

646. Experiments on the Synthesis of the Pyrethrins. Part VII.*
Synthesis of trans-Pyrethronone, trans-Pyrethrolone, and a Pyrethrin-I.

By L. CROMBIE, S. H. HARPER, and D. THOMPSON.

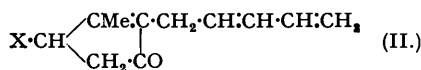
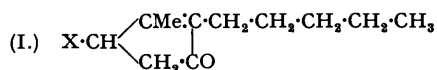
The structure of naturally derived pyrethrolone B-2 is established as (\pm)-4-hydroxy-3-methyl-2-*cis*(or *trans*)-*n*-penta-2': 4'-dienylcyclopent-2-en-1-one by oxidative and reductive degradation.

The use of *trans-n*-pent-2-en-4-yn-1-ol and of *trans-n*-penta-2: 4-dien-1-ol as intermediates for eight- and seven-stage syntheses respectively of (\pm)-*trans*-pyrethrolone is studied. Semihydrogenation of *trans-n*-oct-5-en-7-yn-2-one is not stereospecific, and the resultant pyrethronone and pyrethrolone are impure. Pure products result from the use of *trans-n*-penta-2: 4-dien-1-ol, prepared by the lithium aluminium hydride reduction of *trans-n*-penta-2: 4-dienal. The structure of the resultant (\pm)-*trans*-pyrethrolone is confirmed by oxidative and reductive degradation. Comparison with naturally derived pyrethrolone B-2, in particular through their infra-red absorption spectra, shows lack of identity. By exclusion it is concluded that pyrethrolone B is *cis*-pyrethrolone.

Esterification of (\pm)-*trans*-pyrethrolone with (+)-*trans*-chrysanthemic acid provides the first total synthesis of a pyrethrin-I.

THE structure of pyrethrolone, the major keto-alcoholic component of the pyrethrins (the potent insecticidal constituents of pyrethrum, *Chrysanthemum cinerariifolium*), has been the subject of controversy since its isolation by Staudinger and Ruzicka more than 35 years ago. As experimental evidence accumulated it became increasingly difficult to accommodate in one formula the conflicting requirements of ozonolyses, potassium permanganate oxidations, terminal methyl values, and ultra-violet light absorption data (for a review of this earlier work, see Harper, *Ann. Reports*, 1948, **45**, 162). Then, in 1944, LaForge and Barthel (*J. Org. Chem.*, 1944, **9**, 242; 1945, **10**, 106, 114) showed that pyrethrolone, as isolated from the pyrethrins, is heterogeneous and consists of the (+)- and (\pm)-forms of two isomeric pyrethrolones together with (+)- and (\pm)-cinerolone. Subsequent work by West (*J.*, 1946, 463) confirmed this but suggested that the (\pm)-forms of the keto-alcohols are artefacts and that only the (+)-forms are esterified with the chrysanthemumcarboxylic acids in the pyrethrins. Because of this heterogeneity of crude pyrethrolone much of the earlier evidence as to its structure is of dubious value. Nevertheless, that the pyrethrolones are hydroxy-3-methyl-2-*n*-pentadienylcyclopent-2-en-1-ones had been established by the identity of tetrahydropyrethronone with dihydrojasnone (I; X = H) (LaForge and Haller, *J. Amer. Chem. Soc.*, 1936, **58**, 1777).

The structure of (\pm)-tetrahydropyrethrolone, obtained on hydrogenation of either of the (\pm)-pyrethrolones ("pyrethrolones B-2 and C-2," cf. LaForge and Barthel, *loc. cit.*, and West, *loc. cit.*), as (I; X = OH) was made probable by analogy with dihydrocinerolone and by synthesis of *n*-amylrethrolone (I; X = OH) (for an exposition of this nomenclature, see Harper, *Chem. and Ind.*, 1949, 636) through the action of *N*-bromosuccinimide on tetrahydropyrethronone and subsequent hydrolysis (Dauben and Wenkert, *J. Amer. Chem. Soc.*, 1947, **69**, 2074; Crombie, Elliott, and Harper, Part III, *J.*, 1950, 971). However, no direct comparisons of the synthetic and naturally derived keto-alcohols were made at that time.



Assignment of the side-chain double bonds of the pyrethrolones to the 2': 4'-positions as in (II) was made by LaForge and Barthel (*loc. cit.*) on the basis of quantitative hydrogenations of the semicarbazones and on the light absorption of the semicarbazones which showed a maximum at 2650 Å due to the C=C-C=N chromophore and in addition another maximum at 2280 Å due to the separate C=C-C=C of the side chain (cf. Gillam and West, *J.*, 1942, 671). Additional spectroscopic evidence for this assignment was subsequently provided by West (*loc. cit.*).

* Part VI, *J.*, 1951, 2445.

Such a structure for the pyrethrolones, containing one side-chain methyl group, is in agreement with the terminal methyl contents (1.0—1.1 groups) found by LaForge and Barthel (*loc. cit.*) but is at variance with those (1.2—1.5) found by West (*loc. cit.*). It conflicts, too, with the isolation by earlier workers of acetaldehyde with only small amounts of formaldehyde on ozonisation of pyrethrolone and it was largely on this fact that structures containing the $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CHMe}$ side chain were proposed at various times (cf. Harper, *Ann. Reports*, 1948, 45, 162). However, these discrepancies are now explicable on the assumption that cinerolone was present even in the "purified" pyrethrolone.

As a preliminary to attempting the synthesis of (\pm)-*cis*- and (\pm)-*trans*-pyrethrolone we have clarified some of the uncertainties regarding the structure of the pyrethrolones. We have synthesised *n*-amylrethrolone (I; X = OH) by another method (route D, cf. Part V, *J.*, 1950, 3552) which leaves no doubt as to its structure. Ethyl 2-keto-*n*-octane-1-carboxylate was hydrolysed and the sodium salt condensed with pyruvaldehyde in aqueous solution to give 3-hydroxy-*n*-undecane-2 : 5-dione. Cyclisation of this with aqueous alkali yielded *n*-amylrethrolone, from which the semicarbazone was obtained, though with difficulty. Hydrogenation of a specimen of pyrethrolone B-2 semicarbazone, kindly provided by Dr. F. B. LaForge, and direct comparison (by mixed melting point) of the product with the synthetic semicarbazone established the identity of tetrahydropyrethrolone with *n*-amylrethrolone and its structure as (I; X = OH). Ozonisation of pyrethrolone B-2, regenerated from the semicarbazone, and conversion of the volatile aldehydic product into the dimedon derivative, gave only the derivative of formaldehyde uncontaminated with that of acetaldehyde. As far as we are aware this is the first specimen of pyrethrolone that has not given appreciable or even preponderating amounts of acetaldehyde on ozonisation. This oxidative degradation provides the first clear chemical evidence for the presence of a terminal =CH_2 in the side chain of a pyrethrolone and in conjunction with the evident purity, the spectroscopic evidence, and the structure of tetrahydropyrethrolone establishes pyrethrolone B-2 as (\pm)-*cis*- or (\pm)-*trans*-*n*-penta-2 : 4-dienylrethrolone (II; X = OH). We have not been able to examine a specimen of pyrethrolone C-2 to establish whether it is a geometrical isomer of pyrethrolone B-2 or only an impure form of the latter. Hence our subsequent remarks are concerned only with pyrethrolone B-2.

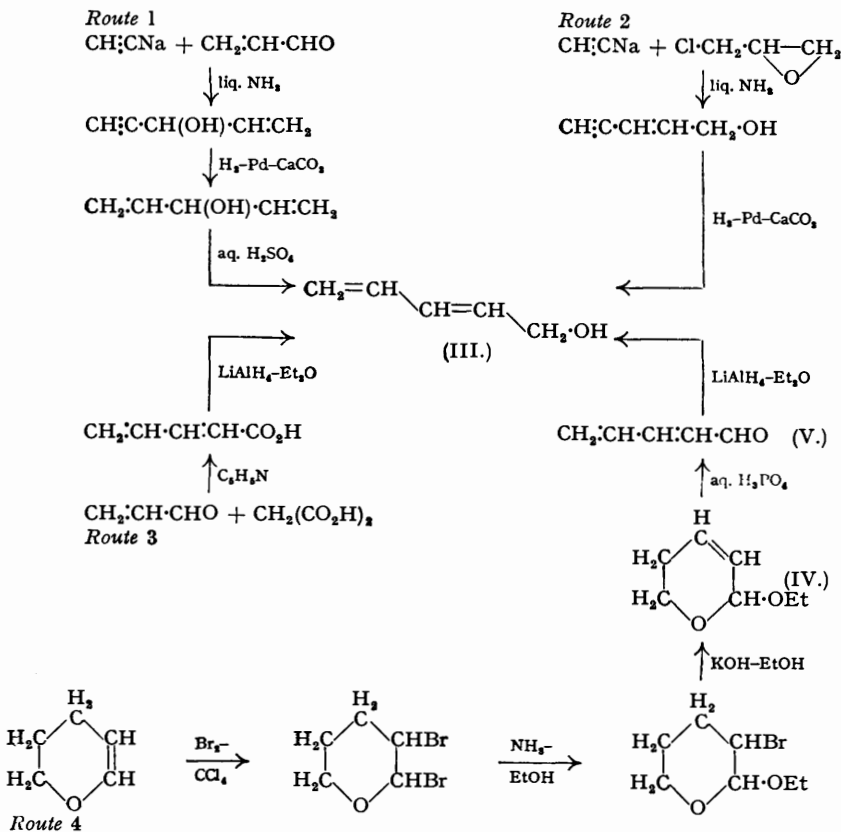
One of the most attractive intermediates for the synthesis of both pyrethron (II; X = H) and pyrethrolone (II; X = OH) is *n*-penta-2 : 4-dien-1-ol (III), which would permit of a subsequent seven-stage synthesis of the latter by the use of our route D (Part V, *loc. cit.*). We therefore studied its preparation and stereochemistry. *n*-Penta-2 : 4-dien-1-ol was first described by Heilbron, Jones, McCombie, and Weedon (*J.*, 1945, 84) as resulting in low yield from the anionotropic rearrangement of penta-1 : 4-dien-3-ol (route 1 of the attached scheme). Its preparation in this manner and the ready formation of a maleic anhydride adduct (Heilbron *et al.*, *loc. cit.*) indicate a *trans*-configuration. It was later prepared in better yield by the semihydrogenation of *n*-pent-2-en-4-yn-1-ol (route 2; Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586), the latter evidently having the *trans*-configuration. Confirmation of this is afforded by the formation of an *erythro*-triol from this *n*-pent-2-en-4-yn-1-ol by performic acid (Raphael, *J.*, 1949, S 44). In agreement with these conclusions we find that lithium aluminium hydride reduction of *n*-penta-2 : 4-dienoic acid (almost certainly having the *trans*-configuration because of its preparation by the Knoevenagel reaction; see Lauer and Gensler, *J. Amer. Chem. Soc.*, 1945, 67, 1171) gives the same alcohol (route 3).

We find that *trans*-*n*-penta-2 : 4-dien-1-ol is also formed in good yield by lithium aluminium hydride reduction of the *n*-penta-2 : 4-dienal obtained on ring fission of 2-ethoxydihydropyran (route 4) (Woods and Sanders, *J. Amer. Chem. Soc.*, 1946, 68, 2483), despite the fact that the internal ethylenic bond is initially constrained into the *cis*-configuration. Inversion appears to occur at the ring-fission stage, for the *n*-penta-2 : 4-dienal itself gives a maleic anhydride adduct (*idem, ibid.*, 1947, 69, 2926). Except for citral *a* and *b*, which are not strictly analogous as they do not contain the $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ structure, we have been unable to find any well-established example of a *cis*- $\alpha\beta$ -ethylenic aldehyde of this type. Semihydrogenation of $\alpha\beta$ -acetylenic acetals followed by acid hydrolysis gives *trans*- $\alpha\beta$ -ethylenic aldehydes (Lohaus, *J. pr. Chem.*, 1928, [ii], 119, 235; Sondheimer, private communication), whereas semihydrogenation of $\alpha\beta$ -acetylenic aldehydes themselves gives either *trans*- or impure products (Lohaus, *loc. cit.*; Bourgeul, *Bull. Soc. chim.*, 1929, [iv], 45, 1067). It would appear that *cis*- $\alpha\beta$ -ethylenic aldehydes are particularly unstable (in the presence of acid?) and difficult to isolate.

The identity of these four preparations of *trans*-*n*-penta-2 : 4-dien-1-ol was established by

the mixed melting points of their 1-naphthylurethanes and of their maleic anhydride adducts. Furthermore they had the same infra-red spectra in the range 8—11 μ . in which differences due to geometrical isomerism should have been evident. The *trans-n-penta-2:4-dien-1-ol* obtained

Routes to *trans-n-penta-2:4-dien-1-ol*.



by route 4 boiled sharply, had a constant refractive index (n_D^{20} 1.4896), and was free from monoethylenic and saturated contaminants. In contrast Heilbron, Jones, and Sondheimer (*loc. cit.*) recorded a boiling point and refractive index spread (n_D^{18} 1.4770—1.4893), which we have confirmed, for *trans-n-penta-2:4-dien-1-ol* made by the semihydrogenation of *trans-n-pent-2-en-4-yn-1-ol* (route 2) over palladium-calcium carbonate. It is evident the semihydrogenation of this enyne system is not entirely selective under these conditions as will be further exemplified below.

We have also made a preliminary examination of the semihydrogenation of *n-pent-4-en-2-yn-1-ol* as a route to *cis-n-penta-2:4-dien-1-ol*. With Isler's palladium-charcoal catalyst (deactivated by quinoline) (Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911) hydrogenation was not fully selective and although hydrogenation was stopped when only 0.9 mol. of hydrogen had been absorbed some monoethenoid or saturated product was present. This process and others for the introduction of the *cis-n-penta-2:4-dienyl* system are being further investigated.

As the enyne system of *trans-n-pent-2-en-4-yn-1-ol* is more stable than the diene system of *trans-n-penta-2:4-dien-1-ol*, the latter alcohol polymerising to a gel in the course of a few days at room temperature, our initial approach to (\pm)-*trans*-pyrethrolone (detailed in the chart below) started from the acetylenic alcohol with the intention of postponing semihydrogenation to as late a stage as possible. Treatment of *trans-n-pent-2-en-4-yn-1-ol* with phosphorus tribromide and pyridine gave impure bromide, but phosphorus trichloride and pyridine gave the pure chloride (VI) in good yield. Alkylation of ethyl sodioacetoacetate with this chloride

followed by ketonic fission gave *trans-n*-oct-5-en-7-yn-2-one (VII), whose structure was confirmed by its light absorption (see Table I) and by quantitative hydrogenation to *n*-octan-2-one, identified as its 2 : 4-dinitrophenylhydrazone.

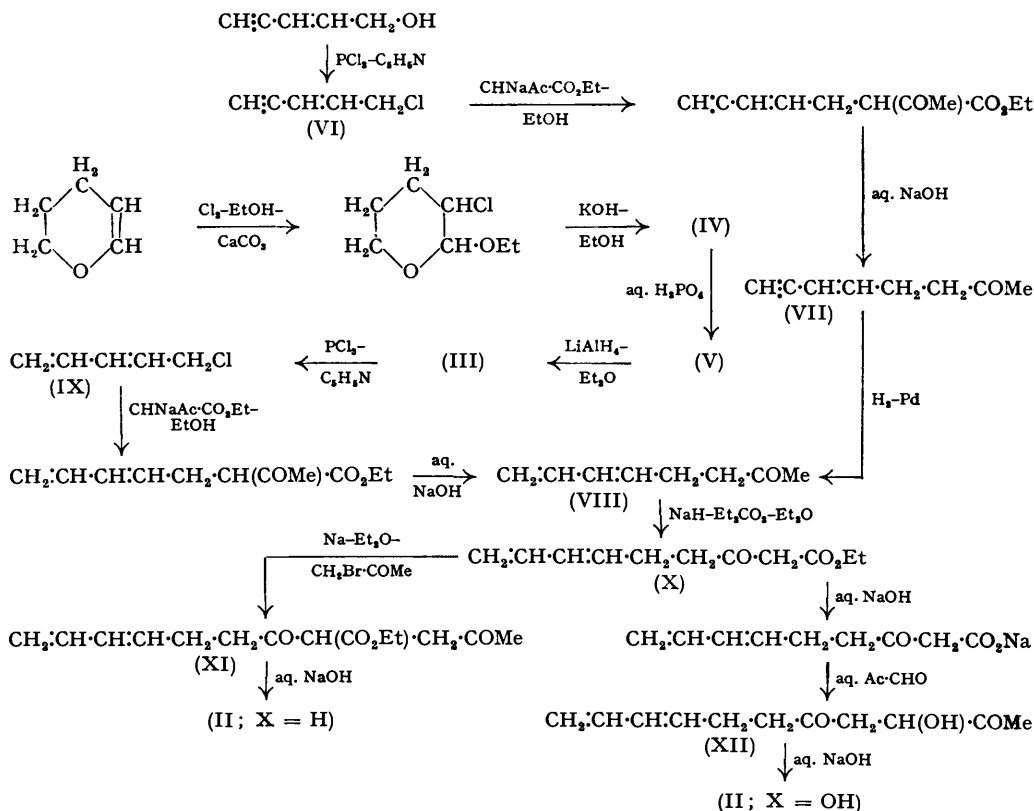
TABLE I.
Ultra-violet light absorption of intermediates.

	$\lambda_{\text{MAX.}}$, Å.	$\epsilon_{\text{MAX.}}$
$\text{CH}_2\text{:C}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{OH}(\text{trans})$	2230	15,000 *
$\text{CH}_2\text{:CH}\cdot\text{C}\text{:C}\cdot\text{CH}_2\cdot\text{OH}$	(Infl. 2290)	10,000 *
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{OH}(\text{trans})$ (III)	2270	11,900
$\text{CH}_2\text{:C}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}(\text{trans})$ (VII)	2260	25,200
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}(\text{trans})$ (VIII)	2230	14,000
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}(\text{trans})$ (X)	2260	23,000
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}(\text{trans})$ (X)	2230	21,500
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}(\text{trans})$ (X)	2260	27,800
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}(\text{trans})$ (X)	2240	23,000
$\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}(\text{trans})$ (XII)	2260	27,500

* Data of Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583.

† The best specimens of dienes obtained from (VII) by the semihydrogenation route; the other dienes were obtained without semihydrogenation from (III) prepared by route 4.

As the next step, carbethoxylation, required the formation of the sodio-derivative of the ketone, semihydrogenation was carried out at this point to avoid the complication due to the ethynyl hydrogen atom. The use of either palladium-calcium carbonate or authentic Isler's



catalyst for the semihydrogenation of the ketone (VII) did not produce exclusively the diene: fractional distillation gave the pure diene (VIII) though in much reduced yield. *trans-n*-Octa-5 : 7-dien-2-one (VIII) was characterised by its light absorption (see Table I), a 2 : 4-dinitrophenylhydrazone, and a maleic anhydride adduct.

To avoid the necessity for semihydrogenation attention was turned to the use of *trans-n*-penta-2:4-dien-1-ol (III), prepared by route 4. We found, in Woods and Sander's procedure (*loc. cit.*), the isolation of 2:3-dibromotetrahydropyran and its subsequent reaction with alcoholic ammonia rather unsatisfactory, uncontrollable decomposition of the dibromide being frequent (cf. Paul, *Bull. Soc. chim.*, 1934, [v], 1, 1397). The use of 2:3-dichlorotetrahydropyran, prepared in ether (cf. Crombie and Harper, *J.*, 1950, 1707), was more satisfactory, as was a procedure based on B.P. 598,080 (Jones, Bremner, and Imperial Chemical Industries Limited, 1948), for without isolation from ethanolic solution the 3-chloro-2-ethoxytetrahydropyran could be treated with potassium hydroxide to give the ethoxydihydropyran (IV). Interaction of *trans-n*-penta-2:4-dien-1-ol with phosphorus trichloride in pyridine at -10° gave *trans-n*-penta-2:4-dienyl chloride (IX) in good yield. We had considered at the outset of these experiments the direct preparation of the corresponding bromide by allylic bromination of *trans*-piperylene. However, we could not induce reaction between *N*-bromosuccinimide and *trans*-piperylene at atmospheric pressure, even in the presence of benzoyl peroxide or of another reacting olefin. Alkylation of ethyl sodioacetoacetate with the chloride (IX) followed by ketonic fission gave *trans-n*-octa-5:7-dien-2-one (VIII), identical with the ketone prepared by semihydrogenation apart from the slightly more intense light absorption (see Table I).

Carbomethoxylation of (VIII) by ethyl carbonate was best effected in presence of sodium hydride, and although hydrogen is liberated reduction of the diene system of the resultant ethyl 2-keto-*trans-n*-octa-5:7-diene-1-carboxylate (X) was negligible as shown by the light absorption of the product (see Table I). Presumably an important factor is the low potential at which hydrogen is liberated from sodium hydride (Hansley and Carlisle, *Chem. Eng. News*, 1945, 23, 1332).

Ethyl sodio-2-keto-*trans-n*-octa-5:7-diene-1-carboxylate and bromoacetone gave ethyl 2:5-diketo-*trans-n*-undeca-8:10-diene-4-carboxylate (XI), which without distillation (cf. Harper, Part II, *J.*, 1946, 892) was cyclised and hydrolysed by 3% sodium hydroxide at 40° to *trans-n*-penta-2:4-dienylrethronone (II; X = H), *i.e.*, *trans*-pyrethronone (purified by way of the semicarbazone). One sample, whose light absorption is recorded in Table II, partly crystallised, but the semicarbazone and ketone, like the naturally derived materials, deteriorated slowly on storage.

By our usual procedure (cf. Part V, *loc. cit.*) ethyl 2-keto-*trans-n*-octa-5:7-diene-1-carboxylate was hydrolysed and the sodium salt condensed with pyruvaldehyde in aqueous solution at pH 8.5 to give 3-hydroxy-*trans-n*-undeca-8:10-diene-2:5-dione (XII), whose light absorption (see Table I) and uptake of hydrogen when hydrogenated over Adams's catalyst in glacial acetic acid (4.04 mols. with a break at 1.96 mols., corresponding to two double bonds and two carbonyl groups) confirmed the expected structure. Cyclisation then gave (\pm)-*trans-n*-penta-2:4-dienylrethrolone, *i.e.*, (\pm)-*trans*-pyrethrolone (II; X = OH). Its gross structure was confirmed by catalytic hydrogenation to *n*-amylrethrolone (I; X = OH), identified as its 3:5-dinitrobenzoate. The presence of the penta-2:4-dienyl side chain was confirmed by the analytical data, the light absorption (see Table II), quantitative hydrogenation, terminal methyl values, and by ozonisation. This last gave only formaldehyde, isolated and identified as its dimedon derivative.

TABLE II.

*Ultra-violet light absorption of final products.**

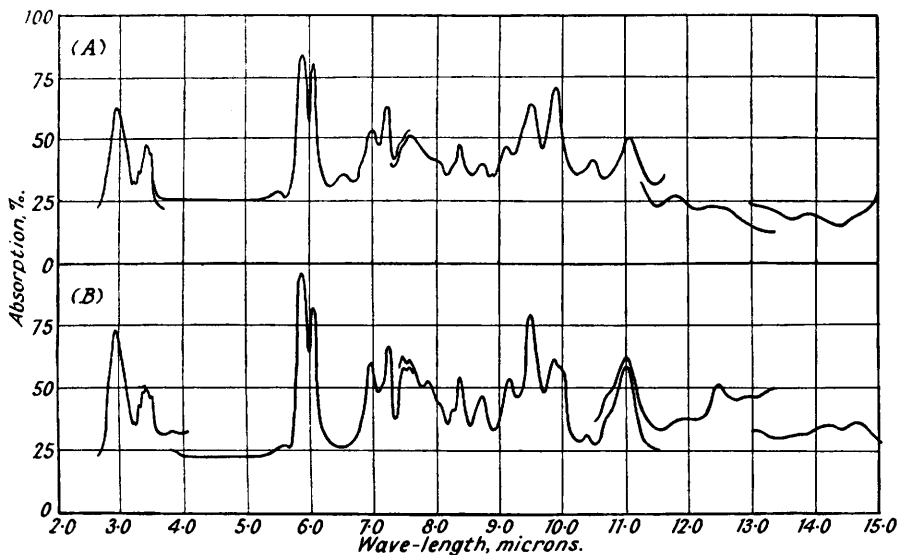
	$\lambda_{\text{max.}}$, Å	$\epsilon_{\text{max.}}$	$\Delta\epsilon$ †
<i>trans</i> -Pyrethronone (II; X = H)	2270	34,000	21,500
Tetrahydropyrethronone (I; X = H) (Part V)	2340	13,800	—
	2270	12,500	—
(\pm)- <i>trans</i> -Pyrethrolone (II; X = OH)	2270	33,000	23,900
(\pm)-Tetrahydropyrethrolone (I; X = OH)	2220	9,100	—
	2270	9,100	—
(\pm)-Pyrethrolone B-2 (naturally derived)	2230	29,900	—
	2270	29,900	20,800
(\pm)- <i>trans</i> -Pyrethronyl (+)- <i>trans</i> -chrysanthemate	2220	47,500	—
	2270	47,500	19,500
(\pm)- <i>trans</i> -Tetrahydropyrethronyl (\pm)- <i>trans</i> -chrysanthemate (Part III)	2230	28,000	—
	2270	28,000	—

* All determined with a Hilger Medium Quartz Spectrograph.

† Increase of ϵ at 2270 Å (*ca.* $\lambda_{\text{max.}}$) due to the $\text{CH}_2\text{:CH:CH:CH}$ chromophore.

It must be mentioned that contamination by quite small amounts of saturated or mono-ethylenic impurities in the intermediates becomes magnified in subsequent stages. This is due to the instability of the diene components which are preferentially destroyed, thus concentrating the impurities, as is shown by the falling off of the ϵ_{max} due to the diene chromophore. A pure diene starting material is thus essential. At each subsequent stage the product was fractionally distilled and the presence of the intact diene system confirmed by ultra-violet light absorption measurement and by quantitative microhydrogenation.

Finally it remains to consider the relation of this synthetic (\pm)-*trans*-pyrethrolone to the naturally derived racemic pyrethrolones. Restricting attention to pyrethrolone B-2, for the

A. (\pm)-*trans*-Pyrethrolone (synthetic).B. (\pm)-Pyrethrolone B-2 (naturally derived).

reason given above, it is evident that any difference must be due to a differing configuration of the side chain. Inspection of their infra-red spectra (see figure) shows that although the main structural features are very similar [see Table III; cf. the infra-red spectra of (\pm)-*cis*- and

TABLE III.

Chief infra-red light absorption structural correlations.*

	Bonded OH.	Unsatd. aliph. C-H.	Satd. C-H, CH ₃ , CH ₂ .	C=O.	C=C.	Satd. CH ₃ , CH ₂ .	C-CH ₃ .	sec. OH.
(\pm)- <i>trans</i> -Pyrethrolone (synthetic)	2.94	3.31	3.42 3.50	5.89	6.05	6.99	7.22	9.52 μ
(\pm)-Pyrethrolone B-2 (naturally derived)	2.93	3.31 (3.36)	3.42 3.50	5.89	6.05	6.98	7.23	9.50 μ

* Discussion of other features is reserved for a later communication.

(\pm)-*trans*-cinerolone (Cupples, *J. Amer. Chem. Soc.*, 1950, **72**, 4522; Crombie, Harper, Stedman, and Thompson, Part VI, *J.*, 1951, 2445)] the spectra are not identical. Non-identity of (\pm)-*trans*-pyrethrolone with pyrethrolone B-2 is supported by the melting point of *trans*-pyrethronone semicarbazone [198—200° (decomp.)] which is some 18° below that recorded for the naturally derived semicarbazone [216—218° (decomp.)]; LaForge and Haller, *J. Org. Chem.*, 1938, **2**, 546]. However, these preparations of pyrethronone semicarbazone were made before the heterogeneity of pyrethrolone was recognised, so that this evidence must not be weighted unduly. Rather similar evidence is the inability to prepare a solid semicarbazone from (\pm)-*trans*-pyrethrolone, but it must be borne in mind that the naturally derived semicarbazones have always been prepared indirectly from the pyrethrin or pyrethronyl acetate semicarbazones. By exclusion, therefore, pyrethrolone B-2 is (\pm)-*cis*-pyrethrolone; a

conclusion which is supported by the analogy of the *cis*-configuration of naturally derived cinerolone and by the repeated failures to obtain a diene adduct from pyrethrolone or its derivatives (LaForge and Haller, *loc. cit.*; West, *J.*, 1944, 239; cf. Robey, *Science*, 1942, 96, 470).

From synthetic (\pm)-*trans*-pyrethrolone the first total synthesis of a pyrethrin-I has now been accomplished by esterification with (+)-*trans*-chrysanthemic acid [for identity of the synthetic and natural (+)-acid see Campbell and Harper, *J.*, 1945, 283]. The acid chloride and *trans*-pyrethrolone in pyridine gave a synthetic pyrethrin-I consisting of the diastereoisomeric pair of esters, (\pm)-*trans*-pyrethronyl (+)-*trans*-chrysanthemate, whose light absorption is recorded in Table II.

EXPERIMENTAL.

M. p.s are uncorrected and were determined in capillary tubes unless otherwise stated. Microanalyses are by Drs. Weiler and Strauss, Oxford, and by Mr. Oliver, Imperial College. Microhydrogenations were carried out in acetic acid over Adams's catalyst, by Mr. Oliver. The ultra-violet light-absorption data were determined in purified ethanol by Drs. Weiler and Strauss, and by Mrs. Boston, Imperial College, with a Hilger Medium Quartz Spectrograph. Infra-red light absorption data were determined by one of us (L. C.) with a Grubb Parsons single-beam spectrometer coupled to a Brown recorder, the pure liquids being used as capillary films of *ca.* 5- μ . thickness.

Naturally Derived Pyrethrolone B-2.—A mixture of pyrethrolone B-2 semicarbazone (500 mg.), m. p. 204—206° (decomp.), oxalic acid (1.0 g.), and water (5 ml.) was heated on the steam-bath with passage of a stream of nitrogen. After 30 minutes the solid had disappeared and the liberated keto-alcohol was taken up in ether, washed with aqueous sodium hydrogen carbonate, dried, and distilled. Pyrethrolone B-2 (200 mg.) was collected as a single pale fraction, n_D^{20} 1.5406 (light absorption: see Table II); uptake on microhydrogenation, 3.80 mols., 3 $\bar{=}$ and 1 carbonyl group.

Ozonisation. Excess of ozone was passed through a carbon tetrachloride solution (5 ml.) of pyrethrolone B-2 (146 mg.) at 20° and then through aqueous dimedon. Water was then added and nitrogen bubbled for 20 hours through the whole. The dimedon derivative was crystallised once from 50% aqueous ethanol, to give the formaldehyde derivative (46 mg.), m. p. 188°, raised to 188—189° on admixture with authentic material.

Hydrogenation. Pyrethrolone B-2 semicarbazone (43 mg.) in ethyl acetate (5 ml.) was hydrogenated over 5% palladium-calcium carbonate (*ca.* 30 mg.). As reduction was slow further catalyst was added (uptake of hydrogen: *ca.* 2 mols.). The catalyst was removed ("Filtercel") and the filtrate concentrated to small bulk, (\pm)-tetrahydropyrethrolone semicarbazone separating as clusters of short needles, m. p. 176.5—177.5° with softening from 172.5°. On a Kofler hot stage this had m. p. 172—174°, whereas a mixture with the synthetic semicarbazone described below had m. p. 170—171°.

(\pm)-*Tetrahydropyrethrolone.*—By procedure A of Part V ethyl 2-keto-*n*-octane-1-carboxylate (23 g., the preparation described in *J.*, 1950, 3552) was shaken with 3% aqueous sodium hydroxide (180 ml.) for 6 hours and then the solution of the sodium salt condensed with aqueous pyruvaldehyde (26 ml.) during 6 hours at 35° and then overnight at room temperature. Isolation as described and distillation at 0.2 mm. gave several fractions, of which those having b. p. 104—124° and n_D^{20} 1.4542—1.4582 (5.24 g.) represented a 23% yield of 3-hydroxy-*n*-undecane-2:5-dione (Found: C, 67.1; H, 10.1. $C_{11}H_{20}O_2$ requires C, 66.1; H, 10.1%).

By the procedure described in Part V, 3-hydroxy-*n*-undecane-2:5-dione (5.24 g.) was cyclised in 3% aqueous sodium hydroxide (90 ml.) at room temperature. Fractional distillation gave (\pm)-tetrahydropyrethrolone (1.9 g., 40%), b. p. 120—128°/0.1 mm., n_D^{20} 1.4856 (light absorption, see Table II; uptake on microhydrogenation, 2.13 mols., 1 $\bar{=}$ and 1 carbonyl group). The 3:5-dinitrobenzoate had m. p. 98—99° (Kofler hot stage), when crystallised from methanol, not depressed when admixed with the derivative of the same m. p. from the reduction of (\pm)-*trans*-pyrethrolone, described below. The semicarbazone had m. p. 167—169° (Kofler hot stage).

trans-n-Oct-5-en-7-yn-2-one.—*trans-n*-Pent-2-en-4-yn-1-ol (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583) is vesicant, and admission of air on to the hot tarry still residue causes an explosion (this tar is soluble in hot pyridine), and its sodium derivative is pyrophoric. It darkens on storage, but a sample kept for 18 months in a refrigerator and then redistilled gave pure material without significant loss.

Phosphorus trichloride (142 g.) was added dropwise to a mixture of *trans-n*-pent-2-en-4-yn-1-ol (230 g.) and pyridine (56 ml.) at -10°, the mixture becoming green and finally blue. The mixture was then kept for 12 hours under nitrogen and the product (242 g.) distilled at 72—82°/150 mm. On redistillation *trans-n*-pent-2-en-4-ynyl chloride (215 g., 76%) had b. p. 80°/175 mm., n_D^{20} 1.4932 (Found: C, 58.7; H, 4.9; Cl, 36.7. Calc. for C_5H_7Cl : C, 59.7; H, 5.0; Cl, 35.3%). Heilbron, Jones, Lacey, McCombie, and Raphael (*J.*, 1945, 77) recorded b. p. 82—84°/200 mm., n_D^{20} 1.4842 for this chloride prepared by another method.

The above procedure gave *trans-n*-pent-2-en-4-ynyl bromide (46% yield) as a turbid unstable product, b. p. 92—100°/16 mm., n_D^{20} 1.538.

trans-n-Pent-2-en-4-ynyl chloride (215 g.) was added dropwise with stirring during 2 hours to a refluxing solution of ethyl sodioacetoacetate [from ethyl acetoacetate (286 g.), sodium (50.6 g.), and

ethanol (1.5 l.). After refluxing for a further 30 minutes the ethanol was distilled off through a short column under reduced pressure. The residual crude ethyl α -pentenylacetoacetate was stirred at room temperature with 5% aqueous sodium hydroxide (2 l.) during 4 hours, then a little undissolved oil removed, and the brown aqueous layer acidified with 50% sulphuric acid (200 ml.). When this was heated to 50° in a flask fitted for steam-distillation decarboxylation started and the ketone thus produced was isolated by steam-distillation, about 2 l. of distillate being collected. This was saturated with salt and extracted twice with ether. Fractional distillation of the dried (Na_2SO_4) extract then gave *trans-n-oct-5-en-7-yn-2-one* (76.8 g., 32%), b. p. 86—88°/10 mm., n_D^{20} 1.4788, having an odour reminiscent of that of *n*-octan-2-one (Found: C, 77.35, 77.2; H, 8.1, 8.35. $\text{C}_8\text{H}_{16}\text{O}$ requires C, 78.65; H, 8.25%); for light absorption, see Table I. The 2 : 4-dinitrophenylhydrazone crystallised in flattened buff-orange needles (from ethanol), m. p. 124° (Found: C, 55.6; H, 5.0; N, 17.9. $\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_4$ requires C, 55.6; H, 5.0; N, 18.5%).

When hydrogenated in ethanol (7 ml.) over 5% palladium-barium sulphate, *trans-n-oct-5-en-7-yn-2-one* (104 mg.) absorbed 59 ml. of hydrogen at N.T.P. (Calc. for 2 $\bar{=}$: 61 ml.). After removal of the catalyst ("Filtercel"), 2 : 4-dinitrophenylhydrazine (170 mg.) and a drop of hydrochloric acid were added to the filtrate and the mixture refluxed briefly. Concentration and crystallisation gave *n*-octan-2-one 2 : 4-dinitrophenylhydrazone (210 mg.), m. p. 58°, not depressed on admixture with an authentic specimen of m. p. 59°.

Semihydrogenation of trans-n-Oct-5-en-7-yn-2-one.—*trans-n-Oct-5-en-7-yn-2-one* (56.4 g.) was shaken in hydrogen over Isler's deactivated palladium-charcoal catalyst (0.8 g.) in ethyl acetate (60 ml.). When 10.15 l. of hydrogen had been absorbed (Calc. for the conversion of an acetylenic to an ethylenic bond: 10.3 l.) hydrogenation was stopped, "Filtercel" added, and the catalyst filtered off. Ethyl acetate was distilled from the filtrate through a column and the residue fractionally distilled at 22 mm., to give the following fractions: (i) b. p. 81—84.0°, n_D^{20} 1.4471 (1.76 g.); (ii) b. p. 84.0—85.0°, n_D^{20} 1.4601 (3.69 g.); (iii) b. p. 85.0—86.0°, n_D^{20} 1.4633 (9.55 g.); light absorption, λ_{max} 2240 Å, ϵ_{max} 13,000; (iv) b. p. 86.0—86.5°, n_D^{20} 1.4663 (9.16 g.); (v) b. p. 86.5—87.0°, n_D^{20} 1.4693 (8.80 g.); light absorption, λ_{max} 2220 Å, ϵ_{max} 20,000; (vi) b. p. 87.0—87.5°, n_D^{20} 1.4712 (7.90 g.); (vii) b. p. 87.5—88.0°, n_D^{20} 1.4724 (5.98 g.); light absorption, λ_{max} 2230 Å, ϵ_{max} 19,500; (viii) b. p. 88.0—89.0°, n_D^{20} 1.4717 (1.11 g.); (ix) b. p. 89—96°, n_D^{20} 1.4797 (2.50 g.). Fractions (v)—(vii) represent a 40% yield of *trans-n-octa-5 : 7-dien-2-one* (Found: C, 77.45; H, 9.75. $\text{C}_8\text{H}_{16}\text{O}$ requires C, 77.45; H, 9.65%). The above is typical of several semihydrogenations carried out with Isler's catalyst; a similar result was obtained with palladium-calcium carbonate. The light absorption quoted in Table I for *trans-n-octa-5 : 7-dien-2-one* is that of the best material isolated.

The 2 : 4-dinitrophenylhydrazone crystallised in long orange needles, m. p. 79°, from ethanol (Found: C, 54.9; H, 5.3; N, 18.4. $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$ requires C, 55.2; H, 5.3; N, 18.2%). A warm mixture of *trans-n-octa-5 : 7-dien-2-one* (124 mg.) and maleic anhydride (98 mg.) in benzene (1 ml.) was set aside until the adduct separated as transparent rectangular plates which became opaque on exposure to air. 3-3'-*Keto-n-butylcyclohex-4-ene-1 : 2-dicarboxylic anhydride* on crystallisation from benzene had m. p. 90—91° (Found, on material dried at 60° *in vacuo*: C, 65.0; H, 6.05. $\text{C}_{12}\text{H}_{14}\text{O}_4$ requires C, 64.85; H, 6.35%).

trans-n-Penta-2 : 4-dien-1-ol.—(a) *Route 3.* To freshly recrystallised vinylacrylic acid (10 g.; *Ber.*, 1937, 70, 2388) covered with ether (50 ml.) and cooled in ice, lithium aluminium hydride (2.85 g.) in ether (200 ml.) was added slowly with stirring. The reaction mixture was cautiously treated with water, then just acidified, and the ethereal layer separated (a ball of polymerised acid remained, consequently the reduction of the unpolymerised acid was carried out with a large excess of reductant). Distillation of the dried ethereal solutions gave *trans-n-penta-2 : 4-dien-1-ol* (1.5 g.), b. p. 66—68°/26 mm., n_D^{20} 1.4838 (this indicates the presence of a trace of more saturated material) (Found: C, 71.1; H, 9.8. Calc. for $\text{C}_5\text{H}_8\text{O}$: C, 71.5; H, 9.6%). The 1-naphthylurethane initially had m. p. 87°, but recrystallisation from light petroleum (b. p. 60—80°) gave superb needles, of m. p. 99.0—99.5° alone or mixed with a specimen (m. p. 97—98°) obtained by Heilbron, Jones, McCombie, and Weedon (*J.*, 1945, 84) (route 1) or with a specimen obtained by route 2, or with the further sample described below. The adduct formed from maleic anhydride (0.25 g.) and *trans-n-penta-2 : 4-dien-1-ol* (0.20 g.) in warm benzene was converted into the γ -lactone of 3-hydroxymethylcyclohex-4-ene-1 : 2-dicarboxylic acid on crystallisation from water and this formed needles, m. p. 177°, not depressed on admixture with a specimen of the same m. p. obtained by Heilbron *et al.* (*loc. cit.*), or with the preparation described below.

(b) *Route 4.* Woods and Sanders's procedure (*J. Amer. Chem. Soc.*, 1946, 68, 2483) was modified as follows: Dihydropyran (504 g.), diluted with carbon tetrachloride (300 ml.), was kept at -35° to -45° (solid carbon dioxide-alcohol) during the slow addition of bromine (960 g.). After removal from the cooling bath excess of bromine was decolorised by a few drops of dihydropyran. The solvent was removed under reduced pressure on a warm water-bath, and the crude yellow (though on several occasions partial decomposition occurred during this process with consequent darkening in colour) 2 : 3-dibromotetrahydropyran added to cooled (0°) anhydrous ethanol (2.5 l.) saturated with ammonia. After 12 hours at room temperature ammonium bromide was filtered off and to the boiling filtrate potassium hydroxide pellets (600 g.) were added in portions. The mixture was refluxed for 6 hours and then as much ethanol as possible was removed by distillation. The residue, diluted with water, was extracted several times with ether, and the extracts were dried (Na_2SO_4) and distilled, to give 2-ethoxy-5 : 6-dihydro-2-pyran (315—330 g., 41—43%), b. p. 153—163°, mainly b. p. 154—158°, n_D^{20} 1.442—1.445. Towards the end of the distillation, if overheating occurs, a violent reaction sets in and penta-2 : 4-dienal distils; presumably acid is liberated, inducing fission of any ethoxydihydropyran remaining undistilled. Appreciable loss occurs on redistillation.

Chlorine was passed into dihydropyran (252 g.), diluted with dry ether (500 ml.), at 0°, until a green

colour persisted. The solution was decolorised by a few drops of dihydropyran, and the solvent removed by distillation under reduced pressure. The crude 2:3-dichlorotetrahydropyran was added to ethanolic ammonia and the preparation completed as described above, to give 2-ethoxy-5:6-dihydro-2-pyran (199 g., 52%), b. p. 50—60°/12 mm., n_D^{20} 1.441—1.444.

In another experiment chlorine was passed into a mixture of dihydropyran (152 g.), ethanol (1 l.), and precipitated calcium carbonate (360 g.), cooled below 10°, until 42 l. had been absorbed. The reaction mixture was heated to boiling, potassium hydroxide (140 g.) added, and the preparation completed as above, to give 2-ethoxy-5:6-dihydro-2-pyran (89 g., 38%), b. p. 154—157°, n_D^{20} 1.443.

By Woods and Sanders's procedure (*loc. cit.*) 2-ethoxy-5:6-dihydro-2-pyran (400 g.) was converted into *trans-n*-penta-2:4-dienal (63 g., 25%), b. p. 38—40°/20 mm., n_D^{20} 1.514. These authors recorded a 55% yield on a 40-g. scale, which we have never achieved on the larger scale, of pentadienal having n_D^{25} 1.5163. Pentadienal was stored at 0° in the presence of quinol.

To a solution of *trans-n*-penta-2:4-dienal (64.5 g.) in dry ether (400 ml.), cooled in ice, an assayed ethereal solution of lithium aluminium hydride (7.48 g. in 177 ml.) was added slowly with stirring. Water was then added cautiously, followed by dilute sulphuric acid, and the product isolated from the dried (Na_2SO_4) ethereal layer by distillation. *trans-n*-Penta-2:4-dien-1-ol (47.4 g., 77%) had b. p. 75—76°/32 mm., 55—57°/12 mm., n_D^{20} 1.4890 (Found: C, 71.3; H, 9.7. Calc. for $\text{C}_5\text{H}_8\text{O}$: C, 71.5; H, 9.6%); light absorption, see Table I. A similar yield of pentadienol, having n_D^{20} 1.4890, was obtained on addition of the ethereal pentadienal to a stirred suspension of lithium aluminium hydride in ether. The pentadienol was stored at 0° in the presence of quinol. The 1-naphthylurethane on crystallisation from light petroleum had m. p. 89°, but on seeding with the derivative described above this m. p. at once rose to 99.5°. The lactonic acid adduct from maleic anhydride had m. p. 177°.

trans-n-Penta-2:4-dien-1-ol (410 mg.), reduced in ethyl acetate over palladium-barium sulphate, absorbed 218 ml. of hydrogen at N.T.P. (Calc. for 2H^+ : 219 ml.). However, microhydrogenation gave an uptake of 2.25 mols., which is attributed to partial hydrogenolysis of the allylic hydroxyl group.

trans-n-Penta-2:4-dienyl Chloride.—Phosphorus trichloride (25 g.) was added slowly to a stirred mixture of *trans-n*-penta-2:4-dien-1-ol (42 g.) and pyridine (10 ml.) at -10° and then the crude chloride was distilled from the reaction mixture under reduced pressure. This product was washed successively with water, aqueous sodium hydrogen carbonate, and hydrochloric acid, dried (CaCl_2), and distilled to give *trans-n*-penta-2:4-dienyl chloride (46 g., 92%), b. p. 80—82°/240 mm., n_D^{20} 1.492—1.493 (Found: Cl, 34.1. $\text{C}_5\text{H}_7\text{Cl}$ requires Cl, 34.6%).

trans-n-Octa-5:7-dien-2-one.—By a procedure similar to that used for the preparation of *trans-n*-oct-5-en-7-yn-2-one, *trans-n*-penta-2:4-dienyl chloride (46 g.) was caused to react with ethyl sodioacetate [from sodium (9.9 g.) and ethyl acetoacetate (56 g.) in ethanol (300 ml.)] and subsequently treated with 5% aqueous sodium hydroxide (800 ml.). Isolation of the product as described above and distillation gave *trans-n*-octa-5:7-dien-2-one (26 g., 47%), b. p. 75—78°/12 mm., n_D^{20} 1.4768 (1.474—1.477); light absorption, see Table I; uptake on microhydrogenation, 3.20 mols. with a break at 2.01 mols. (2H^+ and 1 carbonyl group) (Found: C, 77.5; H, 9.95. Calc. for $\text{C}_8\text{H}_{12}\text{O}$: C, 77.45; H, 9.95%). The 2:4-dinitrophenylhydrazone had m. p. 82.0—82.5° (Found: C, 55.65; H, 5.55. Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$: C, 55.2; H, 5.3%), not depressed on admixture with the somewhat lower-melting derivative obtained from the semihydrogenation of *trans-n*-oct-5-en-7-yn-2-one and described above. *trans-n*-Octa-5:7-dien-2-one was stored at 0° in the presence of quinol.

Ethyl 2-Keto-trans-n-octa-5:7-diene-1-carboxylate.—*trans-n*-Octa-5:7-diene-2-one (26 g.) was added dropwise to a stirred refluxing suspension of sodium hydride (10.1 g.) in ethyl carbonate (47 ml.) and ether (60 ml.) during 2 hours. Next day *ethyl 2-keto-trans-n*-octa-5:7-diene-1-carboxylate (17.3 g., 42%), was isolated by the procedure of Part V; it had b. p. 82—90°/0.1 mm., n_D^{20} 1.477—1.482 (Found: C, 67.5, 66.9; H, 8.35, 8.35. $\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C, 67.3; H, 8.2%); light absorption, see Table I; uptake on microhydrogenation, 2.70 mols. with a break at 2.01 mols. (2H^+ and 1 carbonyl group). Similar experiments with octa-5:7-dien-2-one, prepared by semihydrogenation, yielded products having, e.g., b. p. 75.5—78.0°/0.08 mm., n_D^{20} 1.476—1.479; light absorption, λ_{max} 2250 Å, ϵ_{max} 18,600; (Found: C, 66.4, 66.0, 66.55, 66.35; H, 8.25, 8.65, 8.65, 8.55. $\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C, 66.3; H, 9.05%).

trans-Pyrethron.—Ethyl 2-keto-*trans-n*-octa-5:7-diene-1-carboxylate (3.5 g.) was added to a suspension of powdered sodium (0.54 g.) in ether, and the mixture set aside to complete the formation of the sodio-derivative. Next day freshly distilled bromoacetone (4.0 g.) was added and the mixture refluxed for 2 hours. Aqueous acid was then added, the ethereal layer separated and evaporated, and the residual oil stirred in 3% aqueous sodium hydroxide (90 ml.) at 40° during 3 hours. Acidification, extraction, and distillation gave crude *trans*-pyrethron (0.65 g.), b. p. 92—115°/0.25 mm., n_D^{20} 1.514—1.516. This ketone was converted, in pyridine-ethanol, into the *semicarbazone*, which after crystallisation from aqueous ethanol had m. p. 198—200° (Found: C, 65.45; H, 7.75. $\text{C}_{12}\text{H}_{17}\text{ON}_3$ requires C, 65.8; H, 7.75%); light absorption, λ_{max} 2260 (ϵ 25,100) and 2645 Å (ϵ 22,400); side-chain methyl groups, 1.16, 1.27.

A suspension of the semicarbazone (400 mg.) in water (0.6 ml.) and oxalic acid (600 mg.) was heated under reflux in nitrogen for 1 hour. Cooling, extraction with light petroleum (b. p. 40—60°), and distillation gave *trans*-pyrethron, b. p. 70—72°/0.08 mm., n_D^{20} 1.5350 (Found: C, 78.2; H, 8.6. $\text{C}_{11}\text{H}_{14}\text{O}$ requires C, 81.45; H, 8.7%) (the tendency for these ketones to give low values for carbon was noted in Part II, *f.*, 1946, 892); light absorption, see Table II; uptake on microhydrogenation, 3.5 mols. with a break at 2.82 mols. (3H^+ and 1 carbonyl group). This particular specimen of *trans*-pyrethron partly crystallised and the solid had m. p. ca. 60°.

Similar experiments with ethyl 2-keto-*n*-octa-5:7-diene-1-carboxylate, prepared by the semihydrogenation route, yielded a pyrethron having, e.g., b. p. 85—90°/0.25 mm., n_D^{20} 1.4996, which on

conversion into the semicarbazone (sodium acetate-aqueous ethanol) and crystallisation from methanol gave a product, m. p. 199—200° (decomp.) with softening from 192°; light absorption, λ_{max} , 2270 (ϵ 18,600) and 2640 Å (ϵ 26,300). The less pure products obtained by the semihydrogenation route all had ϵ_{max} , at ca. 2260 Å less than ϵ_{max} , at ca. 2645 Å.

3-Hydroxy-trans-n-undeca-8 : 10-diene-2 : 5-dione.—By procedure A of Part V, ethyl 2-keto-trans-n-octa-5 : 7-diene-1-carboxylate (18 g.) was hydrolysed in 3% aqueous sodium hydroxide (140 ml.) during 6 hours at 20° and the solution of sodium salt then condensed with aqueous pyruvaldehyde (21.2 ml.) during 6 hours at 35° and then 5 hours at 20°. The fractions of the product, isolated as described, boiling within the range 102—128°/0.15 mm., and having n_D^{20} 1.498—1.504 (6.05 g.), represented a 33% yield of 3-hydroxy-trans-n-undeca-8 : 10-diene-2 : 5-dione (Found : C, 67.7; H, 8.2. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%); light absorption, see Table I; uptake on microhydrogenation, 4.04 mols. with a break at 1.96 mols. (2 $\bar{=}$ and 2 carbonyl groups).

(±)-trans-Pyrethrolone.—By the procedure of Part V 3-hydroxy-trans-n-undeca-8 : 10-diene-2 : 5-dione (6.1 g.) was cyclised in 6% aqueous sodium hydroxide (90 ml.) during 2 hours and the product isolated as described. Two distillations gave (±)-trans-pyrethrolone (1.45 g., 26%), b. p. 120—122°/ca. 0.1 mm., n_D^{20} 1.540—1.546 (Found : C, 73.75; H, 8.0. $C_{11}H_{14}O_2$ requires C, 74.1; H, 7.9%); light absorption, see Table II; uptake on microhydrogenation, 4.10, 3.87 mols. with a break at 3.08 mols. (3 $\bar{=}$ and 1 carbonyl group); side-chain methyl groups, 1.14. Attempts to prepare the semicarbazone and the acetate semicarbazone were fruitless.

Ozonisation of (±)-trans-Pyrethrolone.—By the method used for pyrethrolone B-2 (see above), (±)-trans-pyrethrolone (150 mg.) gave formaldehyde dimedon derivative (32 mg.), m. p. 188—189° not depressed on admixture with authentic formaldehyde derivative.

Hydrogenation of (±)-trans-Pyrethrolone.—(±)-trans-Pyrethrolone (100 mg.) in ethyl acetate (15 ml.) was reduced over 5% palladium-barium sulphate (100 mg.) (uptake : ca. 2 mols.). Distillation of the catalyst-free solution then gave (±)-tetrahydropyrethrolone (63 mg.), b. p. 115—116°/0.1 mm., n_D^{20} 1.4902. The 3 : 5-dinitrobenzoate had m. p. 99° (Kofler hot stage), when crystallised from methanol, not depressed when admixed with the derivative described above.

(±)-trans-Pyrethronyl (+)-trans-Chrysanthemate.—By the procedure of Part V, interaction of (±)-trans-pyrethrolone (450 mg.) and (+)-trans-chrysanthemoyl chloride (470 mg.) in benzene (10 ml.)-pyridine (0.4 ml.) gave (±)-trans-pyrethronyl (+)-trans-chrysanthemate (300 mg.), b. p. 112—113°/2 × 10⁻³ mm., n_D^{20} 1.5210 (Found : C, 76.0; H, 8.3. $C_{21}H_{28}O_3$ requires C, 76.8; H, 8.6%); light absorption, see Table II; uptake on microhydrogenation, 5.95 mols. (4 $\bar{=}$, 1 carbonyl group, and hydrogenolysis of one ester group) [for comparison, (±)-tetrahydropyrethronyl (±)-trans-chrysanthemate (Part III) gave an uptake of 3.22 mols. with a break at 2.84 mols. (2 $\bar{=}$, 1 carbonyl group, and hydrogenolysis of one ester group), while a specimen of allethrin gave an uptake of 4.30 mols. (3 $\bar{=}$, 1 carbonyl group, and hydrogenolysis of one ester group)].

We gratefully acknowledge maintenance grants from the Agricultural Research Council (L. C.) and from the County Durham Education Committee (D. T.), and grants from the former, the Royal Society, the Chemical Society, and the Central Research Fund of the University of London. We are indebted to the Distillers Company, Ltd., to Prof. R. Paul and Rhône-Poulenc et Cie, to Dr. Wm. Mitchell and Messrs. Stafford Allen & Sons, Ltd., and to Dr. F. D. Rossini, for gifts of chemicals, and to Prof. E. R. H. Jones and Dr. F. B. LaForge for gifts of reference specimens. We are also indebted to Dr. E. A. Braude for ultra-violet, and to Dr. W. C. Price for infra-red, spectroscopic facilities.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7. (L. C.)

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, W.C.2. (S. H. H., D. T.)

[Received, June 4th, 1951.]