cis*-Jasmone and Other *cis*-Rethrones

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Convenient three-stage syntheses (32—35% overall) of *cis*-jasmone and *cis*-cinerone, from readily available 3-(5-methyl-2-furyl)propionaldehyde (2) are described. Wittig reactions, under 'salt-free' conditions are used for the *cis*-alkenylation (*ca.* 12% *trans* is concurrently produced). Use of an allyl Wittig reagent (3c) led to a mixture (2 : 3) of *cis*- and *trans*-dienes which was converted into a mixture of *cis*- and *trans*-pyrethrone, from which *cis*-pyrethrone was separated and characterised. Thermal rearrangement of *cis*-pyrethrone gave isopyrethrone.

cis-JASMONE (6b), an odorous principle of jasmine flowers, is useful in the reproduction of jasmine fragrance. Syntheses have been described,[1,2] but involve several stages, and proceed in low overall yields; an exception is a recent synthesis due to Büchi and Wüest.[3] Cinerone (6a) and pyrethrone (6c) are degradation products of cinerolone (7a) and pyrethrolone (7c), respectively, which, with jasmololone (7b), are the alcohol components of the insecticidal esters of *Chrysanthemum cinerariaefolium*.[4] There is current interest in conversion of ketones of this type (commonly referred to as 'rethrones') into the corresponding hydroxy-ketones (7),[5] which are generally less accessible.[6] This paper describes convenient syn-

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[1] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1952, 869; S. H. Harper and R. J. D. Smith, *ibid.*, 1955, 1512.

[2] G. Stork and R. Borch, *J. Amer. Chem. Soc.*, 1964, **86**, 936.

[3] G. Büchi and H. Wüest, *J. Org. Chem.*, 1966, **31**, 977.

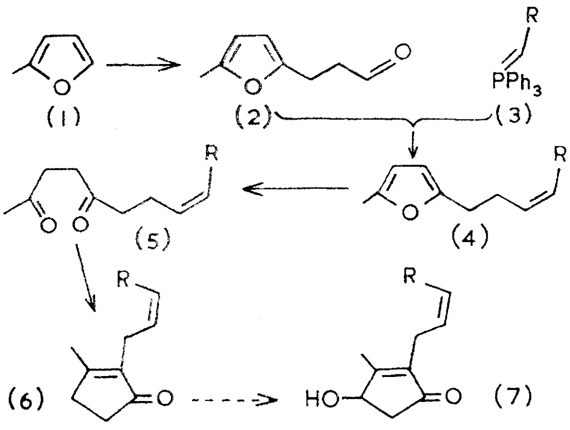
[4] L. Crombie and M. Elliott, *Fortschr. Chem. org. Naturstoffe*, 1961, **19**, 121.

[5] R. A. LeMahieu, M. Carson, and R. W. Kierstead, *J. Org. Chem.*, 1968, **33**, 3660.

[6] See preceding paper and references cited therein.

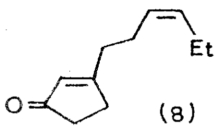
theses of rethrones (6) from 2-methylfuran (1); in the cases of jasmone (6b) and cinerone (6a) overall yields of 32—35% are realised.

Wittig reaction between propylidenetriphenylphosphorane (3b) and the aldehyde (2),[7] obtained from 2-methylfuran (1) and acraldehyde, gave, under 'salt-free' conditions,[8] the *cis*-olefin (4b) containing not more than 12% of the corresponding *trans*-olefin. This Wittig reaction, under different conditions, is reported to yield *trans*-product almost exclusively.[9] It is, however, common to observe predominently (>90%) *cis*-olefination during Wittig condensations between saturated non-stabilised phosphoranes and aldehydes when the reactions are conducted in the absence ('salt-free') of inorganic ions.[8,10] Hydrolysis of (4b) with aqueous acetic acid containing sulphuric acid gave the 2,5-dione (5b), which was cyclised in aqueous ethanolic sodium hydroxide to the ketone (6b).



a; R = Me. b; R = Et. c; R = $CH{:}CH_2$.

cis-Jasmone [32% from (1)] had an i.r. spectrum closely similar to that of an authentic sample, and its 2,4-dinitrophenylhydrazone did not depress the m.p. of the *cis*-jasmone derivative obtained from an earlier synthesis.[1] In view of its origins, however, our *cis*-jasmone must contain some *trans*-contaminant. The n.m.r. spectrum lacked any signals attributable to contamination with the isomeric cyclopentenone (8).



By a similar series of transformations, but with use of ethylidenetriphenylphosphorane (3a) in place of (3b), the aldehyde (2) was converted into *cis*-cinerone (6a) in 35% yield [from (1)]. Once more the Wittig reaction led to *cis*-olefin (4a) containing *ca.* 12% of the *trans*-isomer. The 2,4-dinitrophenylhydrazone had the same m.p. as the derivative of *cis*-cinerone obtained earlier.[11] The i.r. spectrum of synthetic *cis*-cinerone was closely similar to that of *cis*-jasmone; both showed negligible absorption in the region (970 $cm.^{-1}$) associated with the C–H out-of-plane deformation of *trans*-disubstituted double bonds. The n.m.r. spectra of synthetic *cis*-cinerone and synthetic *cis*-jasmone also showed close similarities. Both compounds had complex olefinic proton multiplets (2H) centred at *ca.* τ 4·7 and both showed allylic methylene proton doublets (*J* 6 c./sec.) centred at *ca.* τ 7·15. The cyclopentenone ring methylene protons gave complex multiplets between τ 7·5 and 8·05, and the ring vinyl methyl protons resonated as broad singlets at τ 7·98. In addition, *cis*-cinerone exhibited a vinyl methyl doublet (*J* 5 c./sec.) at τ 8·34, and *cis*-jasmone showed a saturated methyl triplet (*J* 7·5 c./sec.) at τ 9·02 and an additional methylene multiplet (*ca.* τ 7·8).

Wittig reaction between (2) and the phosphorane (3c) from allyltriphenylphosphonium bromide, under 'salt-free' conditions, led to a mixture of diene products containing *ca.* 40% of *cis*-isomer (4c), the remainder being *trans*. The allylphosphorane (3c) is neither a reactive phosphorane [*e.g.* (3a) and (3b)] nor is it a stabilised phosphorane (*e.g.* $Ph_3P{:}CH{\cdot}COR$; R = phenyl, alkyl, OR', *etc.*). Like benzylidenetriphenylphosphorane it is intermediate between these two extremes in reactivity. Wittig reactions between the benzylidene reagent and certain aldehydes, under 'salt-free' conditions, are reported to give olefin products containing not more than 34% of *cis*-isomer;[10] the significance of these findings is discussed elsewhere.[8,10] In the light of this, the percentage of *cis*-isomer (4c) obtained in our Wittig reaction with allylphosphorane (3c) is perhaps not surprising. Hauser *et al.*[12] report that Wittig reactions between (3c) and aldehydes are not satisfactory preparative reactions because of competing aldol condensations; these authors obtained olefin yields of the order 12—30%. House and Cronin,[13] however, who used modified conditions, claim yields of 45% for Wittig reactions with (3c). Under 'salt-free' conditions, we consistently obtained yields of *ca.* 70%.

The isomeric furylalkene mixture was converted into a mixture of *cis*- (6c) and *trans*-pyrethrones *via* the dione (5c), as already described. The final *cis*–*trans*-pyrethrone mixture contained, however, a small amount of additional material, identified by spectral analysis as a thermally rearranged isomer of *cis*-pyrethrone (6c) with structure (10) (isopyrethrone). After separation of the crystalline isopyrethrone, the remaining *cis*–*trans*-pyrethrone mixture was treated with *p*-benzoquinone.

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[7] Yu. K. Yur'ev, N. S. Zefirov, and A. A. Shteinman, *Zhur. obshchei Khim.*, 1963, **33**, 1150.

[8] M. Schlosser, G. Muller, and K. F. Christmann, *Angew. Chem.*, 1966, **78**, 677; M. Schlosser and K. F. Christmann, *Annalen*, 1967, **708**, 1.

[9] Yu. K. Yur'ev, P. V. Kostetskii, and N. S. Zefirov, *J. Gen. Chem.* (*U.S.S.R.*), 1964, **34**, 1061.

[10] L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, 1967, **23**, 2709.

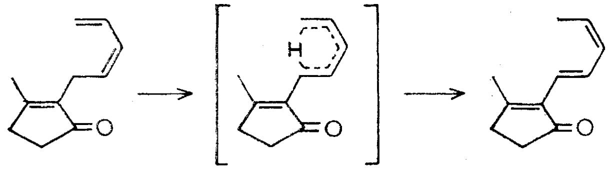
[11] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 1152.

[12] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, 1963, **28**, 372.

[13] H. O. House and T. H. Cronin, *J. Org. Chem.*, 1965, **30**, 1061.

This procedure resulted in removal of the *trans*-pyrethrone as a Diels–Alder adduct, and distillation then afforded pure *cis*-pyrethrone.

Thermal sigmatropic rearrangements of 1,3-dienes are well known,[14,15] and occur by 1,5-hydrogen transfer through cyclic six-membered transition states; such rearrangements are possible when the vinyl and the alkyl groups bear a *cis*-relationship to one another. The diene side chain in *cis*-pyrethrone (6c) has such a relationship [*cf.* cyclic transition state (9)]. Analogous thermal rearrangements have been reported by Elliott[16] for *cis*-pyrethrolone (7c) and its derivatives. Elliott found that only compounds containing the pyrethrolone *cis*-diene side-chain underwent such reactions. Accordingly, the configuration of the side-chain in the iso-compounds was assigned as *trans*-1′,*cis*-3′; i.r. data supported this assignment. Isopyrethrone (10) showed a u.v. spectrum characteristic of a conjugated triene, with maxima at 257, 268, and 278 mμ (*cf.* isopyrethrolone $\lambda_{max.}$ 260, 270, and 279 mμ, in the same solvent). In the olefinic proton region of the n.m.r. spectrum, the C-2′ proton in isopyrethrone was observed to give a double doublet (*J* 9 and 15 c./sec.) at τ 2·75 (the vicinal coupling is characteristic of *trans*-disubstituted double bonds;[17] this supports Elliott's stereochemical proposal), and the remaining olefinic protons gave a complex multiplet (3H) between τ 3·73 and 4·4. The cyclopentenone ring methylene protons in isopyrethrone resonate as a complex multiplet between τ 7·47 and 7·85, the ring vinyl methyl as a singlet at τ 7·92, and the C-4′ methyl protons as a doublet (*J* 5 c./sec.) at τ 8·2.



(6c) (9) (10)

The olefinic protons in the side chain of *cis*-pyrethrone gave signals with similar chemical shifts, and with multiplicities comparable to those of *cis*-pyrethrolone (7c); this spectrum was discussed in the preceding paper.

EXPERIMENTAL

For general experimental details see preceding paper.

3-(5-*Methyl*-2-*furyl*)*propionaldehyde*. The aldehyde, prepared (55%) from 2-methylfuran according to the method of Yur'ev *et al.*,[7] had b.p. 82—100°/17 mm., $n_{\rm D}^{22}$ 1·4758—1·4768, $\nu_{max.}$ (film) 2720, 1730, 1620 and 1575 cm.$^{-1}$, τ 0·29 (t, *J* 1 c./sec., CHO), 4·24 (2 :CH·), 7·26 (4H, m), and 7·79 (Me) (lit.,[7] $n_{\rm D}^{20}$ 1·4770).

Wittig Synthesis of cis-2-(5-*Methylfuryl*)*alkenes*: *General Procedure*.—The finely powdered phosphonium salt (0·1 mol.) was added during 0·25 hr. to a stirred suspension of sodamide [from sodium (2·6 g.)] in liquid ammonia (250 ml.) under nitrogen. The mixture was stirred for 2 hr., and then the ammonia was allowed to evaporate off. The residue was treated with dry benzene (350 ml.), and the mixture was boiled for 0·5 hr. The benzene solution of the phosphorane was decanted in an atmosphere of nitrogen into another flask, and was then treated during 0·75 hr. with 3-(5-methyl-2-furyl)propionaldehyde (12 g.). The mixture was stirred for a further 12 hr., and was then filtered. The filtrate was evaporated to dryness, and the residue was treated with light petroleum (b.p. 60—80°). Triphenylphosphine oxide was filtered off, and the filtrate was evaporated. The residue was chromatographed on alumina (Grade I) in light petroleum (b.p. 60—80°) to remove residual phosphine oxide. Distillation gave the *cis*-alkene.

cis-1-(5-*Methyl*-2-*furyl*)*pent*-3-*ene*. By the general procedure, ethyltriphenylphosphonium bromide[18] and 3-(5-methyl-2-furyl)propionaldehyde gave the *olefin* (10·3 g., 79%), b.p. 76—84°/18 mm., $n_{\rm D}^{23\cdot5}$ 1·4702, $\nu_{max.}$ 1660, 1622, 1575, and 965 cm.$^{-1}$, τ 4·27 (2 :CH·), 4·6 (m, ·*H*C:C*H*·), 7·23—7·9 (4H, m), 7·79 (Me), and 8·41 (d, *J* 5 c./sec., :CH·C*H*$_3$) (Found: C, 79·9; H, 9·5. $C_{10}H_{14}O$ requires C, 79·95; H, 9·4%). G.l.c. analysis (5% saturated $AgNO_3$ in ethylene glycol; 25°) showed that the *cis*-olefin (eluted second) was contaminated with 12% of the *trans* (eluted first).

cis-1-(5-*Methyl*-2-*furyl*)*hex*-3-*ene*. By the general procedure, propyltriphenylphosphonium bromide and 3-(5-methyl-2-furyl)propionaldehyde gave the olefin (9 g., 65%), b.p. 95—100°/13 mm., $n_{\rm D}^{23\cdot5}$ 1·4693, $\nu_{max.}$ 1658, 1623, 1573, and 965 cm.$^{-1}$, τ 4·25 (2 :CH·), 4·65 (m, ·*H*C:C*H*·), 7·16—8·2 (6H, m), 7·78 (Me), and 9·06 (t, *J* 7·5 c./sec., ·CH$_2$·C*H*$_3$) (Found: C, 80·6; H, 9·8. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·8%). G.l.c. analysis (5% saturated $AgNO_3$ in ethylene glycol; 25°) showed that the *cis*-olefin (eluted second) was contaminated with 12% of the *trans* (eluted first) (lit.,[3] $n_{\rm D}^{26}$ 1·4671).

cis- *and* trans-1-(5-*Methyl*-2-*furyl*)*hexa*-3,5-*diene*. By the general procedure, allyltriphenylphosphonium bromide[13] and 3-(5-methyl-2-furyl)propionaldehyde gave a mixture of isomeric dienes (9·4 g., 67%), b.p. 92—95°/19 mm., $n_{\rm D}^{18}$ 1·5055, $\nu_{max.}$ 1653, 1600, 1573, 1050, 950, and 903 cm.$^{-1}$, τ 3·1—5·1 (complex m, 5 :CH·, both isomers), 4·25 (·*H*C:C*H*·, furan ring), 7·21—7·82 (4H, m), and 7·79 (Me) [Found: C, 81·7; H, 8·6%; *M* (mass spectrum), 162. Calc. for $C_{11}H_{14}O$: C, 81·4; H, 8·7%; *M*, 162]. G.l.c. analysis (5% saturated $AgNO_3$ in ethylene glycol; 25°) showed the product to be a mixture of *trans*- (eluted first), and *cis*- (eluted second) isomers (*ca.* 3 : 2) (lit.,[9] $n_{\rm D}^{20}$ 1·5040).

Synthesis of the Alkene-2,5-*diones*: *General Procedure*.—A mixture of the methylfurylalkene and 75% acetic acid containing concentrated sulphuric acid (0·1 ml.) was boiled for 3 hr. The mixture was cooled, then diluted with water, and extracted with ether. The extracts were washed with sodium hydrogen carbonate and water, then dried and evaporated. Distillation gave the alkenediones.

cis-*Dec*-8-*ene*-2,5-*dione*. By the general procedure, *cis*-1-(5-methyl-2-furyl)pent-3-ene (8·5 g.) was treated with 75%

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[14] J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 2775.

[15] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 1966, 999.

[16] M. Elliott, *J. Chem. Soc.*, 1964, 888.

[17] 'Nuclear Magnetic Resonance for Organic Chemists,' ed. D. W. Mathieson, Academic Press, 1967.

[18] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, 1961, **26**, 4278.

acetic acid (36 ml.), and the product was isolated as described. Distillation gave the *dione* (8·5 g., 89%), b.p. 132—136°/19 mm., n_D^{22} 1·4554, $\nu_{max.}$ 1715, 1658, and 970 cm.$^{-1}$, τ 4·66 (m, ·*HC*:*CH*·), 7·44 (2 ·CO·CH$_2$·), 7·32—8·05 (4H, m), 7·89 (Ac), and 8·36 (d, *J* 5 c./sec., :CH·C*H*$_3$) (Found: C, 71·2; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

cis-*Undec*-8-*ene*-2,5-*dione*. By the general procedure, *cis*-1-(5-methyl-2-furyl)hex-3-ene (7·8 g.) was treated with 75% acetic acid (33 ml.) and the product was isolated as described. Distillation gave the dione (7·6 g., 88%), b.p. 135—137°/12 mm., n_D^{17} 1·4568, $\nu_{max.}$ 1714, 1573, and 972 cm.$^{-1}$, τ 4·72 (m, ·*HC*:*CH*·), 7·42 (2 ·CO·CH$_2$·), 7·56—8·19 (6H, m), 7·88 (Ac), and 9·03 (t, *J* 7·5 c./sec., CH$_2$·C*H*$_3$) (Found: C, 72·3; H, 9·7. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%) (lit.,[3] n_D^{26} 1·4521).

cis- *and* trans-*Undeca*-8,10-*diene*-2,5-*dione*. By the general procedure, the *cis–trans* mixture (ratio *ca.* 2 : 3) of 1-(5-methyl-2-furyl)hexa-3,5-dienes (24 g.) was treated with 75% acetic acid (100 ml.) and the product was isolated as described. Distillation gave a mixture of isomeric dienes (18 g., 68%), b.p. 94—100°/0·1 mm., $n_D^{18\cdot5}$ 1·4876, $\lambda_{max.}$ 226 mμ (ε 22,100), $\nu_{max.}$ 1720, 1660, 1510, 1010, 960, and 905 cm.$^{-1}$, τ 3·0—5·16 (complex m, 5 :*CH*·), 7·28—7·78 (4H, m), 7·42 (2 ·CO·CH$_2$), and 7·95 (Ac) [Found: C, 73·2; H, 8·8%; *M* (mass spectrum), 180. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 8·95%; *M*, 180] (lit.,[9] n_D^{20} 1·4877).

Synthesis of the Rethrones: General Procedure.—A solution of the alkenedione in ethanol and 0·5N-sodium hydroxide was boiled for 3 hr. The mixture was diluted with water and then extracted with ether. The extracts were washed with water and then dried. Distillation gave the rethrones.

cis-3-*Methyl*-2-(*but*-2-*enyl*)*cyclopent*-2-*en*-1-*one*[cis-*cinerone*]. By the general procedure, *cis*-dec-8-ene-2,5-dione (7·6 g.) was treated with ethanol (20 ml.) and 0·5 N-sodium hydroxide (76 ml.), and the product was isolated as described. Distillation gave the rethrone (5·5 g., 80%), b.p. 72—80°/1 mm., $n_D^{23\cdot5}$ 1·4994, $\nu_{max.}$ 1700 and 1647 cm.$^{-1}$, τ 4·7 (m, ·*HC*:*CH*·), 7·16 (d, *J* 6 c./sec., :CH·C*H*$_2$), 7·51—8·06 (4H, m), 7·98 (Me), and 8·34 (d, *J* 5 c./sec., :CH·C*H*$_3$) (Found: C, 79·8; H, 9·1. Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·4%) [lit.,[11] n_D^{25} 1·4982 (synthetic); n_D^{25} 1·5002 (natural)]. The 2,4-dinitrophenylhydrazone had m.p. 136—137° (nitromethane) and mixed m.p. 137—138° with the 2,4-dinitrophenylhydrazone (m.p. 137—138°) derivative of *cis*-cinerone from an earlier synthesis.[11] [Found: *M* (mass spectrum), 330. Calc. for $C_{16}H_{18}N_4O_4$: 330].

cis-3-*Methyl*-2-(*pent*-2-*enyl*)*cyclopent*-2-*en*-1-*one*[cis-*jasmone*]. By the general procedure, *cis*-undec-8-ene-2,5-dione (6·5 g.) was treated with ethanol (17 ml.) and 0·5 N-sodium hydroxide (65 ml.), and the product was isolated as described. Distillation gave the rethrone (5 g., 86%), b.p. 93—97°/0·8 mm., n_D^{18} 1·4976, $\nu_{max.}$ 1703 and 1648 cm.$^{-1}$, τ 4·77 (m, ·*HC*:*CH*·), 7·15 (d, *J* 5 c./sec., :CH·C*H*$_2$·) 7·5—8·05 (6H, m), 7·98 (Me), and 9·02 (t, *J* 7·5 c./sec., CH$_2$·C*H*$_3$) (Found: C, 80·35; H, 9·8. Calc. for $C_{11}H_{16}O$: C, 80·5; H, 9·8%) [lit.,[1] n_D^{20} 1·4978 (synthetic); n_D^{20} 1·4987 (natural)]. The 2,4-dinitrophenylhydrazone had m.p. 119°, and mixed m.p. 118—119° with the 2,4-dinitrophenylhydrazone (m.p. 118—119°) derivative of *cis*-jasmone from an earlier synthesis.[1] [Found: *M* (mass spectrum), 344. Calc. for $C_{17}H_{20}N_4O_4$: 344].

cis-3-*Methyl*-2-(*penta*-2,4-*dienyl*)*cyclopent*-2-*en*-1-*one*[cis-*pyrethrone*], *and* 3-*methyl*-2-(*penta*-trans-1,cis-3-*dienyl*)-*cyclopent*-2-*en*-1-*one* [*isopyrethrone*]. By the general procedure, a *cis–trans* mixture of undeca-8,10-diene-2,5-dione (17·6 g.) was treated with ethanol (46 ml.) and 0·5 N-sodium hydroxide (180 ml.) and the product was isolated as described. Distillation gave a mixture (12·2 g., 77%) of *cis*- and *trans*-pyrethrone containing isopyrethrone; b.p. 80—84°/0·1 mm., n_D^{21} 1·5367, $\lambda_{max.}$ (226 mμ (ε 32,900), $\nu_{max.}$ 1700, 1650, 1580, 1050, 950, and 905 cm.$^{-1}$, τ 2·92—5·17 (complex m, 5 :*CH*·), 7·02 (d, *J*, 6 c./sec., ·C*H*$_2$·CH:CH-*cis*), 7·13 (d, *J* 6 c./sec., ·C*H*$_2$·CH:CH-*trans*), 7·5—7·9 (4H, m), and 7·98 (Me). The mixture was kept at 0° for 2 weeks, whereupon colourless crystals of *isopyrethrone* (*ca.* 50 mg.) slowly separated, m.p. 85—88·5° (from cyclohexane), $\lambda_{max.}$ 278, 268, 258, and 249infl mμ, τ 2·75 (dd, *J* 9 and 15 c./sec., ·HC:C*H*·HC:), 3·73—4·4 (m, 3 :*CH*·), 7·47—7·85 (4H, m), 7·92 (Me), and 8·2 (d, *J* 5 c./sec., :CH·C*H*$_3$) [Found: *M* (mass spectrum), 162. $C_{11}H_{14}O$ requires 162]. A portion (920 mg.) of the *cis–trans* mixture of pyrethrones remaining after removal of isopyrethrone was treated with *p*-benzoquinone (65 mg.) in ether (15 ml.), and the mixture was kept at 20° for 4 days under nitrogen. Evaporation of the solution followed by chromatography of the residue in light petroleum (b.p. 60—80°) on alumina (Grade I) gave cis-*pyrethrone* (400 mg.) which was distilled, b.p. 100° (bath)/0·1 mm., n_D^{19} 1·5378, $\lambda_{max.}$ 227·5 mμ (ε 31,500), $\nu_{max.}$ 1703, 1650, 1593, 1000, 950, and 905 cm.$^{-1}$, τ 3·25 (ddd, *J* 16·5 and 10·5 c./sec., ·C*H*:CH$_2$), 4·09 (dd, *J* 10·5 c./sec., ·HC$\overset{cis}{=}$C*H*·CH:, 4·70 (dt, *J* 10·5 and 7·5 c./sec., ·CH$_2$·*HC*:CH·), 4·87 (dd, *J* 16·5 and 1·5 c./sec., ·CH:C*H*H), 4·91 (dd, *J* 10·5 and 1·5 c./sec., ·CH:CH*H*), 7·03 (d, *J* 7·5 c./sec., :CH·C*H*$_2$·), 7·5—7·96 (4H, m), and 7·97 (Me) [Found: C, 81·45; H, 8·55%; *M* (mass spectrum), 162. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%; *M*, 162].

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