

The Chemistry of Terpenes. Part XX.¹ Autoxidation of (+)-Car-3-ene

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Autoxidation of (+)-car-3-ene in the presence or in the absence of cobalt stearate affords the following compounds, their yields being dependent upon the method of decomposition of the initial hydroperoxides: (+)-3 α ,4 α -epoxycarane, (-)-8-methoxy-*m*-mentha-4,6-diene, (-)-car-4-en-3 α -ol, (-)-8-methoxy-*p*-mentha-1,5-diene, eucarvone, (-)-car-4-en-3 β -ol, (+)-*cis*-caran-5 β -ol, (+)-car-2-en-4-one, (-)-*m*-mentha-4,6-dien-8-ol, (+)-*p*-mentha-1,5-dien-8-ol, 3,6,6-trimethylcyclohepta-2,4-dienone, (+)-car-3-en-2-one, 8-hydroxy-*m*- and -*p*-cymenes, and (-)-car-3-en-5-one, in this order of elution from a Carbowax g.l.c. column. A reaction sequence is suggested. Reaction of (+)-car-3-ene with selenium dioxide in pyridine gives (+)-*p*-mentha-1,5-dien-8-ol as the major product.

IN 1931, Owen and Simonsen² isolated *m*-mentha-6,8-dien-5-one (2) from the autoxidation of (+)-car-3-ene (1) with cobalt resinate as catalyst. They also suspected the presence of *m*-mentha-4,6-dien-8-ol (3) in the product. However, they regarded car-3-en-5-ol (4) or the corresponding ketone (5) as the principal autoxidation product, but deemed these to be unstable, readily rearranging to

m-mentha-6,8-dien-5-ol (6) or the corresponding ketone (2) and *p*-mentha-1,8-dien-3-ol (7) or the corresponding ketone (8). Since the degree of stability of (-)-car-3-en-5-one (5) † has been established,³ we have reinvestigated the autoxidation both in the presence and in the absence of catalyst.

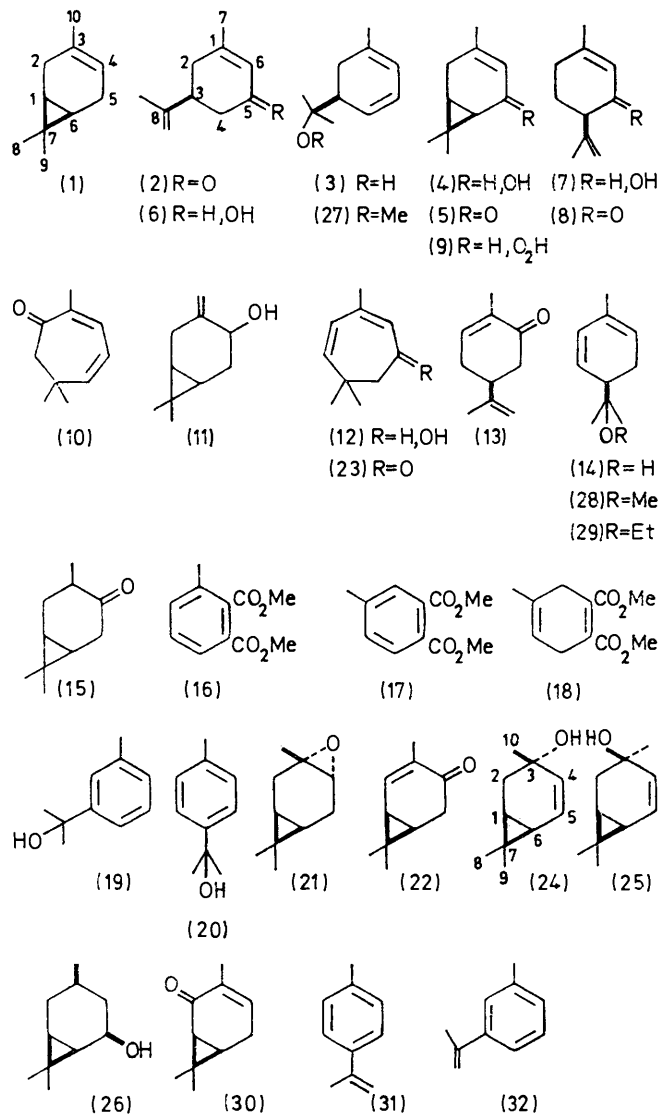
¹ Part XIX, W. Cocker and D. H. Grayson, *J.C.S. Perkin I*, 1975, 1217.

² J. Owen and J. L. Simonsen, *J. Chem. Soc.*, 1931, 3001.

³ W. D. P. Burns, M. S. Carson, W. Cocker, and P. V. R. Shannon, *J. Chem. Soc. (C)*, 1968, 3073.

† Absolute configurations are given for products we obtained from (+)-car-3-ene. Some reports do not specify the car-3-ene used in the experiments described.

Three groups of workers have, in recent years, studied the products of autoxidation of car-3-ene. Car-3-en-5-yl hydroperoxide (9) was isolated and converted into car-3-en-5-ol (4).⁴ In the presence of lead tetra-acetate and



manganese dioxide, autoxidation gave⁵ eucarvone (10), car-3(10)-en-4-ol (11), and 3,6,6-trimethylcyclohepta-2,4-dienol (12). In the latest series of studies⁶⁻⁸ light was used as an initiator; eleven hydrocarbons and eucarvone

(10), the dienol (12), carvone (13), *p*-mentha-1,5-dien-8-ol (14), and *cis*-caran-4-one (15) were identified.

Autoxidation in the Presence of Cobalt Stearate (Table 1).—In our hands, autoxidation of (+)-car-3-ene (1) in the presence of catalyst, followed by reduction, by five methods, of the mixture of hydroperoxides, gave products containing (g.l.c.) up to twenty components. Their number and abundance varied with the method of reductive work-up.

The most abundant product, whose retention time (t_R) relative to that of eucarvone was 1.73, was a 4 : 1 mixture of (–)-*m*-mentha-4,6-dien-8-ol (3) and (+)-*p*-mentha-1,5-dien-8-ol (14). Chromatography gave pure (3), characterised as its adduct with maleic anhydride,⁹ but (14) was always contaminated with (3). Reaction of the mixture of dienols (3) and (14) with dimethyl acetylenedicarboxylate¹⁰ gave dimethyl 3-methylphthalate (16), dimethyl 4-methylphthalate (17), and dimethyl 4-methyl-3,6-dihydrophthalate (18).¹¹ The dihydrophthalate (18), presumably resulting from the reaction of the acetylenic ester with isoprene formed thermally from 2-methylbut-3-en-2-ol (Scheme 1), absorbed in the u.v. at 215 nm and in the i.r. at 1 725, 1 650, 1 590, and 790 cm⁻¹. N.m.r. signals at τ 8.30 (3 H, s, MeC=C), 7.12 (4 H, s, CH₂), 6.30 (6 H, s, CO₂Me), and 4.60 τ (1 H, H-C=C) are in accord with its structure.

(+)-*p*-Mentha-1,5-dien-8-ol (14) was prepared for comparison purposes by reaction of (+)-car-3-ene (1) with selenium dioxide (see later).

The maleic anhydride adduct of the mixture of dienols (3) and (14) was readily resolved on silica giving products identical with those derived from pure specimens of the dienols.

The dienols (3) and (14) afforded, respectively, 8-hydroxy-*m*-cymene (19) and its *p*-isomer (20) in air.

Further chromatography on silica of the mixture of autoxidation products derived from (+)-car-3-ene gave (+)-3 α ,4 α -epoxycarane (21), eucarvone (10), (+)-car-2-en-4-one (22), 3,6,6-trimethylcyclohepta-2,4-dienone (23), 8-hydroxy-*m*-cymene (19), 8-hydroxy-*p*-cymene (20), and (–)-car-3-en-5-one (5). The properties of these compounds are well documented.^{3,12}

(–)-Car-4-en-3 α -ol (24),¹³ (–)-car-4-en-3 β -ol (25), and (+)-*cis*-caran-5 β -ol (26)¹⁴ were isolated from the autoxidation product by preparative g.l.c. The properties of the allylic alcohol (25)¹⁵ are not well described. Both alcohols (24) and (25) absorb in the i.r. near 3 400, 1 630, and 730 cm⁻¹. The n.m.r. spectrum of (24) has signals

⁴ B. V. Erofeev and A. I. Chirko, *Uchenye Zapiski Belorus. Gosudarst. Univ. im V. I. Lenina, Ser. Khim.*, 1956, **29**, 15. (*Chem. Abs.*, 1960, **54**, 6789e).

⁵ B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner, *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, 583 (*Chem. Abs.*, 1961, **55**, 6516i).

⁶ I. I. Bardyshev, V. S. Shavyrin, V. S. Pankova, and G. V. Kabatova, *Gidroliz. desokhim. Prom.*, 1968, **21**, 12 (*Chem. Abs.*, 1968, **69**, 59,392g).

⁷ V. S. Shavyrin, I. I. Bardyshev, and V. V. Budylna, *Sb. Tr., Tsentr. Nauch.-Issled. Proekt. Inst. desokhim. Prom.*, 1968, **19**, 11 (*Chem. Abs.*, 1969, **71**, 102,023t).

⁸ I. Bardyshev and V. S. Shavyrin, *Sb. Tr., Tsentr. Nauch.-Proekt. Inst. desokhim. Prom.*, 1969, **20**, 23 (*Chem. Abs.*, **5**, 20,639s).

⁹ K. Gollnick, G. Schade, and G. Schroeter, *Tetrahedron*, 1966, **22**, 139.

¹⁰ E. D. Parker and L. A. Goldblatt, *J. Amer. Chem. Soc.*, 1950, **72**, 2151.

¹¹ N. P. Sopov and V. S. Miklashevskaya, *Zhur. obshchei Khim.*, 1956, **26**, 1914 (*Chem. Abs.*, 1957, **51**, 4968a).

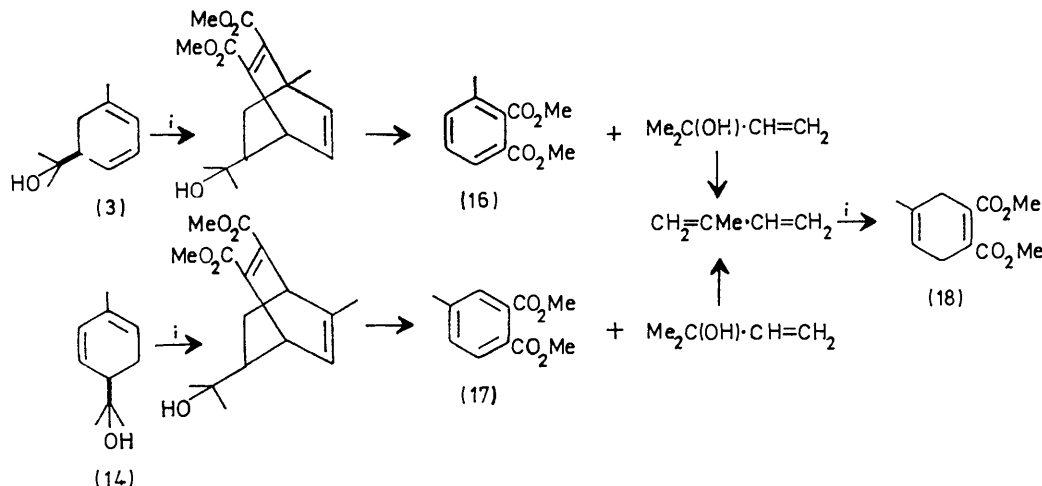
¹² W. Cocker, D. P. Hanna, and P. V. R. Shannon, *J. Chem. Soc. (C)*, 1968, 489.

¹³ K. Gollnick, S. Schroeter, G. Ohloff, G. Schade, and G. O. Schenck, *Annalen*, 1965, **687**, 14.

¹⁴ W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc. (C)*, 1967, 485.

¹⁵ H. Kuczynski and K. Marks, *Roczniki Chem.*, 1969, **43**, 943 (*Chem. Abs.*, 1969, **71**, 61,558a).

at τ 9.16 (3 H, s, 9-H₃), 8.9 (6 H, s, 8- and 10-H₃), and 4.31 (2 H, s, HC=CH); that of its 3-epimer (25) has signals at τ 9.05 (3 H, s, 9-H₃), 8.9 (3 H, s, 8-H₃), 8.75 (3 H, s, 10-H₃), 4.57 (1 H, d, J 10 Hz, 5-H), and 4.32 (1 H, d, J 10 Hz, 4-H). In each case the C-9 methyl group is shielded by the double bond, but in (25), the effect of the β -hydroxy-group is to shift the signal of this methyl group to lower field. In (24), the C-10 methyl group is shielded by the cyclopropane system. The unsaturated alcohols (24) and (25) gave (+)-caran-3 α - and -3 β -ol, respectively, on hydrogenation.



SCHEME 1 i , MeO₂C-C≡C-CO₂Me

In the work-up procedure in which borohydride in methanol was used [Table I, method (b)], and the excess of borohydride was destroyed with dilute acid, the major product was (-)-8-methoxy-*m*-mentha-4,6-diene (27) (*cf.* ref. 16). It absorbed in the u.v. at 264 nm ($\log \epsilon$ 3.6) and its n.m.r. spectrum had signals at τ 8.95 (6 H, s, Me₂C), 8.25br (3 H, s, MeC=C), 6.90 (3 H, s, MeO), and 4.4 (3 H, m, HC=C). It was rapidly aromatised in air.

The compound of t_R 0.86 was possibly 8-methoxy-*p*-mentha-1,5-diene (28) but its instability prevented identification. However when the work-up, by method (b), of the autoxidation product was carried out in ethanol, (+)-8-ethoxy-*p*-mentha-1,5-diene (29) was obtained, identical with a sample prepared by reaction of (+)-car-3-ene with selenium dioxide in ethanol.¹⁷

Work-up of the autoxidation product from (+)-car-3-ene with water [Table I, method (c)], with cold alkali [method (d)], or with hot alkali [method (e)], gave products which varied sequentially. Apart from the dienols (3) and (14), work-up with water gave (-)-car-3-en-5-one (5), (+)-car-2-en-4-one (22), and (+)-car-3-en-2-one (30). Alkali caused rearrangement of (5) and (30) to 3,6,6-trimethylcyclohepta-2,4-dienone (23) and eucarvone (10), respectively.³ The fate of (+)-car-2-en-4-one (22) has still to be examined.

Autoxidation of (+)-Car-3-ene (1) in the Absence of Catalyst (Table 2).—Autoxidation of (+)-car-3-ene

¹⁶ R. K. Murray and K. A. Babiak, *Tetrahedron Letters*, 1974, 311.

without catalyst led to increased yields of the major products, the dienols (3) and (14), but the ratio of these was changed from 4 : 1 to 5 : 4. They were eluted from a silica column as a single fraction and their yields were assessed by the amounts of the dimethyl phthalates, (16) and (17), readily separable on silica, which the mixture afforded.

Work-up of the mixture of hydroperoxides with potassium iodide in acetic acid [method (g)] gave fair yields of two compounds of t_R 0.55 and 0.58 which could not be adequately separated by preparative g.l.c. The more

polar compound was identified as *p*-isopropenyltoluene (31) and the other was probably its *m*-isomer (32). The mixture of these showed a u.v. maximum at 820 cm⁻¹ resulting from aromatic *p*-disubstitution and maxima at 890, 790, and 725 cm⁻¹ resulting from *m*-disubstitution.¹² Dehydration of the mixture of 8-hydroxy-*m*-(19) and -*p*-cymene (20), also obtained in the autoxidation, afforded the anhydro-compounds (32) and (31), respectively.

The hydroperoxides and the initial products derived from them are clearly of such instability that different modes of work-up lead to variations in yields of products. The mild work-up conditions using water alone give higher yields of the $\alpha\beta$ -unsaturated ketones (5), (22), and (30). In the case of the uncatalysed autoxidation, work-up with water also gave (+)-3 α ,4 α -epoxycarane (21) in fair yield.

Free-radical oxidation of allylic centres arising from the use of triplet oxygen is unlikely to give hydroperoxides with migration of the double bonds.¹⁸ Thus the initial autoxidation products of (+)-car-3-ene (1) are likely to be the hydroperoxides (33) and (34), and the epoxide (21). However, the other carane hydroperoxides (35) and (36) can be formed from (33) and (34) by

¹⁷ Z. G. Isaeva, B. A. Arbuzov, and V. V. Ratner, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, 475 (*Chem. Abs.*, 1965, 63, 633f).

¹⁸ D. Swern, 'Organic Peroxides,' Wiley, New York, 1971, vol. 2, p. 22.

allylic rearrangement.¹⁹ The subsequent decomposition products of the hydroperoxides are shown in Scheme 2.

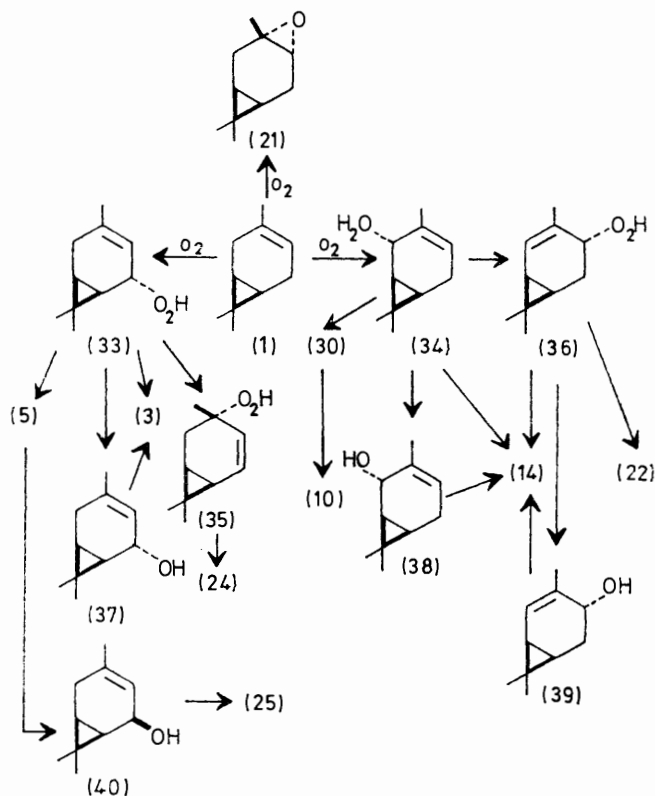
Reduction of the four hydroperoxides (33)—(36) will give the alcohols (37), (38), (24), and (39), respectively. Of these only (—)-car-4-en-3 α -ol (24) is reasonably stable. Of the others, the alcohol (37) will rapidly rearrange to the dienol (3) and the alcohols (38) and (39) will similarly afford the dienol (14); *cf.* the ready rearrangement of caran-2- and -5-ols with acid.¹²

The presence of (—)-car-4-en-3 β -ol (25) among the autoxidation products can be explained on the basis of the reduction of (—)-car-3-en-5-one (5) by borohydride to the alcohol (40) followed by allylic rearrangement.

(—)-Car-4-en-3 α -ol (24) and its epimer (25) are stable to neutral or alkaline work-up, but they readily form the dienol (3) in the presence of acid.⁹

The formation of the epoxide (21) is in competition with that of the hydroperoxy-compounds. Thus in the slower, uncatalysed autoxidation of (+)-car-3-ene, a higher yield of epoxide is formed than in the catalysed reaction.

Other secondary rearrangements which may occur involve the $\alpha\beta$ -unsaturated ketones (5), (22), and (30)



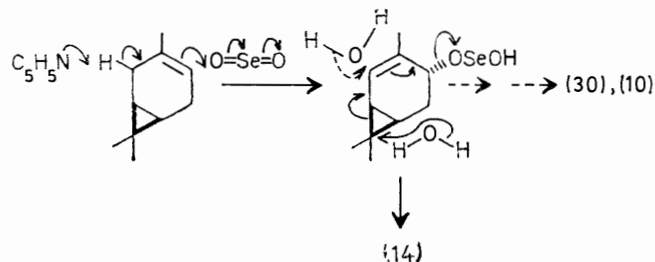
SCHEME 2

which will be reduced by borohydride to the corresponding alcohols, *e.g.* (37), (39), and (38), respectively, from which the dienols (3) and (14) will be formed. (+)-*cis*-

* For details of Supplementary Publications, see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

Caran-5 β -ol (26) is probably formed by reduction by borohydride of (—)-car-3-en-5-one (5).

Oxidation of (+)-car-3-ene (1) with selenium dioxide in pyridine gave a good yield of (+)-*p*-mentha-1,5-dien-8-ol (14), and smaller yields of (—)-car-3-en-5-one (5) (trace), eucarvone (10), 8-hydroxy-*p*-cymene (20), (+)-car-3-en-2-one (30), and *p*-isopropenyltoluene (31) (Table 3). We isolated no *m*-menthane derivatives; a similar specificity was found by earlier workers,¹⁷ who, by using ethanol as solvent, obtained a complex mixture of products. The formation of (+)-*p*-mentha-1,5-dien-8-ol



SCHEME 3

(14), and that of eucarvone (10) and its precursor (+)-car-3-en-2-one (30), can be expressed as proceeding through the common intermediate shown in Scheme 3. The presence of only a trace of product derived *via* oxidation of (+)-car-3-ene (1) at C-5 (a much less hindered position than C-2) argues against initial allylic oxidation by selenium dioxide at the latter position.

EXPERIMENTAL

I.r. spectra were measured either for liquid films (L) or for Nujol mulls (M), u.v. spectra for solutions in ethanol, n.m.r. spectra at 60 MHz for solutions in CCl₄, and mass spectra with a Hitachi-Perkin-Elmer RMS4 instrument. Optical rotations were measured for solutions in CHCl₃. Analytical g.l.c. was carried out on a 2 m × 3 mm 20% Carbowax 20M on Chromosorb W column at 150 °C and preparative g.l.c. on a 2 m × 8 mm 20% Carbowax 20 M column at 150 °C. Cobalt(II) stearate was prepared as described.²⁰ Additional i.r. and mass spectral data, for compounds marked with an obelus (†), are available in Supplementary Publication No. SUP 21513 (11 pp., 1 microfiche).*

Autoxidation of (+)-Car-3-ene (1); General Procedures.—(A) *With catalyst.* Oxygen was bubbled through a fine sintered glass disc, at 40 ml min⁻¹, into a rapidly stirred solution of cobalt(II) stearate (2 g) in (+)-car-3-ene {50 g; $[\alpha]_D^{20} + 14.7^\circ$ (*c* 0.2)} at 15 °C, kept under slight pressure by a mercury bubbler. After 7.5 h the product (peroxide number *ca.* 400) was worked up by one of the methods described below.

(B) *Without catalyst.* The method was as in (A), but the oxygen flow rate was 100 ml min⁻¹, temperature 50–60 °C, and reaction time 6 h. The peroxide number was then 5 500.

Work-up techniques. The same quantity of autoxidation product (50 g) was used in each case. (a) Sodium borohydride (10 g) was added over 1 h to a rapidly stirred solution of hydroperoxides in methanol (500 ml) kept at 0 °C. After

¹⁹ Ref. 18, p. 14.²⁰ R. Lombard and L. Rommert, *Bull. Soc. chim. France*, 1956, 36.

a further 2 h, water (500 ml) was added and the product was collected in ether (3 × 200 ml). (b) As in method (a) except that the excess of borohydride was destroyed with hydrochloric acid (2*N*; 250 ml). Water (250 ml) was added, the product was extracted with ether (3 × 200 ml) and the extract was washed with sodium hydrogen carbonate (5%; 2 × 100 ml) and water (2 × 100 ml). (c) Water (500 ml) was used; the mixture was rapidly stirred for 4 h, and extracted with ether (3 × 250 ml). (d) Sodium hydroxide

TABLE 1

Autoxidation of (+)-car-3-ene in the presence of catalyst

t_R (g.l.c.)	Product	Conditions of work-up and % yield †				
		(a)	(b)	(c)	(d)	(e)
0.64	(21)	1.7	T	3.0	2.4	3.8
0.72	(27)	1.1	44.5			
0.76		T		1.5	1.8	1.0
0.82	(24)	10.5	T	0.5	T	T
0.86	(28) *	T	11.1			
1.0	(10)	T	T	T	1.2	11.5
1.17	(25)	5.1	3.2	T	T	0.7
1.22		1.1				
1.39		T		0.5		
1.47	(26)	10.0				
1.58	(22)	6.3	3.0	16.0	12.8	2.8
1.73	(3), (14)	31.8	27.0	21.0	19.4	21.0
1.90	(23)	3.8			11.4	48.0
2.10		1.7				
2.15	(30)	10.1	6.4	14.0	15.6	3.5
2.35		T		2.0	2.4	T
2.54		2.0				
2.85	(19), (20)	3.6	4.8	2.0	3.9	2.8
3.34		T		T	T	
4.0	(5)	11.2		39.5	29.1	4.9

* Tentative assignment. † T = Trace.

TABLE 2

Autoxidation of (+)-car-3-ene in the absence of catalyst

t_R (g.l.c.)	Product	Conditions of work-up and % yield †				
		(a)	(b)	(c)	(f)	(g)
0.55	(32)				4.3	10.0
0.58	(31)					
0.64	(21)	5.5		17.0	22.2	13.0
0.72	(27)	7.6	49.5			
0.76				2.7		T
0.82	(24)	1.3		9.5	1.1	
0.86	(28) *	9.1	15.0		0.6	3.7
0.94						T
1.0	(10)					T
1.13					1.1	
1.17	(25)	1.0		1.4		T
1.39						0.6
1.47	(26)	0.5				
1.58	(22)	2.0		10.9	3.2	8.1
1.73	(3), (14)	68.0	35.5	12.3	26.7	15.2
2.01				5.4	0.6	2.2
2.15	(30)	2.5		10.9	8.5	6.2
2.35						T
2.54						0.6
2.84	(19), (20)	2.5		2.7	16.1	26.1
3.34						1.6
3.78						T
4.0	(5)			27.2	13.9	12.7

* † See Table 1.

solution (10%; 500 ml) was used; the mixture was stirred for 4 h and extracted with ether (3 × 250 ml), and the extract washed successively with hydrochloric acid (2*N*; 250 ml), sodium hydrogen carbonate (5%; 250 ml), and water (250 ml). (e) As in (c) except that the alkaline mixture was refluxed for 4 h. (f) The peroxide mixture was slowly added to a stirred solution of sodium disulphite (40 g), in water (300 ml), kept at 0 °C. Stirring was continued for 1 h

longer and the mixture was worked up as in (c). (g) As in (f), the reducing agent being a stirred solution of potassium iodide (20 g), water (200 ml), and acetic acid (20 ml), kept at 0 °C. After 1 h, the mixture was extracted with ether (3 × 250 ml), and the extract was washed with sodium hydrogen carbonate (5%; 4 × 250 ml) and water (2 × 250 ml).

Specific Examples.—(A) *Autoxidation in the presence of catalyst.* Work-up by method (a) gave an oil (48 g) which on distillation at 0.7 mmHg gave (+)-car-3-ene (22 g), b.p. 30°, other volatile products (16.6 g), b.p. 60–110°, and a residue (7.8 g) which was not investigated.

(B) *Without catalyst.* The product from method (a) when distilled at 0.2 mmHg, gave (+)-car-3-ene (20.5 g), b.p. 21–25°, other volatile products (21.1 g), b.p. 35–70°, and a residue (9 g).

Isolation of products. The fraction of b.p. 60–110° at 0.7 mmHg from (A) was redistilled at 0.8 mmHg giving fraction (i) (6.7 g), b.p. 65–78°, and fraction (ii) (3.5 g), b.p. 78–110°. Fraction (ii) (2.8 g) was chromatographed on silica (100 g) and eluted with increasing amounts of ether in light petroleum giving (+)-3 α ,4 α -epoxycarane (21) (0.1 g; 6% ether), $[\alpha]_D^{20} + 12.1^\circ$ (lit.,³ +12.5°); (+)-car-2-en-4-one (22) (0.3 g; 15% ether), $[\alpha]_D^{20} + 360^\circ$ (*c* 3.6) (lit.,³ +428); (+)-car-3-en-2-one (30) (0.2 g; 20% ether), $[\alpha]_D^{20} + 251^\circ$ (*c* 2.5) (lit.,³ +243°); eucarvone (10) (0.01 g; 20% ether); 3,6,6-trimethylcyclohepta-2,4-dienone (23) (0.15 g; 20% ether); (–)-*m*-mentha-4,6-dien-8-ol (3) and (+)-*p*-mentha-1,5-dien-8-ol (14) isolated as a mixture (0.6 g, 25% ether) (see below); and (–)-car-3-en-5-one (5) (1.1 g, 30% ether), $[\alpha]_D^{20} - 244^\circ$ (*c* 20) (lit.,³ –271°). The $\alpha\beta$ -unsaturated ketones and dienones were identical (g.l.c., i.r., and n.m.r.) with authentic specimens.³

*8-Hydroxy-*m*- and -*p*-cymenes.* Chromatography of fraction (i) (3 g) on silica (100 g) gave the range of compounds described above and a mixture of 8-hydroxy-*m*-cymene (19) and 8-hydroxy-*p*-cymene (20) (0.2 g; 20% ether). Rechromatography of this mixture on silica (10 g) gave first a fraction rich in the *p*-isomer (20)¹⁷ (for n.m.r. data see Supplementary Publication) and finally a fraction rich in the *m*-isomer (19).³ Each was identical (g.l.c. and i.r.) with an authentic specimen.

(–)-*m*-Mentha-4,6-dien-8-ol (3). The mixture (0.6 g) of this compound and *p*-mentha-1,5-dien-8-ol (14), obtained as described above, rechromatographed on silica (40 g), gave (–)-*m*-mentha-4,6-dien-8-ol (3), † $[\alpha]_D^{20} - 158^\circ$ (*c* 2.5) (lit.,⁹ –165.4°), λ_{max} 264 nm (log ϵ 3.7), ν_{max} (L) 3360 and 1650 cm^{-1} , τ 8.87 (6 H, s, Me₂C), 8.23 (3 H, s, MeC=C), and 4.1–4.7 (3 H, m, olefinic H). Its maleic anhydride adduct † (0.3 g) obtained by refluxing the dienol (0.25 g) with maleic anhydride (0.2 g) in benzene (10 ml), had m.p. 118–119° (from acetone–benzene) (lit.,⁹ 118°), $[\alpha]_D^{20} - 47^\circ$ (lit.,⁹ –50°), ν_{max} (N) 1845 and 1775 cm^{-1} (anhydride) (Found: C, 67.3; H, 7.4. Calc. for C₁₄H₁₈O₄: C, 67.2; H, 7.25%).

Reaction of the mixture of dienols (3) and (14) with dimethyl acetylenedicarboxylate. The dienols (1.4 g) and the ester (2.2 g) were refluxed for 2.5 h. The product (2 g) was chromatographed on silica (50 g) and eluted with increasing amounts of ether in light petroleum. Dimethyl 4-methyl-3,6-dihydrophthalate (18) † (0.3 g) was eluted first (15% ether), *m/e* 210 (*M*⁺) (Found: C, 62.8; H, 6.6. Calc. for C₁₁H₁₄O₄: C, 62.85; H, 6.7%). Elution with 30% ether gave dimethyl 3-methylphthalate (16) † (0.8 g), ν_{max} (L) 1730 and 1590 cm^{-1} , τ 7.69 (3 H, s, ArMe), 6.18 (6 H, s, MeO), 2.6–2.8 (2 H, m, ArH), and 2.2–2.42 (1 H, m, ArH), *m/e* 208 (*M*⁺) (Found: C, 63.1; H, 5.8. Calc. for C₁₁H₁₂O₄:

C, 63.45; H, 5.8%). Elution with 40% ether gave dimethyl 4-methylphthalate (17) † (0.5 g), ν_{\max} (L) 1 725 and 1 600 cm^{-1} , τ 7.65 (3 H, s, ArMe), 6.21 (6 H, s, MeO), and 2.4—2.95 (3 H, m, ArH), m/e 208 (M^+) (Found: C, 63.2; H, 5.6. Calc. for $\text{C}_{11}\text{H}_{12}\text{O}_4$: C, 63.45; H, 5.8%).

(-)-*Car-4-en-3 α -ol* (24). This compound † (t_R 0.82) was isolated by preparative g.l.c. as a liquid, ν_{\max} 3 380 and 1 630 cm^{-1} .

Reduction of compound (24) to (+)-caran-3 α -ol. The unsaturated alcohol (15 mg) in ethyl acetate (2 ml) was hydrogenated over palladised charcoal (5%; 30 mg) during 1 h, giving (+)-*caran-3 α -ol* (10 mg)²¹ as the only product (g.l.c.).

(-)-*Car-4-en-3 β -ol* (25). The 3 β -ol † (t_R 1.17) was isolated by preparative g.l.c. as a liquid, ν_{\max} (L) 3 350 and 1 630 cm^{-1} .

Reduction of compound (25) to (+)-caran-cis-3 β -ol. This was performed as for (24) giving the saturated alcohol²¹ as the only product.

(+)-*cis-Caran-5 β -ol* (26). The 5 β -ol (t_R 1.47)¹⁴ was isolated by preparative g.l.c.

(-)-*8-Methoxy-m-mentha-4,6-diene* (27). Compound (27) † (t_R 0.72), isolated by preparative g.l.c. had $[\alpha]_D^{20} -14^\circ$, ν_{\max} (L) 2 810 and 1 640 cm^{-1} , m/e 166 (M^+) (Found: C, 79.95; H, 10.9. Calc. for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.5; H, 10.9%).

(+)-*8-Ethoxy-p-mentha-1,5-diene* (29). *Car-3-ene* (50 g) was autoxidised in the presence of catalyst and worked up by method (b), with ethanol instead of methanol. Three main products were observed on g.l.c., the main fraction being the mixed dienols (3) and (14). Preparative g.l.c. of the least abundant fraction gave (+)-*8-ethoxy-p-mentha-1,5-diene* (29) †,¹⁷ b.p. 40° at 0.25 mmHg, λ_{\max} 264 nm ($\log \epsilon$ 3.45), ν_{\max} 1 650, 1 600, 745, and 730 cm^{-1} , τ 8.93 (6 H, s, Me_2C), 8.93 (3 H, t, J 7 Hz, $\text{CH}_3\text{-CH}_2\text{O}$), 8.34 (3 H, s, MeC=C), 7.30—8.20 (3 H, m, CH_2 and CH), 6.7 (2 H, q, J 7 Hz, CH_2O), 4.67br (1 H, s, HC=C), and 4.32 (2 H, s, HC=CH), m/e 180 (M^+) (Found: C, 79.7; H, 11.0. Calc. for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 79.9; H, 11.2%), identical (g.l.c., i.r., and n.m.r.) with a specimen prepared by the reaction of (+)-*car-3-ene* with selenium dioxide in ethanol.¹⁷

m- (32) and *p-* (31) *Isopropenyltoluene*. These were isolated by preparative g.l.c. as a 7 : 5 mixture from the uncatalysed autoxidation reaction [work-up by method (c)]. The mixture showed ν_{\max} (L) 2 860, 1 620, 1 595, 1 570, 1 510, 1 490, 1 440, 1 300, 1 230, 1 110, 890, 820, 790, and 725 cm^{-1} .

²¹ P. J. Kropp, *J. Amer. Chem. Soc.*, 1966, **88**, 4926; W. Cocker, D. P. Hanna, and P. V. R. Shannon, *J. Chem. Soc. (C)*, 1969, 1302.

A similar mixture of hydrocarbons was obtained by stirring a mixture (1 g) of 8-hydroxy-*m*-cymene (19) and its *p*-isomer (20), acetone (25 ml), and water (25 ml) for 20 min with sulphuric acid (10 ml) at 15 °C.

Reaction of (+)-Car-3-ene (1) with Selenium Dioxide.—Powdered selenium dioxide (80 g) was added over 0.5 h to a stirred solution of (+)-*car-3-ene* (100 g) in dry pyridine (250 ml) at 70 °C. The mixture was refluxed for 3 h and distilled in steam, and the distillate (2 l) was extracted with ether (3 × 500 ml). The extract, washed with hydrochloric acid (10%; 2 × 500 ml), sodium hydrogen carbonate (5%; 2 × 500 ml), and water (500 ml), dried, and distilled at 0.2 mmHg, gave (+)-*car-3-ene* (32.5 g), b.p. 25—35°, oxidation products (39.5 g), b.p. 35—85°, and a residue (9 g) which was not further investigated. The second fraction contained (g.l.c.) the components shown in Table 3. The oxidation pro-

TABLE 3

Oxidation of (+)-*car-3-ene* with selenium dioxide in pyridine

t_R (g.l.c.)	Product and % yield †	
0.58	(31)	11.4
1.00	(10)	5.0
1.05		1.0
1.40		2.4
1.73	(14)	55.4
2.14	(30)	12.3
2.48		1.8
2.90	(20)	10.7
4.0	(5)	T

† T = trace.

ducts were absorbed on silica, eluted with ether-light petroleum mixtures, and compared (g.l.c., i.r., and n.m.r.) with authentic specimens.

(+)-*p*-*Mentha-1,5-dien-8-ol* (14) † had $[\alpha]_D^{20} +183.5^\circ$ (c 3.1), λ_{\max} 264 nm ($\log \epsilon$ 3.4), ν_{\max} (L) 3 350, 1 645, 795, and 715 cm^{-1} , τ 8.85 (6 H, s, Me_2C), 8.3br (3 H, s, MeC=C), 7.82 (2 H, m, CH_2), 7.45 (1 H, m, CH), 4.6br (1 H, s, HC=C), and 4.22 (2 H, s, HC=CH), m/e 152 (M^+). The *maleic anhydride adduct* † of the dienol (14) consisted of needles (from ether), m.p. 98°, $[\alpha]_D^{20} +4^\circ$, ν_{\max} (N) 3 540, 1 835, and 1 775 cm^{-1} (Found: C, 67.4; H, 7.0. $\text{C}_{14}\text{H}_{18}\text{O}_4$ requires C, 67.2; H, 7.25%).

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