

The Chemistry of Terpenes. Part XVI.¹ Some Oxidation Products of β -Pyronene

By Wesley Cocker,* Kevin J. Crowley, and Krishnaswamy Srinivasan, Trinity College, Dublin 2, Ireland

Oxidation of β -pyronene (1,2,6,6-tetramethylcyclohexa-1,3-diene) (1) with Brown's chromic acid reagent gave 4-hydroxy-3,4,5,5-tetramethylcyclohex-2-enone (5), which was reduced to *cis*- (7) and *trans*-1,2,6,6-tetramethylcyclohex-2-ene-1,4-diol (8).[†] The *cis*-isomer (7) was also obtained by reduction of the peroxide (9) formed on photo-oxidation of β -pyronene. The diols (7) and (8) and 1,6,6-trimethyl-2-methylenecyclohex-3-enol (12) were obtained when β -pyronene was oxidised in ether with monoperphthalic acid. Oxidation of β -pyronene with peracetic acid in acetic acid, and with perbenzoic acid in chloroform gave the dienol (12), and as main products, respectively the 4-acetate (14) and 4-benzoate (15) of the *cis*-diol (7). Oxidation of β -pyronene in ether with perbenzoic acid gave the epoxide (16) as main product, the benzoate (15), and the dienol (12). Pyrolysis of the diol (8) over pyridine-treated alumina gave 1,2,3,4-tetramethylbenzene (13) and 2,2,6,6-tetramethylcyclohex-3-enone (18) which was also the major product of the similar pyrolysis of the dienol (12). The hydroxy-ketone (5), which has the same ring structure as abscisin II [5-(1-hydroxy-2,6,6-trimethyl-4-oxocyclohex-2-enyl)-3-methylpenta-2,4-dienoic acid] (6), lacks the latter's growth regulatory properties.

THE oxidation of β -pyronene (1,2,6,6-tetramethylcyclohexa-1,3-diene) (1) has been carried out using several reagents. Thus selenium dioxide affords the unsaturated aldehyde (2),² while oxidative hydroboration gives³ the allylic alcohol (3) in good yield. This, and the

isomeric allylic alcohol (4) are formed⁴ on hydrochlorination of β -pyronene followed by treatment of the product with acetic anhydride and then lithium aluminium hydride.

The work now described was initiated by the investigation of the two-phase⁵ oxidation of β -pyronene (1) with

[†] The terms *cis* and *trans* refer to the relative configurations of the hydroxy-groups or their derivatives.

¹ Part XV, W. Cocker, K. J. Crowley, and K. Srinivasan, *J.C.S. Perkin I*, 1972, 1971.

² A. Uzarewicz and W. Zacharewicz, *Roczniki Chem.*, 1961, **35**, 541, 887 (*Chem. Abs.*, 1961, **55**, 23,378d; 1962, **56**, 443c).

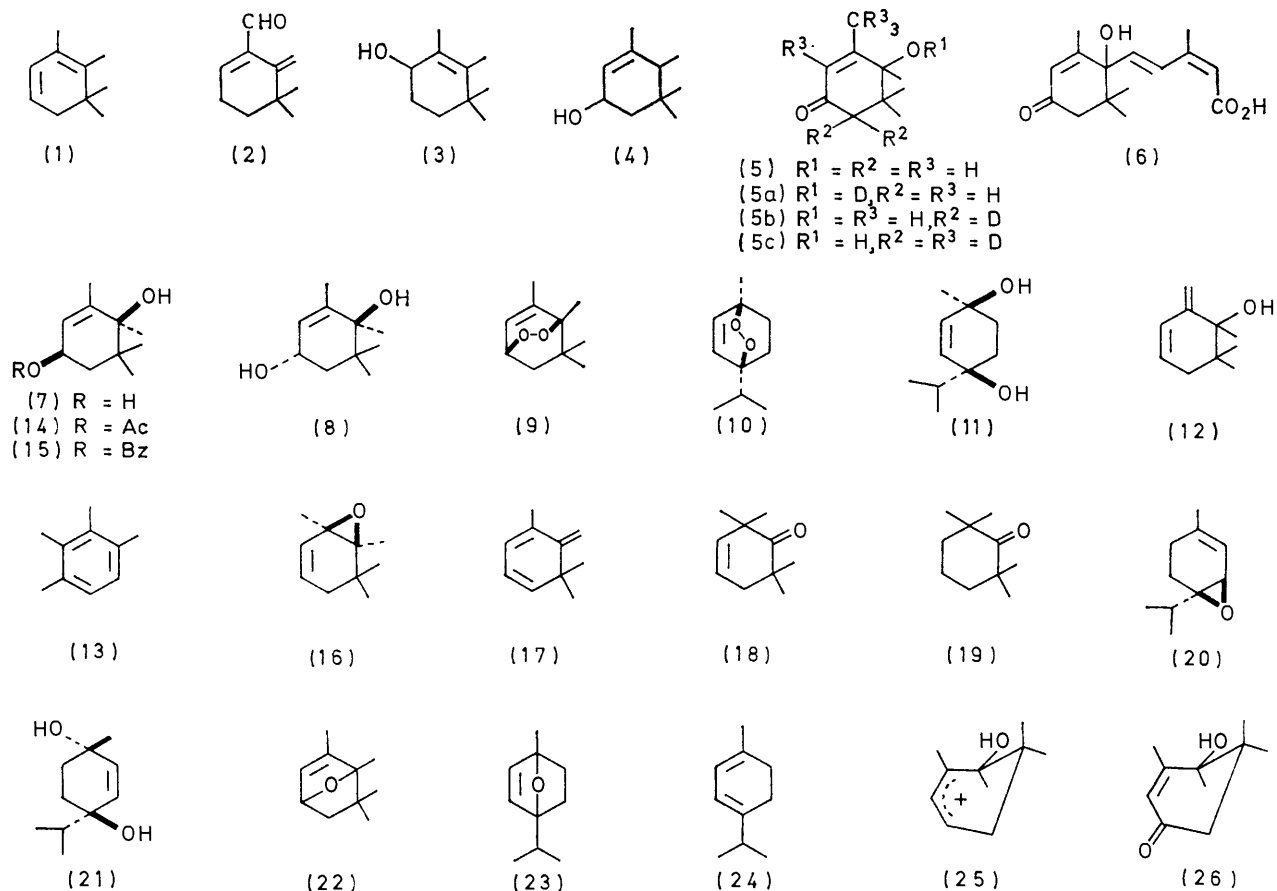
³ A. Uzarewicz, *Roczniki Chem.*, 1964, **38**, 385 (*Chem. Abs.*, 1964, **61**, 1771b).

⁴ A. Uzarewicz and M. Zaidlewicz, *Roczniki Chem.*, 1970, **44**, 313 (*Chem. Abs.*, 1970, **72**, 132,138).

⁵ H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

chromic acid. This yielded a neutral fraction (*ca.* 50%) which consisted (g.l.c.) of a complex mixture of high-boiling products. The only crystalline product was 4-hydroxy-3,4,5,5-tetramethylcyclohex-2-enone (5) whose

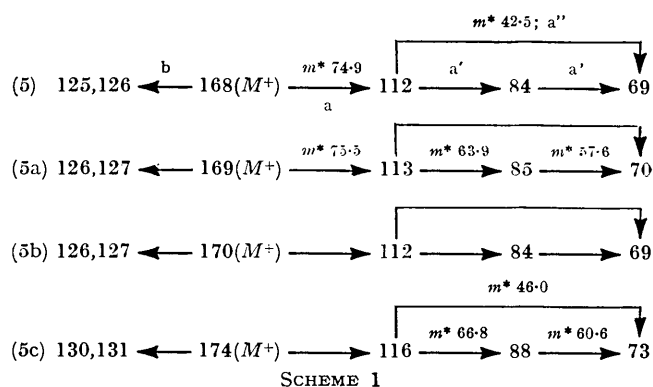
The other major fragmentation pathway of (5) involves the elimination of either C_3H_8 or C_3H_7 , giving rise to the fragments, m/e 126 and 125, one of the hydrogens apparently originating from C-6 in both cases. The



u.v. spectrum displayed a maximum at 238.5 nm, indicative of a disubstituted $\alpha\beta$ -unsaturated ketone.⁶ Maxima in the i.r. at 3380, 1675sh, 1660sh, 1640, and 1609sh cm^{-1} were reminiscent of those of abscisin II [5-(1-hydroxy-2,6,6-trimethyl-4-oxocyclohex-2-enyl)-3-methylpenta-2,4-dienoic acid] (6),^{7,8} and signals at τ 8.9 (CMe_2), 8.62 ($MeCOH$), 8.0 ($MeC=C$), and 4.2 ($HC=C$) in its n.m.r. spectrum were compatible with structure (5). This was fully confirmed by the mass spectra of (5) and those of its deuteriated derivatives (5a—c).

The two major decomposition pathways of (5) and its deuteriated derivatives are shown in Schemes 1 and 2. The principal route (path a) proceeds by a retro Diels-Alder fission, for which analogy exists in similar systems.⁹ The resulting ion can lose CO followed by CH_3 (path a'), or it can transfer its hydroxy-hydrogen atom either by a [1,5] or a [1,6] shift and then lose $COCH_3$ in one step (path a'').

formation of the ion of m/e 126 can be depicted as in path b', while the ion of m/e 125 can be formed as in path b''. These mechanisms are necessitated by the results of



deuteriation studies given in Scheme 1. Similar hydrogen shifts have been reported.¹⁰ The low eV spectrum

⁶ L. F. Fieser and M. Fieser, 'Steroids,' Reinhold, New York, 1959, p. 19.

⁷ J. W. Cornforth, B. V. Milborrow, G. Ryback, and P. F. Wareing, *Nature*, 1965, **205**, 1269.

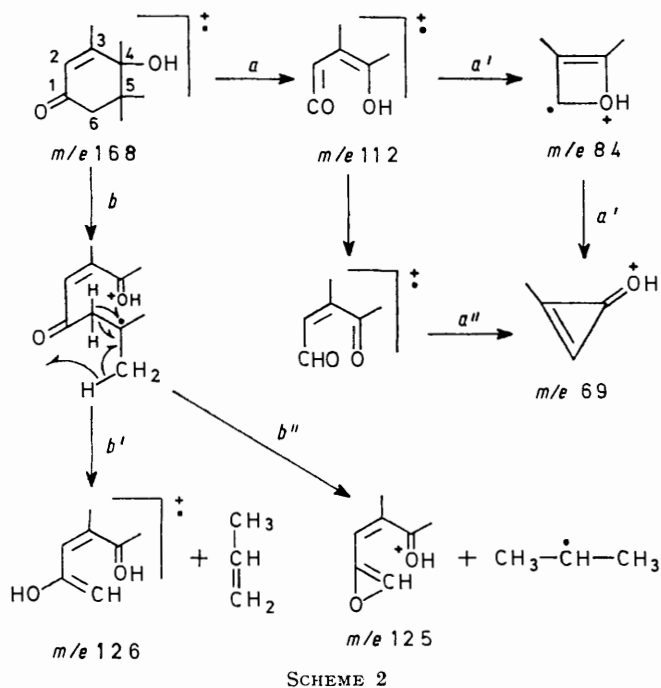
⁸ J. W. Cornforth, B. V. Milborrow, and G. Ryback, *Nature*, 1965, **206**, 715.

⁹ A. F. Thomas, B. Willhalm, and J. H. Bowie, *J. Chem. Soc. (B)*, 1967, 392.

¹⁰ See for example U. T. Bhalarao and H. Rapoport, *J. Amer. Chem. Soc.*, 1971, **93**, 105.

of (5) shows the absence of other major breakdown pathways.

Borohydride reduction of the hydroxy-ketone (5) gave a mixture of *cis*-1,2,6,6-tetramethylcyclohex-2-ene-1,4-diol (7) (56%), m.p. 125–127°, and its *trans*-isomer (8) (44%), m.p. 94–95°. Both were oxidised with chromium trioxide in pyridine to the hydroxy-ketone (5). Assignment of configuration to the diols (7 and 8) by i.r. dilution studies failed, owing to their low solubilities in appropriate solvents. Neither diol yielded a volatile



oxalate on treatment with oxalyl chloride and pyridine, and an attempt to form a derivative of the *cis*-diol (7) with benzaldehyde was also unsuccessful. However the configuration of the *cis*-diol (7) was established as follows. Photo-oxidation of β -pyronene (1) in the presence of Methylene Blue gave a mixture of products in which the peroxide (9)¹¹ was predominant (52% by n.m.r.). Chromatography on silica gave the peroxide in *ca.* 80% purity (g.l.c.). Its structure followed from its spectra. In the i.r. it showed a characteristic band at 869 cm^{-1} , and in its Raman spectrum, bands at 865 cm^{-1} , characteristic¹² of the O–O group, 792, 890, and 1643 cm^{-1} (C=C). Ascaridole (10) (kindly supplied by Professor H. B. Henbest) showed bands at 812, 850, 876 (O–O), 890, and 1616 cm^{-1} in its Raman spectrum. The peroxide (9) showed resonances at τ 9.16 and 8.81 (Me_2C), 8.78 (MeC-O-O), 8.14 (MeC=C), 5.55 (HC-O-O), and 3.78 (HC=C). Apart from the molecular ion at m/e 168 and an ion at m/e 136 ($M^+ - \text{O}_2$), its mass spectrum closely resembled that of β -pyronene. Structure (9) is thus established. Reduction of the peroxide with lithium aluminium hydride gave

¹¹ G. O. Schenck and K. Ziegler, Ger.P. 913,892 (*Chem. Abs.*, 1958, **52**, 14,704g).

¹² D. C. McKean, J. L. Duncan, and R. K. M. Hay, *Spectrochim. Acta*, 1967, **23A**, 605.

the *cis*-diol (7). Similar reduction of ascaridole (10) affords¹³ the analogous *cis*-diol (11).

Oxidation of β -pyronene, in ether, with monopero-phthalic acid gave, as major products, the *cis*-diol (7) and its *trans*-isomer (8), the latter slightly predominating, and 1,6,6-trimethyl-2-methylenecyclohex-3-enol (12). We were unable to carry out this oxidation in chloroform because of the low solubility of the perphthalic acid in this solvent. Oxidation with peracetic acid in acetic acid also afforded the unsaturated alcohol (12) and 1,2,3,4-tetramethylbenzene (13), both in low yield. It gave as major product the 4-acetate (14) of diol (7). Perbenzoic acid, in chloroform, similarly gave (12) and (13), and, as major product the 4-benzoate (15). The esters (14) and (15) were related to the diol (7) by alkaline hydrolysis and by reacylation. The diol showed maximum absorption at 230 nm in agreement with structure (12),⁶ and its i.r. spectrum included peaks at 3500 (OH), 895 ($\text{C}=\text{CH}_2$), 768 (*cis*- $\text{HC}=\text{CH}$), and 1604 and 1643 cm^{-1} (conjugated C=C). Its n.m.r. spectrum had signals at τ 9.12 and 9.01 (Me_2C), 8.76 (MeCOH), 5.13 and 4.73 ($\text{H}_2\text{C}=\text{C}$), and an AB quartet with sub-splitting centred on 4.13 ($\text{HC}=\text{CH}$).¹⁴

Oxidation of β -pyronene (1), in ether, with perbenzoic acid gave the epoxide (16) as major product and also the diol (12), 1,2,3,4-tetramethylbenzene (13), and the benzoate (15). Minor quantities of epoxide (16) were formed along with the diol (12) and the *cis*- (7) and *trans*- (8) diols when β -pyronene was treated with monopero-phthalic acid in ether containing sodium phthalate.

The epoxide (16) showed bands at 1644 and 730 (*cis*- $\text{HC}=\text{CH}$) and 868 cm^{-1} (epoxide) in the i.r. and n.m.r. signals at τ 9.09 and 8.9 (6H, 2s, Me_2C), 8.69 (3H, s,

$\text{Me}-\overset{\text{O}}{\text{C}}-\text{C}$), 8.6 (3H, s, $\text{C}=\text{C}-\text{Me}$), and 4.33 (2H, m, $\text{HC}=\text{CH}$). Its mass spectrum included a relatively weak molecular ion at m/e 152 and other ions at 134 ($M^+ - \text{H}_2\text{O}$), 137 ($M^+ - \text{Me}$), 119 ($M^+ - \text{H}_2\text{O} - \text{Me}$), and 43 (base peak). The structure of the epoxide was thus established.

The epoxide (16) was rapidly decomposed by nucleophiles. Stirring, in chloroform, with benzoic acid gave a mixture containing the diol (12), 1,2,3,4-tetramethylbenzene (13), and, mainly, the *cis*-benzoate (15). In acetic acid, the epoxide (16) afforded the *cis*-acetate (14). Stirring with water (pH 6.96), dilute hydrochloric acid (pH 5.96–1.0), or with water and solid carbon dioxide (*cf.* ref. 1), gave the *trans*-diol (8) with no evidence of the formation of the *cis*-isomer (7). Indeed attempts to purify the epoxide by chromatography on silica failed owing to hydrolysis, but it was purified by chromatography on basic alumina.

Pyrolytic dehydration of the diol (8) was attempted with a view to obtaining the linearly conjugated triene (17). It has been reported¹⁵ that when cyclic, tertiary

¹³ F. Richter and W. Presting, *Ber.*, 1931, **64**, 878; K. Bodendorf, *Arch. Pharm.*, 1933, **271**, 1; M. Matic and D. A. Sutton, *J. Chem. Soc.*, 1952, 2679; *cf.* K. H. Overton and P. Owen, *J.C.S. Perkin I*, 1973, 226.

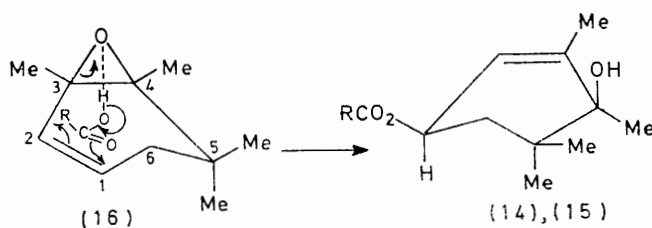
¹⁴ *Cf.* W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, 1968, **90**, 802.

¹⁵ E. von Rudloff, *Canad. J. Chem.*, 1961, **39**, 1860.

hydroxy-compounds are heated with pyridine-treated alumina, exocyclic dehydration takes place preferentially. In our hands however, the only identifiable products obtained from the diol (8) were 1,2,3,4-tetramethylbenzene (13) and 2,2,6,6-tetramethylcyclohex-3-enone (18), whose structure follows from its spectra (see Experimental section) and its reduction to the known¹⁸ saturated ketone (19). A similar pyrolytic reaction with the dienol (12) also afforded the unsaturated ketone (18) as the main product.

In the reaction of a conjugated diene with a peracid, the more highly substituted double bond is preferentially attacked.¹⁷ Thus the initial formation of the allylic epoxide (16) from β -pyronene was expected. However, in our early experiments this was not encountered owing to the relative instability of these compounds towards nucleophiles. Thus the analogous epoxide (20) affords¹⁸ the *trans*-diol (21) on stirring with water and our epoxide (16) similarly yields the *trans*-diol (8). Nor did we encounter the 1,4-epoxide (22) in our oxidations of β -pyronene. The analogous 1,4-epoxy-*p*-menth-2-ene (23) obtained¹⁹ in the oxidation of α -terpinene (24) with perbenzoic acid was presumably formed *via* the epoxide (20) or its isomer.

The conversion of the epoxide (16) into the diols (7) and (8) and the esters (14) and (15) can be likened to the reaction of nucleophiles with allylic halides, whose mechanism has provoked much discussion.²⁰ Our results suggest that three mechanisms can operate according to the reaction conditions. The stereospecific formation of the *cis*-esters (14) and (15) on treatment of the epoxide (16) with acetic acid or with benzoic acid in chloroform suggests that it is the configuration of the epoxide (*cf.* ref. 21) that controls the direction of attack of the acids. The nature of the solvent is also important. In chloroform, which will not complex with peracid or carboxylic acid, co-ordination of the latter with the epoxide oxygen atom can take place. Concurrent attack of the acid on C-1 can take place thus yielding a *cis*-ester (Scheme 3).



SCHEME 3

Models show that the geometry of the transition state is favourable, but the reaction could take place *via* the 3-ester followed by allylic rearrangement. In ether, which can complex with benzoic acid, co-ordination of the latter

with the epoxide oxygen atom is minimised. This is reflected in the formation of the epoxide (16) and very little *cis*-ester (15) when β -pyronene is treated with perbenzoic acid in ether. The reaction is also slow which is in accord with the fact²² that the epoxidation of cyclohexene with perbenzoic acid is over a hundred times faster in chloroform than in ether.

The formation of the *cis*- (7) and *trans*- (8) diols and only a minor amount of epoxide (16) from β -pyronene and monopero-phthalic acid in ether requires another mechanism. No hydrogen phthalate was encountered although the hydrogen phthalate of the *cis*-diol (7) is stable under the work-up conditions of the oxidation reaction. The absence of ester is perhaps not surprising since phthalic acid is sparingly soluble in ether. It would seem therefore that the precursor of the diols is the carbonium ion whose preferred conformation is (25). The less-hindered, underside attack of this by water should result in the formation of more *trans*-diol (8) than *cis*-diol (7). This accords with experimental results.

A third mechanism must be invoked to explain the aqueous hydrolysis of the epoxides (16) and (20) which affords only the *trans*-diols (8) and (21) respectively. Even with 0.1M-hydrochloric acid the epoxide (16) gives only the *trans*-diol (8). Clearly the carbonium ion (25) cannot be an intermediate since hydration should yield both *cis*- and *trans*-diols. We make the suggestion that solvation of the oxonium ion of (16) prevents attack of water on the upper side of the molecule, thus precluding the formation of *cis*-diol (7). The stereospecific formation of the *trans*-diol (8) could also be explained if the 1,4-epoxide (22) [*cf.* (23)] were an intermediate. This would suffer from intense strain and would readily undergo hydrolysis. Further work is in progress.

The formation of the unsaturated alcohol (12) in the peracid oxidation of β -pyronene can be explained on the basis of loss of a proton from the 2-methyl group of the carbonium ion (25).

The formation of the hydroxy-ketone (5) in the oxidation of β -pyronene (1) with Brown's chromic acid reagent⁵ no doubt takes place through the intermediate epoxide (16) and the diols (7) and (8). The low yield of product may result from the sensitivity of the diols to mineral acid; this is under further investigation.

The predominance of the *cis*-diol (7) over the *trans*-diol (8) on borohydride reduction of (5) may result from underside attack on the preferred conformer (26). As expected the more stable *trans*-diol is the main product of lithium aluminium hydride reduction.

The formation of the unsaturated ketone (18) on heating the diol (8) and dienol (12) with the amphoteric catalyst,¹⁵ pyridine on alumina may be portrayed as shown in Scheme 4.

¹⁶ E. G. Cummins and J. E. Page, D.M.S. spectrum 4086.

¹⁷ D. Swern, 'Organic Peroxides,' Wiley, New York, 1971, vol. II, p. 454.

¹⁸ G. O. Pierson and O. A. Runquist, *J. Org. Chem.*, 1969, **34**, 3654.

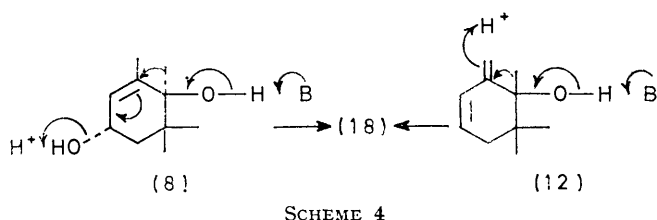
¹⁹ L. A. Elson, C. S. Gibson, and J. L. Simonsen, *J. Chem. Soc.*, 1929, 2732.

²⁰ F. G. Bordwell, *Accounts Chem. Res.*, 1970, **3**, 281 where many other references are given.

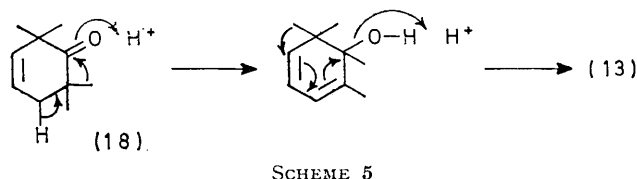
²¹ H. B. Henbest, *Proc. Chem. Soc.*, 1963, 159.

²² Ref. 17, p. 460.

The ketone (18) may be the precursor of 1,2,3,4-tetramethylbenzene (13) formed in the above dehydration



and in the peracid oxidations of β -pyronene. The reaction may be portrayed as in Scheme 5.



Abscisin II (6)^{7,8} has the same ring system as the hydroxy-ketone (5), but tests of the growth regulatory properties of (5) showed it to have little activity.

EXPERIMENTAL

I.r. spectra were measured for liquid films (L) or Nujol mulls (N). N.m.r. and u.v. spectra were measured for solutions in [²H]chloroform and ethanol respectively, unless otherwise stated. Other experimental conditions were similar to those described in Part XV.¹ With the exception of peaks of particular diagnostic value, i.r. and mass spectral data are given in Supplementary Publication No. SUP 20805 (16 pp.).* β -Pyronene used in this work was obtained by pyrolysis of α -pinene and had b.p. 47.6–48.3° at 7 mmHg (89% pure by g.l.c.).

4-Hydroxy-3,4,5,6-tetramethylcyclohex-2-enone (5).—A solution of β -pyronene (1) (7.9 g) in ether (80 ml) was stirred for 2 h with Brown's reagent⁵ (30 ml), while the temperature rose from 0 to 25°. The solid from the neutral fraction (4.2 g) of the product was crystallised from ethyl acetate–light petroleum giving the hydroxy-ketone (5) as rhombs (0.28 g), m.p. 108–109°, λ_{\max} (MeOH) 238.5 (log ϵ 3.95) and 313 nm (1.68), τ 8.9 (6H, s, Me₂C), 8.62 (3H, s, MeCOH), 8.0 (3H, d, J 1.5 Hz, MeC=C), 7.7 (1H, s, OH), 7.67 (2H, s, CH₂), and 4.2 (1H, q, J 1.5 Hz, HC=C) (Found: C, 71.6; H, 9.4. C₁₀H₁₆O₂ requires C, 71.4; H, 9.6%). Its deuterated derivatives (5a–c) were prepared by the methods described in ref. 9.

Reduction of the Hydroxy-ketone (5). *cis*-1,2,6,6-Tetramethylcyclohex-2-ene-1,4-diol (7) and its *trans*-Isomer (8).—A solution of the hydroxy-ketone (5) (0.27 g) in methanol (10 ml) was kept overnight with sodium borohydride (0.15 g). The usual work-up, extracting with ethyl acetate and crystallising from ether–light petroleum gave first the *cis*- and then the *trans*-diol. The *cis*-diol (7) consisted of needles (88 mg), m.p. 125–127°, λ 210 nm (log ϵ 2.9), ν_{\max} (N) 3300 and 837 cm⁻¹, τ [(CD₃)₂SO] 9.20 and 9.09 (6H, 2s, Me₂C), 8.99 (3H, s, MeC–OH), 8.35–8.6 (2H, m, 5-H₂), 8.33br (3H, s,

MeC=C), 6.0 (1H, m, 4-H), 5.97 (1H, s, MeCOH), 5.66 (1H, m, CHOH), and 4.72br (1H, s, 3-H), mass spectrum similar to that of its isomer (8) (Found: C, 70.6; H, 10.6. C₁₀H₁₈O₂ requires C, 70.5; H, 10.7%). Its benzoate (15), made in pyridine, was a thick oil, ν_{\max} (L) 3450, 1710, and 835 cm⁻¹, τ 9.0 and 8.88 (6H, 2s, Me₂C), 8.77 (3H, s, MeCOH), 8.18 (3H, s, MeC=C), 4.24–4.7 (2H, m, HC=C and HCOBz), and 2.44–2.77 and 1.9–2.09 (5H, m, ArH) (Found: C, 74.1; H, 8.2. C₁₇H₂₂O₃ requires C, 74.4; H, 8.1%).

The *trans*-diol (8) was obtained as an amorphous solid (55 mg), m.p. 94–95°, λ 210 nm (log ϵ 3.0), ν_{\max} (N) 3400, 3180, and 846 cm⁻¹, τ [(CD₃)₂SO] 9.12 (6H, s, Me₂C), 8.88 (3H, s, MeC–OH), 8.4–8.65 (2H, m, 5-H), 8.34br (3H, s, MeC=C), 6.05 (1H, s, MeCOH), 6.0 (1H, m, 4-H), 5.6 (1H, d, J 6 Hz, CHOH), and 4.78br (1H, s, 3-H), m/e 170 (M^+ , 8%), 152 (M^+ – H₂O, 8), 137 (M^+ – H₂O – Me, 24), and 134 (M^+ – 2H₂O, 38) (Found: C, 63.2; H, 10.2. C₁₀H₁₈O₂·H₂O requires C, 63.8; H, 10.7%). Its benzoate, made in pyridine, was a thick oil, τ 8.94 and 8.91 (6H, 2s, Me₂C), 8.67 (3H, s, MeCOH), 8.19br (3H, s, MeC=C), 6–6.5 (1H, OH), 4.3–4.7 (2H, m, HC=C and HC–OBz), and 2.5–2.8 and 1.9–2.1 (5H, m, ArH), ν_{\max} (L) 3420, 1708, and 842 cm⁻¹ (Found: C, 74.5; H, 8.2%).

The dienol (12) (see below) was formed in low yields in the benzylation of (7) and (8).

The hydroxy-ketone (5) (0.2 g) was reduced in ether (15 ml) with lithium aluminium hydride (80 mg) and worked up by careful addition of ice–water (5 ml) and continuous extraction with ether. In a similar manner reduction was carried out with lithium aluminium triethoxy- and tri-*t*-butoxy-hydrides. The yields of gummy product were 187, 178, and 197 mg respectively. By n.m.r. the relative proportions of *cis*- (7) and *trans*- (8) diols were 40 : 60, 44 : 56, and 44.5 : 55.5.

Oxidation of the Diols (7) and (8).—Pyridine (10 ml) was stirred and cooled while chromium trioxide (0.9 g) followed by the *cis*-diol (107 mg) in pyridine (2 ml) were slowly added. After 24 h, ether was added, and then sufficient dilute hydrochloric acid to bring the acidity to pH 3. The brown emulsion was continuously extracted for 10 h with ether, the extract was washed with water, dried, and evaporated. The residue (103 mg), crystallised from ethyl acetate–light petroleum, afforded the hydroxy-ketone (43 mg). The *trans*-diol was similarly oxidised.

Photo-oxidation of β -Pyronene. *3,6-Epidioxy-1,5,5,6-tetramethylcyclohexene (9).*—A stirred solution of β -pyronene (1) (5.4 g) in propan-2-ol (160 ml) containing Methylene Blue (0.2 g) was kept in an atmosphere of oxygen and irradiated with a 250 W Philips sunlamp. The solution was kept at 40°. After 36 h, when oxygen uptake had ceased, the solvent was removed under reduced pressure, and the dark residue (5.72 g) was chromatographed on silica (300 g). Elution with light petroleum–ether (9 : 1) gave the peroxide (9) (2.6 g) (77% pure by g.l.c.), τ 9.16 and 8.81 (6H, 2s, Me₂C), 8.78 (3H, s, MeC–O–O), 8.14 (3H, d, J 2.3 Hz, MeC=C), 5.55 (1H, m, HC–O–O), and 3.78 (1H, m, J_{tot} 9 Hz, HC=C).

Reduction of the Peroxide (9). *cis*-Diol (7).—A solution of the peroxide (9) (270 mg; 77% pure) in ether (10 ml) was added dropwise to an ice-cold stirred suspension of lithium aluminium hydride (150 mg) in ether (5 ml). After stirring for 18 h at room temperature, ice-cold water (5 ml) was added. The usual work-up gave the *cis*-diol (mixed m.p., i.r. and n.m.r. spectra) (70 mg). The residual gum from the crystallisation contained (n.m.r.) ca. 15% of *cis*-diol.

* Details of Supplementary Publications are given in Notice to Authors No. 7, *J.C.S. Dalton*, 1972, Index Issue.

Oxidation of β -Pyronene with Mono-perphthalic Acid. *cis*-(7) and *trans*-(8) *Diols* and 1,6,6-*Trimethyl-2-methylenecyclohex-3-enol* (12).— β -Pyronene (1) (2.73 g) in ether (25 ml) was stirred at -5 to 0° while a solution in ether (50 ml) of mono-perphthalic acid²³ [prepared from phthalic anhydride (3.7 g)] was added over 5 h. Stirring was continued at -5 to 0° for 5 h and at room temperature overnight. The mixture was neutralised with solid sodium hydrogen carbonate and the ether layer was separated and washed twice with water. Removal of solvent afforded a thick oil (1.9 g) which was chromatographed on silica (190 g) and eluted with light petroleum and increasing quantities of ether. The first fraction consisted of the *dienol* (12) (0.21 g) as an oil (99% by g.l.c.), n_D^{19} 1.5052 which crystallised on long standing and then had m.p. 23–26°, λ_{\max} 230 nm ($\log \epsilon$ 4.15), τ 9.12 and 9.01 (6H, 2s, Me₂C), 8.76 (3H, s, MeCOH), 5.13br and 4.73br (2H, 2s, H₂C=C), and 4.13 (2H, AB quartet with sub-splitting, $\delta_A - \delta_B$ 0.49, J_{AB} 10 Hz, *cis*-HC=CH),¹⁴ *m/e* 152 (M^+ , 8%), 134 ($M^+ - H_2O$, 23), and 119 ($M^+ - Me - H_2O$, 22) (Found: C, 79.4; H, 10.5. C₁₀H₁₆O requires C, 78.9; H, 10.6%).

The second fraction consisted of the *trans*-diol (8) (0.19 g), m.p. 93–95°, identical in all other respects with the compound described above. A residual gum (0.65 g) consisted largely (n.m.r.) of the *trans*-diol (8) with some *cis*-diol (7). Continuous extraction with ether of the aqueous mother liquors from the peracid oxidation afforded the crude *cis*-diol (7) which after crystallisation from light petroleum–ether afforded the pure diol (7) (0.5 g), m.p. 124–126°, identical with the compound described above.

Oxidation of β -Pyronene with Peracetic Acid. Acetate (14).—Peracetic acid (12.5 ml), prepared by adding hydrogen peroxide (7.5 ml; 30%) to stirred acetic anhydride (5 ml) at -5 to 5° , was added during 0.25 h to a stirred solution of β -pyronene (1) (6.8 g) and sodium acetate (6 g) in methylene chloride (50 ml) at -5 to 0° . After 24 h the mixture was filtered, stirred at 0° , and potassium carbonate was added until in slight excess. Water was added, the organic layer was separated, washed with water, dried, and evaporated. Elution of the residue (10 g) from silica gel (500 g) with light petroleum and increasing amounts of ether gave β -pyronene (2.8 g), the *dienol* (12) (0.32 g), 1,2,3,4-tetramethylbenzene (13) (0.12 g), and the *hydroxy-ester* (14) (3.18 g) which on short path distillation at 2 mm (bath temp. 115–120°) was obtained as an oil, λ 210 nm ($\log \epsilon$ 3.08), ν_{\max} (L) 3450, 1720, 1250, and 840 cm⁻¹, τ 9.07 and 8.97 (6H, 2s, Me₂C), 8.83 (3H, s, MeCOH), 8.29 (2H, d, J 6 Hz, CH₂), 8.21br (3H, s, MeC=C), 8.0 (3H, s, MeCO₂), 4.8br (1H, s, CHOH), and 4.65br (1H, s, HC=C), *m/e* 212 (M^+ , 0.2%), 195 ($M^+ - OH$, 0.6), 194 ($M^+ - H_2O$, 1.4), 156 ($M^+ - C_4H_8$, 9), and 152 ($M^+ - AcOH$, 23), m^* 114 $\xrightarrow{63-3}$ 85 and 152 $\xrightarrow{123-3}$ 137 (Found: C, 67.5; H, 9.8. C₁₂H₂₀O₃ requires C, 67.9; H, 9.5%).

Hydrolysis of the ester with sodium methoxide in methanol afforded the diol (7).

Oxidation of β -Pyronene with Perbenzoic Acid. Benzoate (15).—A solution in chloroform (120 ml) of perbenzoic acid, prepared²⁴ from benzoyl peroxide (10 g) was added dropwise to a stirred mixture of β -pyronene (6 g), sodium benzoate (6 g), and chloroform (25 ml) kept at 0 to 5° . Stirring was continued for a further 5 h at this temperature and overnight at room temperature. Water (50 ml) was added, the

organic layer was separated, washed with sodium carbonate (4 × 25 ml; 10%), with water, dried, and the solvent removed. The residual oil was first distilled, b.p. 32–62° at 1 mmHg, the distillate (2.43 g) was chromatographed on silica (190 g), and eluted, first with light petroleum, and then with light petroleum–ether (90 : 10). β -Pyronene (1.1 g) was first eluted, followed by 1,2,3,4-tetramethylbenzene (45 mg), identified by its i.r. spectrum,²⁵ and g.l.c. comparison with an authentic specimen, and the *dienol* (12) (0.93 g) identified by g.l.c. and i.r. and n.m.r. spectra.

The residue (2.99 g) from the distillation was chromatographed on silica (240 g) and eluted with light petroleum–ether (80 : 20) giving a product (1.56 g) which was subjected to short-path distillation at 1 mmHg (bath at 140°). The benzoate (15) (1.04 g) was obtained as a gum, identical in all respects with a specimen prepared as described above. Similar results were obtained when sodium benzoate was omitted from the reaction mixture.

Hydrolysis of the ester (0.31 g) in methanol (5 ml) with potassium hydroxide (2 ml; 10%) at room temperature afforded the *cis*-diol (7) (95 mg), m.p. and mixed m.p. 124–126°.

3,4-Epoxy-3,4,5,5-tetramethylcyclohexene (16).— β -Pyronene (1.8 g) was oxidised with perbenzoic acid [from benzoyl peroxide (3 g)] in ether (55 ml) overnight at 20°. Work-up afforded a mobile liquid (2.02 g), which contained (g.l.c. and n.m.r.) unchanged β -pyronene, the epoxide (16), the *dienol* (12), 1,2,3,4-tetramethylbenzene (13), and the *cis*-benzoate (15) in the approximate proportions, 8 : 12 : 3 : 1 : 2. Distillation and collection at 50–70° at 10 mmHg gave the crude epoxide (50% by g.l.c.) free from *dienol* (12), and ester (15). It was chromatographed on Merck's basic alumina and eluted first with light petroleum to remove β -pyronene and then with light petroleum containing 3% ether to give the *epoxide* (16) (0.5 g) as a camphoraceous oil, b.p. 68–70° at 12 mmHg, n_D^{22} 1.4596, λ 215 nm ($\log \epsilon$ 3.54) (Found: C, 78.5; H, 10.5. C₁₀H₁₆O requires C, 78.9; H, 10.6%).

Hydrolysis of the Epoxide (16).—(a) *With water.* The epoxide (0.1 g; 50% pure) was stirred with deionised water (0.56 g; pH 6.96, for 1 h at room temperature. The solid product was collected, washed with light petroleum, and dried, giving the *trans*-diol (8) (42 mg), m.p. 93–94°. Continuous extraction of the aqueous liquor with ethyl acetate afforded no *cis*-diol (7).

(b) *With dilute acid.* The reaction was repeated using dilute hydrochloric acid (pH 5.96, 3.56, 2.0, and 1.0) with similar results.

(c) *With water and solid carbon dioxide* (cf. ref. 1). Using epoxide (0.1 g; 50% pure), water (300 mg), and solid carbon dioxide (ca. 200 mg), *trans*-diol (8) (43 mg) was obtained.

Pyrolysis of the trans-Diol (8) and the *Dienol* (12). 2,2,6,6-Tetramethylcyclohex-3-enone (18).—An intimate mixture of the diol (8) (0.58 g) and pyridine-treated alumina¹⁵ (1.74 g) was heated slowly to 240° in a stream of nitrogen, and maintained at 240° for 1.5 h. The product, extracted with light petroleum, was a brown oil (0.43 g) which was chromatographed on silica (40 g). Elution with light petroleum gave 1,2,3,4-tetramethylbenzene²⁵ (13) (88 mg), and with light petroleum–ether (90 : 10), the *ketone* (18) (55 mg) which was subjected to short path distillation at 10 mmHg (bath temp. 140°). The product, pure by g.l.c., had n_D^{20} 1.4508, λ_{\max} 295 ($\log \epsilon$ 1.41) and 215 nm (2.3), ν_{\max} (L) 2960, 1705, 1470,

²⁴ G. Brown, *Org. Synth.*, 1941, 1, 431.

²³ L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. 1, p. 819.

²⁵ P. J. Launer and D. A. McCaulay, *Analyt. Chem.*, 1951, 23, 1875.

1046, 1001, and 718 cm^{-1} , τ 8.87 (12H, s, $2\text{Me}_2\text{C}$), 7.76 (2H, d, J 4 Hz, CH_2), and 4.1—4.4 (2H, m, $\text{HC}=\text{CH}$), m/e 152 (M^+ , 19%), 124 ($M^+ - \text{CO}$, 35), 109 ($M^+ - \text{CO} - \text{Me}$, 58) (Found: C, 78.5; H, 10.8. $\text{C}_{10}\text{H}_{16}\text{O}$ requires C, 78.9; H, 10.6%). Hydrogenation of the ketone (18) in ethyl acetate over 5% palladised charcoal yielded an oil having an i.r. spectrum identical with that reported¹⁶ for 2,2,6,6-tetramethylcyclohexanone (19).

The dienol (12) (0.39 g; 96% pure by g.l.c.), was similarly

pyrolysed; after 1 h at 240° pressure was reduced to 10 mmHg and the products of reaction were collected in a cold trap. The cyclohexenone (18) (80 mg) was obtained after chromatography.

We thank the National Science Council of the Republic of Ireland for the award of a Research Grant, and An Foras Taluntais for the growth tests.

[3/1045 Received, 18th May, 1973]
