1006. *Some Addition Reactions of β-Pinene Derivatives.*

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Reaction of hydrogen bromide with *trans*- and *cis*-pinocarveol (Ia and c) gives rearranged products of the fenchane and bornane types, respectively. In contrast, pinocarvone (Ie), on reaction with either hydrogen bromide or bromine, gives products in which the pinane skeleton remains intact.

It has been reported recently [1] that *trans*-pinocarveol (Ia) underwent reaction with hydrogen bromide with retention of the pinane skeleton to give a bromo-alcohol (IIa) which, on oxidation, gave a bromo-ketone (IIb). As we required compounds with structures (IIa and b) in the course of other investigations we repeated the earlier work.

As an initial step we investigated an alternative to reaction with selenium dioxide [2] for the conversion of β-pinene into *trans*-pinocarveol. Reaction of β-pinene with lead tetra-acetate in benzene kept neutral with calcium carbonate gave largely *trans*-pinocarvyl acetate (Ib) instead of myrtenyl acetate (IIIb) which is formed [3] as a major product when acetic acid is present. This is analogous [4] to the reaction of α-pinene with lead tetra-acetate, which yields first 2-acetoxy-*cis*-pin-3-ene (IV) which is converted in the presence of acetic acid into *trans*-verbenyl acetate (IIIa).

Addition of hydrogen bromide to *trans*-pinocarveol (Ia) gave a bromo-alcohol which could be oxidised under mild conditions to a bromo-ketone, both compounds having similar melting points to those reported by Treibs *et al.*[1] However, the evidence given below [5] is not consistent with the pinane-type structures (IIa and b), which had been assigned to the alcohol and ketone, respectively, but supports structure based on a fenchane skeleton (Va and f).

The infrared spectrum of the bromo-ketone, which exhibits a band at 1745 cm.$^{-1}$, is consistent with either a fenchane (Vf) or a camphane (VIe), but not with a pinane, structure (IIb). Furthermore, the nuclear magnetic resonance (n.m.r.) spectra of the bromo-alcohol and the bromo-ketone exhibit a singlet (230 c./sec.), which was assigned to a proton deshielded by a bromine atom. This is consistent only with the fenchane structures (Va and f). The absence of a band characteristic of a partial structure [6] $>$C(Me)Br excludes the pinane-type structures (IIa and b) proposed by Treibs *et al.*[1]

Chemical evidence also supports the assignment of a fenchane skeleton. Mild dehydrobromination of the bromo-alcohol (Va) with silver acetate–acetic acid gave the aldehyde [7] (VII) in good yield, rather than aldehyde (VIII) reported by Treibs *et al.*[1] Reductive debromination of the bromo-ketone (Vf) with zinc–acetic acid gave a product identified as (+)-isofenchone by physical constants and conversion into the corresponding oxime.

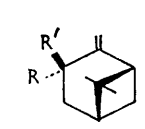
Reductive debromination of the bromo-alcohol (Va) gave *exo*-isofenchol (Vc) in addition to the aldehyde (VII). Reduction of the bromo-ketone (Vf) with sodium borohydride in methanol gave a new bromo-alcohol (Vd) which, on reductive debromination, gave *endo*-isofenchol (Ve) again accompanied by some aldehyde (VII).

Whilst the bromine atom in compounds (Va and f) could on mechanistic grounds be assigned the *endo*-configuration, no formal proof has been given above for such an assignment. However, an *X*-ray crystal-structure analysis recently carried out by Williams [8] has shown the bromine atom to have the *endo*-configuration.

[1] Treibs, Mühlstädt, Megges, and Klotz-Herdmann, *Annalen*, 1960, **634**, 118.
[2] Joshel and Palkin, *J. Amer. Chem. Soc.*, 1942, **64**, 1008.
[3] Matsubara, *J. Chem. Soc. Japan*, 1954, **75**, 894.
[4] Whitham, *J.*, 1961, 2232.
[5] Hartshorn and Wallis, *Chem. and Ind.*, 1963, 1878.
[6] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, London, 1959.
[7] King and Farber, *J. Org. Chem.*, 1961, **26**, 326.
[8] Williams, *Chem. and Ind.*, 1964, 1583.

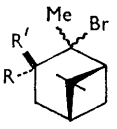
In view of the specificity of the reaction of *trans*-pinocarveol (Ia) with hydrogen bromide leading to the bromo-alcohol (Va), it was decided to extend the study to reactions of *cis*-pinocarveol (Ic) and pinocarvone (Ie).

Addition of hydrogen bromide to *cis*-pinocarveol (Ic) gave a mixture, the infrared spectrum of which exhibited a band in the carbonyl region. Chromatography on silica gel allowed the separation of a mixture of pinocamphone (IXa) and isopinocamphone (IXb) from a bromo-alcohol, shown below to be 6-*endo*-bromoisoborneol (VIb). The mixture of compounds (IXa and b) was shown to have arisen from an acid-catalysed isomerisation of *cis*-pinocarveol (Vc). Treatment of the alcohol (Vc) with toluene-*p*-sulphonic acid in ether partly converted the alcohol into the mixed ketones. In order to avoid this side-reaction, *cis*-pinocarvyl acetate (Id) was reacted with hydrogen bromide to give the bromo-acetate (VIc), which could be hydrolysed under mild alkaline conditions to the bromo-alcohol (VIb). Mild dehydrobromination of this alcohol, using silver acetate in acetic acid, gave the known



(I)

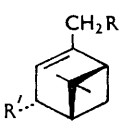
	R	R′
a:	OH	H
b:	OAc	H
c:	H	OH
d:	H	OAc
e:	RR′ = O	



(II)

a: R = OH, R′ = H.

b: RR′ = O

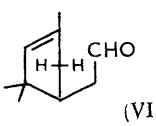


(III)

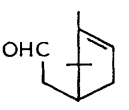
a: R = H, R′ = OAc

b: R = OAc, R′ = H

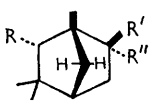
(IV)



(VII)

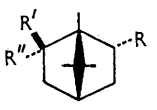


(VIII)



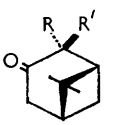
(V)

	R	R′	R″
a:	Br	OH	H
b:	Br	OAc	H
c:	H	OH	H
d:	Br	H	OH
e:	H	H	OH
f:	Br	R′R″ = O	
g:	H	R′R″ = O	



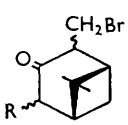
(VI)

	R	R′	R″
a:	Br	H	OH
b:	Br	OH	H
c:	Br	OAc	H
d:	H	OH	H
e:	Br	R′R″ = O	
f:	H	R′R″ = O	



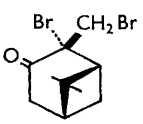
(IX) a: R = Me; R′ = H

b: R = H; R′ = Me

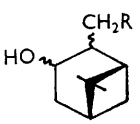


(X) a: R = H;

b: R = Br.



(XI)



(XII) a: R = Br;

b: R = H.

aldehyde (VIII). Reductive debromination of the bromo-alcohol (VIb) gave isoborneol (VId). The bromo-alcohol (VIb) on oxidation gave a bromo-ketone (VIe), the infrared spectrum of which was consistent with the structure assigned. The n.m.r. spectrum of the bromo-ketone exhibited a quartet (248, 251, 257, and 260 c./sec.) characteristic [9] of a bornane derivative with the *exo*-CHBr proton split only by the vicinal methylene group. Reductive debromination of the bromo-ketone (VIe) gave a product which was shown to be camphor (VIf) by comparison of physical constants and derivatives.

In contrast to the reactions of hydrogen bromide with *trans*- and *cis*-pinocarveol (Ia and c), which gave stable products, the corresponding reaction with pinocarvone (Ie) gave an unstable addition product (Xa), which tended to eliminate hydrogen bromide spontaneously. Treatment of this crude product with pyridine at 30° for 15 minutes gave a good

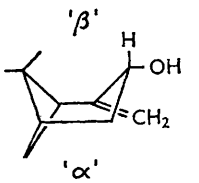
[9] Musher, *Mol. Phys.*, 1963, **6**, 93.

yield of pinocarvone. At this point it was decided to examine the reaction of bromine with pinocarvone (Ie). The product from this addition reaction proved to have the 2,10-dibromo-ketone structure [10] (XI). The n.m.r. spectrum indicated the presence of the C·CH_2Br group (223, 235, 249, and 261 c./sec.) and the absence of any further protons of the CHBr type. The infrared spectrum of the dibromo-ketone (XI), which exhibited a band at 1724 cm.$^{-1}$,[11] was consistent also with the presence of a six-membered-ring ketone in the molecule. When treated with hydrogen bromide in acetic acid the 2,10-dibromo-ketone (XI) was converted into an isomeric dibromo-ketone to which the 4,10-dibromo-structure (X) was assigned. The n.m.r. spectrum now revealed the structural feature CH·CH_2Br (193, 202, 212; 227, 231; 236 and 239 c./sec.) and a further proton deshielded by a CHBr bromine atom (286 c./sec.). The infrared spectrum of the ketone (Xb), which exhibited a band at 1728 cm.$^{-1}$,[11] was again more consistent with a six-membered- than with a five-membered-ring ketone.

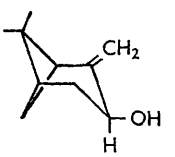
The stability of the 2,10-dibromo-ketone (XI) prompted us to re-examine the addition product of pinocarvone and hydrogen bromide. Addition of one mole of bromine to the crude reaction product of hydrogen bromide and pinocarvone, gave a mixture which, when seeded with the pure 2,10-dibromo-compound (XI), afforded a sample of the dibromo-ketone (XI). In addition, it was shown by infrared spectroscopy that the remaining oil consisted largely of a mixture of the 2,10- and 4,10-dibromo-compounds (XI) and (Xb) which could not be separated by chromatography.

The product of the reaction of hydrogen bromide with pinocarvone thus gives 10-bromo-ketones (Xa) with the pinane skeleton. This assignment was supported by the n.m.r. spectrum of the ketones (Xa) which indicated the presence of the >CH·CH_2Br feature (187, 197, 207; 224, 227; 234 and 237 c./sec.). Reduction of the bromo-ketone mixture (Xa), epimeric at C-2, with sodium borohydride gave a mixture of bromo-alcohols (XIIa). This was immediately reductively debrominated with zinc–acetic acid to a mixture of pinocampheols (XIIb) contaminated with 13% of the corresponding acetates. Chromic acid oxidation of the alcohols (XIIb) gave a mixture (6 : 1) of pinocamphone (IXa) and isopinocamphone (IXb). This evidence supports the assignment of a pinane skeleton to the ketones (Xa).

It is pertinent at this point to examine the stereochemistry of the addition reactions which have been described above. It has been shown that addition of hydrogen bromide to *trans*-pinocarveol (Ia) or its acetate (Ib) gave only the corresponding bromo-alcohol (Va) or the acetate (Vb). Similarly, addition of hydrogen bromide to *cis*-pinocarvyl acetate (Ia) gave only the bromo-acetate (VIc). It seems probable that, in the case of *trans*-pinocarveol, the preferred conformation tends towards (XIII), to which Markownikoff addition of a



(XIII)



(XIV)

proton, presumably solvated, from the β-face, may be followed by transoid attack by C-7 on C-2 and bromide ion on C-1 to give the observed product. With *cis*-pinocarveol, where the preferred conformation tends towards (XIV), the proton approaches C-10 from the α-face, followed by transoid attack by C-6 on C-2 and bromide ion on C-1 to give a camphane skeleton.

The corresponding addition of hydrogen bromide to pinocarvone probably occurs by a Michael addition to the conjugated system to give immediately an equilibrated mixture of

[10] Schmidt, *Ber. Schimmel and Co.*, 1941, 56.
[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

the ketones (Xa), analogous to the proved addition [12] of hydrogen bromide to cholest-5-en-4-one to give 6α-bromocholestan-4-one. An alternative mode of formation of the ketones (Xa), involving *anti*-Markownikoff addition of hydrogen bromide, cannot, however, be excluded on the information given above.

The addition of bromine to pinocarvone to give a compound with a pinane skeleton is of greater interest, since Michael addition may now not be involved. This reaction is visualised as proceeding by attack of Br^+, or some equivalent, on the α-face of the ethylenic linkage. The subsequent attack by bromide ion to give the dibromide may be governed by two contributing factors. The first is that attack on the β-face at C-2 is hindered to a greater extent than that at C-10 by the bulky methyl groups at C-6. The second is that the $-I$ effect of the C-3 carbonyl group will tend to stabilise the partly formed C(2)–Br bond in the bromonium complex, leading to bromide ion attack at C-10. This argument allows the 2,10-dibromo-ketone to be assigned the 2,10-dibromo-*cis*-pinan-3-one structure (XI). The formation of this compound on bromination of the 10-bromo-ketones (Xa) may be rationalised on the basis of α-face attack at C-2 on the $\Delta^{2(3)}$-enol. The configuration of the 4,10-dibromo-ketone (Xb) cannot be deduced from the above data but further work directed at the determination of its detailed structure is in progress.

Experimental

Rotations were measured for benzene solutions at room temperature. Unless otherwise specified, infrared and ultraviolet spectra were recorded for carbon disulphide and methanol solutions, respectively. Silica gel used was Crosfield Sorbsil Grade 60—120. Identity by gas–liquid chromatography (g.l.c.) was established by identical retention times for the sample and an authentic compound using columns of 10% Apiezon M and poly(ethylene glycol adipate) on Celite in a Pye Argon gas chromatograph. N.m.r. spectra were measured at 60 Mc. in $CDCl_3$, using tetramethylsilane as internal standard. Light petroleum had b. p. 50—70°.

trans-*Pinocarveol* (Ia).—Lead tetra-acetate (71 g.) as added during 10 min. to a stirred suspension of calcium carbonate (5 g.) in dry benzene (400 c.c.) containing β-pinene (45 g.; $[\alpha]_D$ −20°) and the mixture stirred at 60° for a further 20 min. The solid was removed by filtration, and the filtrate washed with aqueous sodium hydrogen carbonate solution and water, and dried. Distillation under reduced pressure afforded (i) benzene, (ii) an alkene mixture (10·2 g.), b. p. 55—65°/20 mm., and (iii) a monoacetate fraction (33·2 g.), b. p. 120—125°/20 mm. The monoacetate fraction was shown by g.l.c. to consist mainly of *trans*-pinocarvyl acetate (*ca.* 75%) and myrtenyl acetate (*ca.* 15%). Treatment of this fraction in methanol (50 c.c. with aqueous potassium hydroxide (5 g. in 3 c.c. H_2O) at 20° for 12 hr., followed by isolation with ether and fractionation by an 18 in. spinning-band column at 2 mm., gave *trans*-pinocarveol (15·9 g.), b. p. 59—60°/2 mm., n_D^{20} 1·4992 (lit.,[13] n_D^{20} 1·5005), $[\alpha]_D$ +60° (*c*, 0·93), $\nu_{max.}$ (liquid film) 3356 (OH), 3030, 1639, and 895 cm.$^{-1}$ (C:CH_2), *p*-nitrobenzoate, m. p. 95·0—95·5°, $[\alpha]_D$ +42° (*c*, 0·94) (lit.,[13] m. p. 91—92°, $[\alpha]_D$ +40°).

A further pure fraction obtained was identified as myrtenol (2·2 g.), b. p. 65—66°/2 mm., n_D^{19} 1·4975 (lit.,[14] n_D^{20} 1·4968), $[\alpha]_D$ −38° (*c*, 0·95), $\nu_{max.}$ (liquid film) 3280 (OH), 1642 and 803 cm.$^{-1}$ (R_2C:CHR), *p*-nitrobenzoate, m. p. 96—97°, $[\alpha]_D$ +5° (*c*, 1·03).

Pinocarvone (Ie).—Selenium dioxide (144 g.) was added during 15 min. to a stirred solution of β-pinene (180 g.; $[\alpha]_D$ −20°) in carbon tetrachloride (270 c.c.) and the mixture stirred and heated under reflux for 10 hr. The supernatant liquid was decanted and the residue washed with ether (2 × 100 c.c.). The combined carbon tetrachloride and ether solutions were reduced to *ca.* 200 c.c. by distillation and the residue steam-distilled. The distillate was extracted with ether, dried, and the resulting solution fractionated on an 18 in. spinning-band column to give pinocarvone (32·5 g.), b. p. 48—49°/1·5 mm., n_D^{20} 1·4940 (lit.,[15] n_D^{20} 1·4947), $[\alpha]_D$ +46° (*c*, 1·02), $\nu_{max.}$ 1709 and 1626 (C:C·C:O), $\lambda_{max.}$ 2420 Å (ε 5100), oxime, m. p. 129—130° (lit.,[15] m. p. 132—133°).

cis-*Pinocarveol* (Ic).—Bromine (23·5 g.) in acetic acid (40 c.c.) was added dropwise during

[12] Shoppee and Lack, *J.*, 1960, 4846.
[13] Schmidt, *Ber.*, 1944, **77**, 167.
[14] Schmidt, *Ber. Schimmel and Co.*, 1941, 70.
[15] Stallcup and Hawkins, *J. Amer. Chem. Soc.*, 1941, **63**, 3339.

30 min. to a stirred solution of pinocarvone (21 g.) in ether (100 c.c.) at 0°. Isolation with ether gave a solid (44 g.) which was dissolved in a mixture of acetic acid (400 c.c.) and water (50 c.c.). Zinc powder (90 g.) was added during 20 min. to the stirred solution kept at 10°, followed by the addition of potassium hydroxide (300 g.) in water (500 c.c.). Isolation with ether and fractionation on an 18 in. spinning-band column gave *cis*-pinocarveol (14·6 g.), b. p. 64—65°/1·5 mm., m. p. 50—50·5° (lit.,[13] 51°), $[\alpha]_D$ −41° (*c*, 1·04), $\nu_{max.}$ (liquid film) 3289 (OH), 3030, 1642, and 893 cm.$^{-1}$ ($RC_2^{\cdot}CH_2$).

6-endo-*Bromo*-1,5,5-*trimethyl*-2-exo-*norbornanol* (Va).—A solution of *trans*-pinocarveol (12·6 g.) in ether (60 c.c.) was saturated with hydrogen bromide and kept at 0° for 16 hr. Isolation with ether gave a solid (19·56 g.) which crystallised from light petroleum as *needles*, m. p. 118—119°, $[\alpha]_D$ −9° (*c*, 0·96) (Found: Br, 34·7. $C_{10}H_{17}BrO$ requires Br, 34·3%), $\nu_{max.}$ 3534 cm.$^{-1}$ (OH).

2-exo-*Acetoxy*-6-endo-*bromo*-1,5,5-*trimethylnorbornane* (Vb).—An ice-cold solution of *trans*-pinocarvyl acetate (2·5 g.) in ether (12 c.c.) was saturated with hydrogen bromide and kept at 0° for 12 hr. Isolation with ether gave an oil (4·23 g.), which, on distillation, afforded the *bromo-acetate* (2·25 g.), b. p. 140—145°/15 mm., n_D^{17} 1·5124, $[\alpha]_D$ +14° (*c*, 0·92) (Found: Br, 29·6. $C_{12}H_{19}BrO_2$ requires Br, 29·0%), $\nu_{max.}$ 1734, 1235, and 1221 cm.$^{-1}$ (OAc).

Hydrolysis of the Bromo-acetate (Vb).—A solution of the bromo-acetate (1·01 g.) and potassium hydroxide (500 mg.) in ethanol–water (10·5 c.c.; 20 : 1) was kept at 20° for 6 hr. Dilution with water (500 c.c.) gave the bromo-alcohol (Va) as needles (375 mg.), m. p. and mixed m. p. 118—119° (from light petroleum), $[\alpha]_D$ −10° (*c*, 1·00).

2,2,4-*Trimethylcyclopent*-3-*enylacetaldehyde* (VII).—The bromo-alcohol (Va) (200 mg.) was mixed with acetic acid (1 c.c.) and silver acetate (200 mg.) and the whole kept at 80—90° for 1 hr. Isolation with ether gave a liquid (120 mg.), n_D^{17} 1·4611, $[\alpha]_D$ +10° (*c*, 0·96), $\nu_{max.}$ 2670 and 1724 cm.$^{-1}$ (CHO), semicarbazone, m. p. 112—113°. The infrared spectrum and retention time on g.l.c. of the liquid were identical with those of an authentic sample of the aldehyde prepared from α-pinene oxide.[7]

Debromination of the Bromo-alcohol (Va).—The bromo-alcohol (1·03 g.) in ethanol (5 c.c.) was heated under reflux with zinc powder (550 mg.) for 15 hr. Removal of the zinc by filtration, and isolation of the product from the filtrate with ether, gave a liquid (650 mg.). Adsorption of the liquid, in pentane, on silica gel and elution with pentane–ether (100 : 3) gave the aldehyde [7] (VII) (80 mg.), identified by its infrared spectrum and retention time on g.l.c. Further elution gave a solid (400 mg.), m. p. 42—46°, which, on sublimation at 0·1 mm., afforded 1,5,5-trimethyl-2-*exo*-norbornanol (Vc), m. p. 57—59° (lit.,[16] 61—62°), $[\alpha]_D$ +10° (*c*, 1·01), $\nu_{max.}$ 3534 cm.$^{-1}$ (OH), phenylurethane, m. p. 110—111° (lit.,[16] 106—107°).

6-endo-*Bromo*-1,5,5-*trimethylnorbornan*-2-*one* (Vf).—To the complex formed from chromium trioxide (5·0 g.) and pyridine (75 c.c.) was added the bromo-alcohol (Va) (3·05 g.) in pyridine (5 c.c.) and the mixture kept at 20° for 48 hr. Isolation with ether gave a solid (2·95 g.) which crystallised from light petroleum as *needles*, m. p. 62—63°, $[\alpha]_D$ −32° (*c*, 1·02) (Found: Br, 35·0. $C_{10}H_{15}BrO$ requires Br, 34·6%), $\nu_{max.}$ 1745 cm.$^{-1}$ (C:O), *oxime*, plates, m. p. 209—210° (from ethanol), $[\alpha]_D$ −11° (*c*, 0·96) (Found: C, 48·6; H, 9·7 $C_{10}H_{17}NO$ requires C, 48·8; H, 9·6%).

Debromination of the Bromo-ketone (Vf).—The bromo-ketone (1·0 g.), in acetic acid (5 c.c.) and water (2 c.c.), was heated under reflux with zinc powder (1·0 g.) for 1 hr. Removal of the zinc by filtration and isolation of the product from the filtrate with ether gave an oil (640 mg.). Adsorption on silica gel (40 g.) in pentane and elution with pentane–ether (100 : 3) gave pure isofenchone (5 g.) (140 mg.), n_D^{18} 1·4635 (lit.,[17] $n_D^{18\cdot5}$ 1·4621), $[\alpha]_D$ +36° (*c*, 0·92), $\nu_{max.}$ 1736 cm.$^{-1}$ (C:O), oxime (sublimed), m. p. 83—84° (lit.,[17] 82°), $[\alpha]_D$ −11° (*c*, 0·99).

6-endo-*Bromo*-1,5,5-*trimethyl*-2-endo-*norbornanol* (Vd).—The bromo-ketone (Vf) (500 mg.) was added to sodium borohydride (500 mg.) in ethanol (20 c.c.) and kept at 20° for 14 hr. Isolation with ether gave an oil (690 mg.) which, in pentane, was adsorbed on silica gel (50 g.). Elution with pentane–ether (100 : 3) gave a solid (340 mg.) which, on sublimation at 0·1 mm., gave the *bromo-alcohol*, m. p. 81—82°, $[\alpha]_D$ −25° (*c*, 1·04) (Found: Br, 33·9. $C_{10}H_{17}BrO$ requires Br, 34·3%), $\nu_{max.}$ 3497 cm.$^{-1}$ (OH).

Debromination of the Bromo-alcohol (Vd).—The bromo-alcohol (550 mg.) in ethanol (5 c.c.) was heated under reflux for 16 hr. with zinc powder (260 mg.). Removal of the zinc by filtration

[16] Wallach, *Annalen*, 1907, **357**, 49.
[17] Wallach and Vivck, *Annalen*, 1908, **362**, 174.

and isolation of the product from the filtrate with ether gave an oil (430 mg.), which was adsorbed in pentane on silica gel (30 g.). Elution with pentane–ether (100 : 3) gave the aldehyde [7] (VII) (60 mg.), identified by its infrared spectrum and retention time on g.l.c. Further elution gave 1,5,5-trimethyl-2-*endo*-norbornanol (310 mg.), n_D^{18} 1·4763 (lit.,[18] n_D^{20} 1·4726), $[\alpha]_D$ −3° (*c*, 0·97), $\nu_{max.}$ (liquid film) 3356 cm.$^{-1}$ (OH).

Addition of Hydrogen Bromide to cis-*Pinocarveol* (Ic).—An ice-cold solution of the alcohol (Ic) (1·98 g.) in ether (10 c.c.) was saturated with hydrogen bromide and kept at 0° for 17 hr. Isolation with ether gave an oil (2·71 g.) which was dissolved in pentane and adsorbed on silica gel (250 g.). Elution with pentane–ether (50 : 1) gave an oil (1·28 g.) which was identified as a mixture (3 : 1) of pinocamphone (IXa) and isopinocamphone (IXb) by infrared spectra and g.l.c. Further elution gave 6-endo-*bromoisoborneol* (VIb) (825 mg.) which crystallised as needles (440 mg.), m. p. 145—146° (from light petroleum), $[\alpha]_D$ −41° (*c*, 1·07) (Found: C, 52·4; H, 7·6; Br, 33·3. $C_{10}H_{17}BrO$ requires C, 51·5; H, 7·3; Br, 34·3%), $\nu_{max.}$ 3584 cm.$^{-1}$ (OH).

cis-*Pinocarvyl Acetate* (Id).—*cis*-Pinocarveol (5·3 g.) was treated at 20° for 24 hr. with pyridine (7 c.c.) and acetic anhydride (7 c.c.). Isolation with ether and distillation of the crude product gave the acetate (6·1 g.), b. p. 78—80°/1·5 mm., n_D^{23} 1·4775 (lit.,[13] n_D^{20} 1·4802), $[\alpha]_D$ −58° (*c*, 1·0), $\nu_{max.}$ (liquid film), 1727, 1235 (OAc), 2611, 1637, and 887 cm.$^{-1}$ ($R_2C{:}CH_2$).

Addition of Hydrogen Bromide to cis-*Pinocarvyl Acetate*.—A solution of the acetate (Id) (3·05 g.) in ether (15 c.c.) at 0° was saturated with hydrogen bromide and kept at 0° for 24 hr. Isolation with ether gave a solid (4·34 g.) which crystallised from light petroleum to give 6-endo-*bromoisobornyl acetate* (VIc) as prisms (2·6 g.), m. p. 70—74°, $[\alpha]_D$ −74° (*c* 1·03) (Found: Br, 31·1. $C_{12}H_{19}BrO_2$ requires Br, 29·0%), $\nu_{max.}$ (Nujol) 1736, 1245 cm.$^{-1}$ (OAc).

Hydrolysis of the Bromo-acetate (VIc).—A solution of the acetate (1·0 g.) in methanol (10 c.c.) containing potassium hydroxide (500 mg.) and water (0·5 c.c.) was kept at 20° for 10 hr. Isolation with ether gave a solid (825 mg.) which crystallised from light petroleum (50/70) to give the bromo-alcohol (VIb) as needles (690 mg.), m. p. and mixed m. p. 145—146°.

2,2,3-*Trimethylcyclopent*-3-*enylacetaldehyde* (VIII).—The bromo-alcohol (VIb) (100 mg.) was treated with silver acetate (100 mg.) in acetic acid (0·5 c.c.) at 80—90° for 1 hr. Isolation with ether gave the aldehyde (VIII), n_D^{20} 1·4710, $[\alpha]_D$ +5° (*c* 1·01), $\nu_{max.}$ 3021, 2691, 1727, and 797 cm.$^{-1}$, semicarbazone, m. p. 140—145°. The aldehyde was identical (infrared spectra and g.l.c.) with an authentic sample [7] prepared from α-pinene oxide.

Debromination of 6-endo-*Bromoisoborneol* (VIb).—The bromo-alcohol (700 mg.) was heated under reflux with zinc powder (1·0 g.) in ethanol (10 c.c.) for 24 hr. Removal of the zinc by filtration and isolation of the product from the filtrate with ether gave a waxy solid (460 mg.) which could not be purified by sublimation, $[\alpha]_D$ +23° (*c* 0·98), $\nu_{max.}$ (liquid film) 3333 and 1066 cm.$^{-1}$, *p*-nitrobenzoate, m. p. 119—120°, $[\alpha]_D$ +49° (*c* 1·02). Huckel [19] gives m. p. 120°, $[\alpha]_D$ +54° for (−)-isobornyl *p*-nitrobenzoate.

Oxidation of 6-endo-*Bromoisoborneol* (VIb).—The alcohol (300 mg.) in pyridine (3 c.c.) was added to the complex formed from chromium trioxide (500 mg.) and pyridine (5 c.c.) and the mixture kept at 20° for 2 days. Isolation with ether gave a solid (305 mg.), which crystallised from light petroleum to give 6-endo-*bromocamphor* as plates (160 mg.), m. p. 133—134°, $[\alpha]_D$ +44° (*c* 1·04) (Found: C, 52·4; H, 6·8; Br, 34·6. $C_{10}H_{15}BrO$ requires C, 52·0; H, 6·8; Br, 34·3%), $\nu_{max.}$ 1757 cm.$^{-1}$ (C:O).

Debrominatjon of 6-endo-*Bromocamphor* (VIe).—The bromo-ketone (96 mg.) was heated under reflux for 1 hr. with a mixture containing zinc powder (100 mg.), acetic acid (0·5 c.c.), and water (0·2 c.c.). Isolation with ether gave a solid (52 mg.), $[\alpha]_D$ +36° (*c* 1·02), $\nu_{max.}$ 1748 cm.$^{-1}$, identified as camphor by infrared spectra and g.l.c.

Bromination of Pinocarvone (Ie).—Bromine (11·5 g.) in carbon tetrachloride (36·5 c.c.) was added dropwise during 40 min. to a stirred ice-cold solution of pinocarvone (9·75 g.) in carbon tetrachloride (10 c.c.). Isolation with ether gave a solid (20·5 g.) which crystallised from methanol to give 2,10-dibromo-*cis*-pinan-3-one (XI) (13·6 g.) as needles, m. p. 72—73° (lit.,[10] 73—74°), $[\alpha]_D$ −159° (*c* 1·01), $\nu_{max.}$ 1724 cm.$^{-1}$ (C:O).

Hydrogen Bromide-catalysed Isomerisation of the Dibromo-ketone (XI).—A solution of the dibromo-ketone (500 mg.) in acetic acid (3 c.c.) saturated with hydrogen bromide was heated to 50° and set aside for 18 hr. Isolation with ether gave a solid (460 mg.) which yielded the 4,10-*dibromopinan*-3-*one* (Xb) (210 mg.) as needles, m. p. 103—104° (from methanol), $[\alpha]_D$ −39°

[18] Schmidt and Todenhöfer, *Ber. Schimmel and Co.*, 1937, 113.
[19] Huckel, *Annalen*, 1941, **549**, 206.

(*c* 1·04) (Found: C, 38·4; H, 4·9; Br, 51·7. $C_{10}H_{14}Br_2O$ requires C, 38·7; H, 4·6; Br, 51·5%), $\nu_{max.}$ (CCl_4) 1728 cm.$^{-1}$ (C:O).

Addition of Hydrogen Bromide to Pinocarvone (Ie).—A solution of the ketone (3·0 g.) in dry ether (15 c.c.) was saturated with hydrogen bromide and kept at 0° for 16 hr. Isolation with ether gave an oil (4·1 g.), identified as 10-bromopinan-3-ones (Xa), n_D^{18} 1·5179, $[\alpha]_D$ −30° (*c* 1·48), $\nu_{max.}$ (CCl_4) 1716 cm.$^{-1}$.

Dehydrobromination of 10-*Bromopinan*-3-*ones* (Xa).—A solution of the bromo-ketones (1·0 g.) in pyridine (5 c.c.) was kept at 30° for 15 min. Isolation with ether gave an oil (670 mg.) identified as pinocarvone (Ie) by infrared and ultraviolet spectra and by g.l.c.

Bromination of 10-*Bromopinan*-3-*ones* (Xa).—Bromine (2·24 g.) in acetic acid (9·95 c.c.) was added during 3 min. to a solution of the 10-bromo-ketones (Xa) produced by saturating an ice-cold solution of pinocarvone (Ie) (2·0 g.) in ether (10 c.c.) with hydrogen bromide and storing the solution for 8 hr. Isolation with ether gave an oil (4·25 g.) which, on seeding with 2,10-dibromo-*cis*-pinan-3-one (XI), afforded a solid (450 mg.) which crystallised from methanol as needles, m. p. and mixed m. p. 73—74°, $[\alpha]_D$ −162° (*c* 0·98). The identity of the dibromo-ketone was confirmed by infrared spectra.

The remaining oil gave an infrared spectrum which exhibited bands characteristic of both 2,10- and 4,10-dibromopinan-3-ones.

Reduction of 10-*Bromopinan*-3-*ones* (Xa).—A solution of the bromo-ketones (Xa) (3·0 g.) in ethanol (10 c.c.) was added to a solution of sodium borohydride (3 g.) in ethanol (30 c.c.) and kept at 20° for 8 hr. Isolation with ether gave an oil which was distilled. The first fraction (710 mg.), b. p. up to 120°, 0·1 mm., was shown by g.l.c. to consist mainly of *cis*-pinocarveol (Ic). The second fraction (1·8 g.) was identified as the bromo-alcohols (XIIa), b. p. 120—125°/0·1 mm., m. p. 40—45° (Found: Br, 32·9. Calc. for $C_{10}H_{17}BrO$: Br, 34·3%), $\nu_{max.}$ (liquid film) 3320 and 1078 cm.$^{-1}$ (OH).

Pinocamphone (IXa) *and Isopinocamphone* (IXb) *from the Bromo-alcohols* (XIIa).—The bromo-alcohols (450 mg.) were heated under reflux with zinc powder (500 mg.), acetic acid (3 c.c.), and water (2 c.c.). Isolation with ether gave an oil (300 mg.) which was oxidised using 8N-chromic acid in acetone. The product (270 mg.) was shown by g.l.c. to contain pinocamphone (75%), isopinocamphone (12%), and acetates (13%), the latter being formed at the debromination stage.

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