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# THE BROMINATION OF ISOPINOCAMPHONE

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**Abstract**—Bromination of isopinocamphone gives 2α,4α-dibromo-10β-pinan-3-one (III) which is rearranged to 3-*endo*-6-*endo*-6-dibromocamphor (IV) when heated with aqueous acetic acid. Analogous rearrangements of 2α-bromo-10β-pinan-3-ones are described.

BROMINATION of either pinocamphone or isopinocamphone has been reported[1] to give the same mixture of two dibromoketones, the structures of which were not described. In order to determine the structures of these two bromoketones we studied the bromination of the more readily available isopinocamphone.

Attempted monobrominations of isopinocamphone (I) using either molecular bromine or trimethylphenylammonium perbromide[2] gave only oily products which were later shown to consist of mixtures of isopinocamphone, 2α-bromo-10β-pinan-3-one[3] (II) and one of the dibromoketones reported earlier, 2α,4α-dibromo-10β-pinan-3-one (III). These mixtures could not be resolved into their components by preparative gas-liquid chromatography (GLC) or by adsorption chromatography on silica gel. Repetition of the dibromination of isopinocamphone gave only the 2α,4α-dibromo-10β-pinan-3-one (III); the second dibromoketone reported by Schmidt[1] was not obtained from this experiment. Furthermore it has been demonstrated that the second dibromoketone, shown below to be 3-*endo*-6-*endo*-bromocamphor (IV), was not formed by acid catalysed isomerization when the 2α,4α-dibromoketone (III) was recovered unchanged from lengthy treatment with hydrogen bromide in acetic acid.

In an attempt to obtain monobromoketones from isopinocamphone the enol acetylation of the ketone was studied. Under either isopropenyl acetate-toluene-*p*-sulphonic acid[4] or perchloric acid–acetic anhydride in carbon tetrachloride[5] conditions, isopinocamphone was converted into the $\Delta^2$-enol acetate (V). No trace of the $\Delta^3$-isomer (VI) was detected. The structure of the enol acetate was revealed by IR and NMR spectra. In particular, the absence of signals due to olefinic protons[6] and the presence of signals (8·45 τ) characteristic of the $CH_3—\overset{|}{C}=C\diagup\diagdown$ system in the NMR spectrum defined the structure of the enol acetate. Bromination of this enol acetate

[1] H. Schmidt, *Chem. Zentr.* I, 2531 (1942); *Chem. Abstr.* **37**, 4380 (1943).
[2] A. Marquet and J. Jacques, *Tetrahedron Letters* No. 9, 24 (1959).
[3a] M. P. Hartshorn and A. F. A. Wallis, *Chem. & Ind.* 1878 (1963); *J. Chem. Soc.* 1964, in press.
[b] W. Treibs, M. Muhlstadt, R. Megges and I. Klotz-Herdmann, *Liebig's Ann.* 634, 118 (1960).
[4] W. G. Dauben, J. F. Eastham, R. A. Micheli, K. H. Takemura, L. Mandell and J. M. Chemerda, *J. Amer. Chem. Soc.*, **75**, 3255 (1953).
[5] D. H. R. Barton, R. M. Evans, J. C. Hamlet, P. G. Jones and T. Walker, *J. Chem. Soc.* 747 (1954).
[6] L. M. Jackman, *Applications of Nuclear Mcgnetic Resonance Spectroscopy in Organic Chemistry*. Pergamon Press (1959).

gave 2α-bromo-10β-pinan-3-one (II) as an oil. The structure was assigned on the basis of preferred bromination of the enol acetate at $C_2$ from the α-face rather than from the β-face of the molecule which is shielded from attack by the $C_8$ methyl group. The NMR spectrum (8·04 τ) was consistent[6] with the presence of the $Br—\overset{|}{\underset{|}{C}}—CH_3$ feature and the absence of —CHBr —protons. Attempted isomerization of the 2α-bromoketone using hydrogen bromide–acetic acid gave a mixture, the NMR spectrum of which exhibited signals (5·34 τ) consistent with the formation among other products of some 4-bromoketone (VII).

Monobromination using either bromine–acetic acid or under bromination conditions using trimethylphenylammonium perbromide[2] gave the 2α,4α-dibromoketone (III) obtained by dibromination of isopinocamphone. The NMR spectrum of the dibromoketone exhibited signals (7·98 and 5·30 τ) characteristic of both —$CBr(CH_3)$— and —CHBr— features. In view of the isolation of the $\Delta^2$-enol acetate (V) from a reaction (isopropenyl acetate-toluene-*p*-sulphonic acid) which might have been expected to favour $\Delta^3$-enol acetate (VI) formation, it seems probable that kinetically controlled dibromination of isopinocamphone proceeds *via* α-face attack by $Br^+$, or some equivalent, on the $\Delta^2$-enol of isopinocamphone followed by subsequent attack of $Br^+$ on the $\Delta^3$-enol (VIII) of the monobromoketone (II) again from the less hindered α-face. The recovery of the 2α,4α-dibromoketone from treatment with hydrogen bromide-acetic acid demonstrated that it was also the product of thermodynamic control.

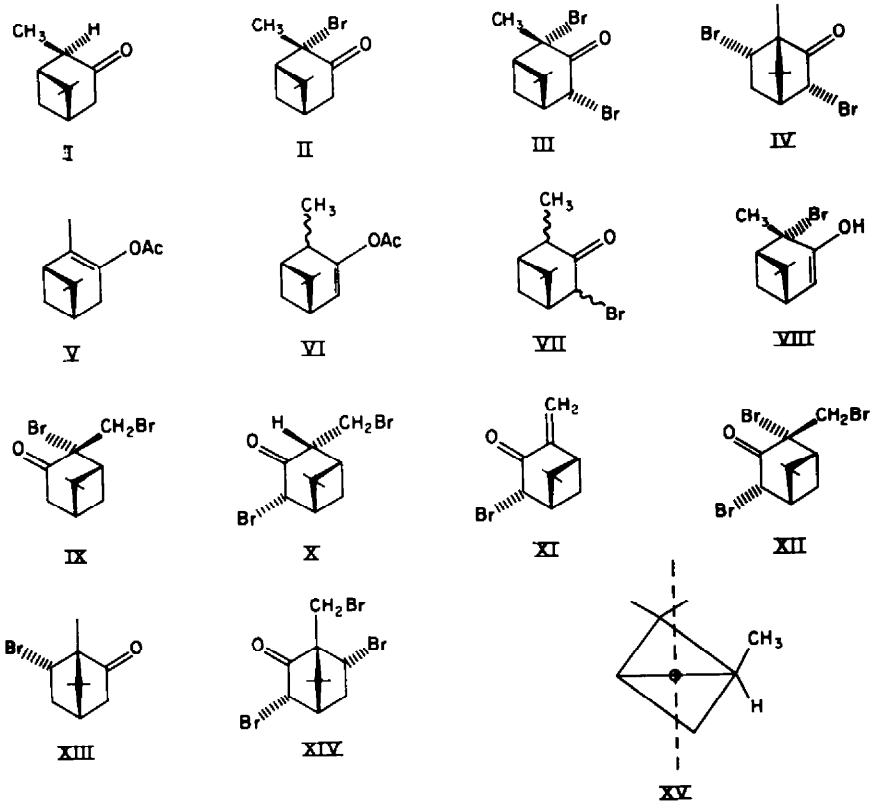
Reductive debromination of the 2α,4α-dibromoketone with zinc and aqueous acetic acid gave a product shown by GLC to consist largely (ca. 80%) of isopinocamphone contaminated with pinocamphone. The isolation of isopinocamphone may be adduced in support of the 2α-bromo-2β-methyl structure if it may be assumed that such debromination reactions occur with retention of configuration at the site of the bromine atom.

In an earlier paper we reported[3] the isomerization of the 2α,10-dibromo-10β-pinan-3-one (IX) with hydrogen bromide to give a 4,10-dibromoketone. This compound has now been assigned the 4α,10-dibromo-10α-pinan-3-one structure (X). Reductive debromination of X with zinc and aqueous acetic acid gave mainly pinocamphone contaminated with isopinocamphone. As it was shown that isopinocamphone was not significantly converted into pinocamphone under the reaction conditions (control experiment) and that X was homogeneous, the isolation of pinacamphone supports the 2α-methyl structural assignment.

Dehydrobromination of X with pyridine gave 4α-bromopinocarvone (XI). The structural features were confirmed by IR, UV and NMR spectra. Addition of hydrogen bromide to 4α-bromopinocarvone proceeded by the expected[3] Michael addition to give X. Addition of bromine to XI gave 2α,4α,10-tribromo-10β-pinan-3-one (XII). The NMR spectrum exhibited signals characteristic of both —$CBr—CH_2Br$ and —CHBr— features, consistent with the assigned structure. The addition of bromine to 4α-bromopinocarvone (XI) is assumed to proceed in a manner analogous to the addition[3] of bromine to pinocarvone, namely by attack of $Br^+$ on the α-face of the double bond followed by bromide ion addition at $C_{10}$. Acid catalysed bromination of the 4α,10-dibromoketone (X) or of the 2α,10-dibromoketone (IX) also gave the

same 2α,4α,10-tribromoketone (XII). Under the above acid catalysed bromination conditions the 2α,10-dibromoketone (IX) was not appreciably isomerized into the 4α,10-dibromoketone (X) (control experiment).

At no time in the work described above was the second dibromoketone described[1] by Schmidt obtained. However, in an attempt to dehydrobrominate the 2α,4α-dibromoketone (III) using lithium carbonate–dimethyl formamide the crude product was shown to contain, in addition to 4α-bromopinocarvone (XI), a dibromoketone, m.p. 113·5–114·5°, $[\alpha]_D$ −156°, similar in properties to the second[1] dibromination




product. This dibromoketone, now assigned the 3-*endo*-6-*endo*-dibromocamphor structure (IV), was later shown to be produced from the 2α,4α-dibromoketone (III) in good yield by heating it under reflux with aqueous acetic acid. The dibromo-compound was shown to have the camphane skeleton by reductive debromination using zinc and aqueous acetic acid to yield camphor identified by IR spectra and GLC. The *endo,endo*- configuration of the bromine atoms follows from the NMR spectrum. In the NMR spectrum of 6-*endo*-bromocamphor[3] (XIII) the signal due to the C*H*Br appeared as a quartet (centred 5·82τ) due to coupling with the adjacent methylene group ($J_{5-exo,6-exo} = 9$, $J_{5-endo,6-exo} = 3$ c/s). The C$^6$*H*Br feature in 3-*endo*-6-*endo*-dibromocamphor was revealed by a quartet (centered 5·85τ) ($J_{5-exo,6-exo} = 8$, $J_{5-endo,6-exo} = 6$ c/s). The change in splitting pattern is attributed to molecular distortion due to the non-bonded interactions between the two *endo*-bromine atoms in the molecule. In addition the C$^3$*H*Br feature produces a quartet centered at 5·32τ($J_{3-exo,4} = 6$,

$J_{3-exo,5-exo} = 1$ c/s). These data are consistent only with a 3-*endo*-6-*endo*-formulation[7] for the dibromoketone (IV).

In view of the ready formation of the dibromoketone (IV) from the 2α,4α-dibromoketone (III) on heating with aqueous acetic acid its mode of formation in the original dibromination experiments is not obscure. The earlier workers isolated by crystallization the bulk of the 2α,4α-dibromoketone. Steam distillation of the residue from the crystallization in the presence of aqueous acetic acid converted the remaining 2α,4α-dibromoketone into the camphor derivative which was isolated as the second 'product' of dibromination of isopinocamphone.

*Rearrangement of* 2α-*bromo*-10β-*pinan*-3-*ones*. The ready conversion of the 2α,4α-dibromoketone (III) into an isomeric dibromoketone (IV) having a camphone skeleton prompted us to examine the reactions of other 2α-bromoketones under similar conditions. The simplest member of the series, the 2α-bromoketone (II) gave only intractible oils as products of reaction either with aqueous acetic acid or dimethylformamide–lithium carbonate, although GLC suggested the formation of some 6-*endo*-bromocamphor (XIII) in the former case. In contrast the 2α,4α,10-tribromoketone (XII) was isomerized by boiling aqueous acetic acid to the corresponding camphor derivative, to which the 3-*endo*-6-*endo*-,10-tribromocamphor (XIV) structure has been assigned by analogy with the 2α,4α-dibromoketone reaction. The NMR spectrum of XIV contained signals consistent with the $-\overset{|}{\underset{|}{C}}-CH_2Br$ (6·07, 6·26, 6·50, 6·72τ) and —CHBr— features (multiplet centred at 5·3τ). However, reaction of the 2α,4α,10-tribromoketone (XII) with lithium carbonate–dimethylformamide resulted in loss of bromine to give the known 4α-bromopinocarvone (XI).

Treatment of the 2α,10-dibromoketone (IX) with lithium carbonate–dimethylformamide gave pinocarvone in good yield. The attempted isomerization using aqueous acitic acid however gave no identifiable camphone derivative in a crude product, the IR spectrum of which showed peaks due to both hydroxyl and carbonyl groups.

*Optical rotatory dispersion data.* The optical rotatory dispersion data for the bromopinan 3-ones reported above proved to be anomalous when compared with predicted values on the basis of the Octant Rule[8] for the more probable conformations of each ketone. Unless systematic deviations from the Octant Rule are applied the Cotton curve ($a$ +17) for isopinocamphone (1) may only be explained on the basis of twist structures (XV) where $C_6$ and $C_7$ outweigh the $C_2$ methyl group which lies in the far upper right octant. Extension of this to the 2α-bromo-10β-pinan-3-one (II) would suggest a more positive Cotton curve than for the unsubstituted compound as the $C_2$-Br lies in the far lower right octant and would thus reinforce the contributions due to $C_6$ and $C_7$; in fact the Cotton curve ($a$ +7) shows instead a negative shift ($\Delta a$ −10). In view of the changes in physical constants on the introduction of the $C_2$-Br into isopinocamphone, IR spectrum[9] a shift from 1712 to 1726 $cm^{-1}$ ($\Delta\nu$ 14 $cm^{-1}$) and UV spectrum[10] a shift from 285 mμ to 310 mμ ($\varepsilon$ 20 → 130), it seems

[7a] J. Musher, *Mol. Phys.* **6**, 93 (1963); [b] T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.* **85**, 3212 (1963).

[8] W. Moffit, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerass, *J. Amer. Chem. Soc.* **83**, 4013 (1961).

[9] R. N. Jones, D. A. Ramsey, F. Herling and K. Dobriner, *J. Amer. Chem. Soc.* **74**, 2828 (1952).

[10] R. C. Cookson, *J. Chem. Soc.* 282 (1954).

probable that the data may not in this case be rationalized on the basis of a normal cyclohexanone analogy.

## EXPERIMENTAL

Rotations, unless otherwise stated, were measured for benzene solutions. IR and UV spectra were recorded for $CS_2$ and MeOH solutions respectively, unless stated otherwise. Silica gel used for adsorption chromatography was Crosfield Sorbsil Grade 60–120. The NMR spectra were measured at 60 Mc in $CDCl_3$ solution using tetramethylsilane and $CHCl_3$ as internal standards.

*Isopinocampheol.* Prepared by the method of Brown and Zweifel[11] from α-pinene ($[\alpha]_D$ +47°, neat) to give m.p. 54–56°, $[\alpha]_D$ −31° (*c* 2·37). (Lit.[11]: m.p. 54–6°, $[\alpha]_D$ −32°.)

*Isopinocamphone* (I). Prepared by oxidation of isopinocampheol to give b.p. (11 mm) 86–88°, $n_D^{20}$ 1·4739, $[\alpha]_D$ +29° (*c* 1·9), $\nu_{max}$ ($CCl_4$) 1712 $cm^{-1}$ $\lambda_{max}$ 289 mμ (ε 20). O.R.D. $[\phi]_{311}$ +705°, $[\phi]_{266}$ −1050°, $[\phi]_{244}$ −850°. (Lit.[11]: $n_D^{20}$ 1·4745, $[\alpha]_D$ +11° (neat).)

*Dibromination of isopinocamphone* (I)

(a) Bromine (4·3 g) in acetic acid (12 ml) was added during 10 min to a stirred ice-cold solution of isopinocamphone (2·0 g) in acetic acid (5 ml). After a further 30 min the product, isolated by use of ether, was a solid (4·13 g), which on crystallization from methanol afforded 2α,4α-*dibromo*-10β-*pinan*-3-*one* (2·85 g) as prisms, m.p. 96–97°, $[\alpha]_D$ +52° (*c* 0·97). (Found: C, 39·1; H, 4·6; Br, 51·8. $C_{10}H_{14}Br_2O$ requires: C, 38·7; H, 4·6; Br, 51·5%). $\nu_{max}$ ($CCl_4$) 1731 and 717 $cm^{-1}$, $\lambda_{max}$ 328 mμ (ε 225), 336 mμ (ε 240), 346 mμ (ε 195). O.R.D. in MeOH: $[\phi]_{400}$ +575°; $[\phi]_{353}$ +1760°; $[\phi]_{308}$ −1195°; $[\phi]_{278}$ −98°; $[\phi]_{258}$ −555° (Lit.[1]: m.p. 95–96°, $[\alpha]_D$ +50°.)

(b) A solution of isopinocamphone (500 mg) in tetrahydrofuran (5 ml) was added to phenyltrimethylammonium perbromide (2·6 g) in tetrahydrofuran (10 ml) and the mixture kept at 20° for 20 min. Isolation by means of ether gave the 2α,4α-dibromoketone (720 mg) as prisms, m.p. 96–97°, $[\alpha]_D$ +52° (*c* 0·99).

*Debromination of* 2α,4α-*dibromo*-10β-*pinan*-3-*one* (III)

To the dibromoketone (200 mg) in acetic acid–water (5 ml − 1 ml) was added Zn powder (200 mg) and the mixture heated to 40°. The Zn was filtered off and the terpene isolated by means of ether from the filtrate to give an oil (110 mg) shown to consist (IR spectra and GLC) of isopinocamphone–pinocamphone (4:1).

*Monobromination of isopinocamphone* (I)

(a) Bromine (1·12 g) in acetic acid (5 ml) was added during 5 min to a stirred ice-cold solution of isopinocamphone (1·01 g) in ether (10 ml), and the stirring continued for a further 5 min. The product isolated by means of ether was an oil (1·54 g) which proved to be a mixture of isopinocamphone, II and III. (IR spectra and GLC.)

(b) To a solution of isopinocamphone (500 mg) in tetrahydrofuran (5 ml) was added a solution of phenyltrimethylammonium perbromide (1·3 g) in tetrahydrofuran (5 ml) and the mixture kept at 20° for 10 min. The product, isolated by means of ether, was an oil (780 mg) consisting of isopinocamphone and the 2α-bromo- and 2α-4α-dibromoketones.

3-*Acetoxy-pin*-2-*ene* (V)

(a) A solution of isopinocamphone (10 g) in $CCl_4$ (230 ml) was treated with acetic anhydride (11·4 g) and perchloric acid aq (1·0 ml; 60%) and kept at 20° for 18 hr. Isolation of the product by means of ether gave an oil (14·4 g) which was adsorbed on silica gel (600 g) in pentane. Elution with pentane–ether (100:1) gave the *enol-acetate* (8·51 g), $n_D^{21.5}$ 1·4692, $[\alpha]_D$ +36° (*c* 1·00). (Found: C, 74·3; H, 9·3. $C_{12}H_{18}O_2$ requires: C, 74·2; H, 9·3%) $\nu_{max}$ 1751, 1224 and 1205 $cm^{-1}$ (OAc).

Further elution with pentane–ether (100:1) gave an equilibrium mixture of isopinocamphone and pinocamphone (1·06 g) identified by IR spectra and GLC.

(b) The solvent was fractionally distilled at 96° from a solution of isopinocamphone (10·1 g) and toluene-*p*-sulphonic acid (1·3 g) in isopropenyl acetate (200 ml). After 9 hr, during which time 50 ml

[11] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.* **83**, 2544 (1961).

of solvent had distilled over, the product was isolated by means of ether. The crude product (14·0 g) was fractionally distilled to give the enolacetate (9·1 g), b.p. (1·5 mm) 72–74°, $n_D^{19}$ 1·4705.

*2α-Bromo-10β-pinan-3-one* (II)

Bromine (930 mg) in $CCl_4$ (4 ml) was added during 5 min to a stirred solution of 3-acetoxy-pin-2-ene (1·07 g) and anhydrous $Na_2CO_3$ (1·0 g) in $CCl_4$ (5 ml) at 0°. After a further 5 min the terpene was isolated by means of ether to give the *bromoketone* (1·08 g) as an oil, $n_D^{15}$ 1·5247, $[\alpha]_D$ +124° (*c*, 1·09). (Found: C, 51·4; H, 6·3; Br, 34·8. $C_{10}H_{15}BrO$ requires: C, 52·0; H, 6·5; Br, 34·6%). $\nu_{max}$ ($CCl_4$) 1726 $cm^{-1}$ (C=O) and 708 $cm^{-1}$ (C—Br), $\lambda_{max}$ 312·5 mμ (ε 130). O.R.D. in MeOH: $[\phi]_{429}$ +380°; $[\phi]_{400}$ +675°; $[\phi]_{336}$ +1545°.

*Hydrogen bromide catalysed isomerization of 2α-bromo-10β-pinan-3-one* (II)

A solution of the bromoketone (1·0 g) and HBr in acetic acid (2 ml; 45%) was kept at 20° for 24 hr. The product isolated by means of ether was an oil (980 mg) $n_D^{18}$ 1·5179, $[\alpha]_D$ +43° (*c* 1·11) $\nu_{max}$ ($CCl_4$) 1727 $cm^{-1}$ (C=O) and 711 $cm^{-1}$ (C—Br) $\lambda_{max}$ 301 mμ (ε 220) the NMR spectrum of which was consistent with the presence of 4-bromopinan-3-one as a component of the mixture.

*Bromination of 2α-bromo-10β-pinan-3-one* (II)

A solution of the bromoketone (250 mg), $Br_2$ (180 mg) in acetic acid (4 ml) was kept at 20° for 15 min. Isolation of the product by means of ether gave a solid (330 mg) and crystallization from MeOH afforded 2α,4α-dibromo-10β-pinan-3-one (240 mg), m.p. and m.m.p. 96–97°, $[\alpha]_D$ +51° (*c* 1·02).

*Pinocarvone*

Prepared from β-pinene ($[\alpha]_D$ −20°, neat) by the literature method[12] to give pinocarvone, b.p. (1·5 mm) 48–49°, $n_D^{20}$ 1·4940, $[\alpha]_D$ +46° (*c* 1·02), $\nu_{max}$ 1709 and 1626 $cm^{-1}$ (C=C—C=O), $\lambda_{max}$ 242 mμ (ε 5100). O.R.D. in MeOH: $[\phi]_{287}$ +6750°; $[\phi]_{324}$ −15400°; $[\phi]_{317}$ −14000°. Oxime m.p. 129–130°. (Lit.[12]: $n_D^{20}$ 1·4947, oxime m.p. 132–133°).

*2α,10-Dibromo-10β-pinan-3-one* (IX)

Prepared from pinocarvone[12] to give the dibromoketone, m.p. 73–74°, $[\alpha]_D$ −159° (*c* 1·01), $\nu_{max}$ ($CCl_4$) 1724 $cm^{-1}$ (C=O) and 740 $cm^{-1}$ (C—Br), $\lambda_{max}$ 313 mμ (ε 115), 320 mμ (ε 105). O.R.D. in MeOH: $[\phi]_{500}$ −580°; $[\phi]_{400}$ −960°; $[\phi]_{351}$ −505°; $[\phi]_{300}$ −5440°. (Lit.[13] for dibromopinocarvone m.p. 73–74°, $[\alpha]_D$ +130°).

*4α,10-Dibromo-10α-pinan-3-one* (X)

Prepared[3] from 2α,10-dibromo-10β-pinan-3-one to give the 4α,10-dibromoketone, m.p. 103–104°, $[\alpha]_D$ −39° (*c* 1·04), $\nu_{max}$ ($CCl_4$) 1728 $cm^{-1}$ (C=O) and 718 $cm^{-1}$ (C—Br), $\lambda_{max}$ 305 mμ (ε 140), 315 mμ (ε 180), 324 mμ (ε 190), 335 mμ (ε 140). O.R.D. in MeOH: $[\phi]_{500}$ −225°; $[\phi]_{342}$ −3430°; $[\phi]_{324}$ +5710°; $[\phi]_{285}$ +5950°.

*Debromination of 4α-,10-dibromo-10α-pinan-3-one* (X)

The dibromoketone (200 mg) was heated under reflux for 30 min with Zn dust (200 mg) in acetic acid–water (5 ml:1 ml). Isolation of the terpene by means of ether gave an oil (95 mg) shown (IR spectra and GLC) to consist of a mixture of pinocamphone and isopinocamphone (9:1).

*4α-Bromopinocarvone* (XI)

4α-10-Dibromo-10α-pinan-3-one (500 mg) was heated under reflux with pyridine (5 ml) for 1 hr. The product isolated using ether was a solid (360 mg) which on crystallization from light petroleum gave *4α-bromopinocarvone* as needles, m.p. 62–63°, $[\alpha]_D$ +166° (*c* 0·99). (Found: C, 52·5; H, 6·0; Br, 35·0. $C_{10}H_{13}BrO$ requires: C, 52·9; H, 5·7; Br, 34·8%). $\nu_{max}$ ($CCl_4$) 1716 $cm^{-1}$ (C=O) and

[12] W. D. Stallcup and J. E. Hawkins, *J. Amr. Chem. Soc.* **63**, 3339 (1941).
[13] H. Schmidt, *Ber. Schimmel and Co.* 56 (1941); *Chem. Abstr.* **37**, 4714 (1943).

717 $cm^{-1}$ (C—Br), $\lambda_{max}$ 251 m$\mu$ ($\varepsilon$ 4500). O.R.D. in MeOH: $[\phi]_{400}$ 0°; $[\phi]_{374}$ +15600°; $[\phi]_{343}$ −25800°; $[\phi]_{328}$ −14100°.

*Addition of hydrogen bromide to* 4α-*bromopinocarvone* (XI)

The bromoketone (80 mg) was treated with a saturated solution of HBr in ether (5 ml) and kept at 0° for 4 hr. Isolation by means of ether gave a solid (116 mg) which on crystallization from light petroleum gave 4α,10-dibromo-10α-pinan-3-one (63 mg) m.p. and m.m.p. 103–104°, $[\alpha]_D$ −40° (*c* 0·99).

2α,4α,10-*Tribromo*-10α-*pinan*-3-*one* (XII)

(a) Bromide (455 mg) in acetic acid (2·5 ml) was added to 2α-10-dibromo-10β-pinan-3-one (800 mg) in acetic acid (5 ml) containing HBr in acetic acid (0·2 ml; 45%) and the mixture kept at 50° for 10 min. Isolation by means of ether gave a solid (1·0 g) which on crystallization from light petroleum gave the *tribromoketone* (840 mg) as needles, m.p. 82–3°, $[\alpha]_D$ −94° (*c* 0·96). (Found: C, 31·2; H, 3·5; Br, 61·0. $C_{10}H_{13}Br_3O$ requires: C, 30·9; H, 3·4; Br, 61·7%). $\nu_{max}$ ($CCl_4$) 1728 $cm^{-1}$ (C=O) $\lambda_{max}$ 327 m$\mu$ ($\varepsilon$ 150), 336 m$\mu$ ($\varepsilon$ 165), 347 m$\mu$ ($\varepsilon$ 135). O.R.D. in MeOH: $[\phi]_{400}$ −360°; $[\phi]_{366}$ −430°; $[\phi]_{345}$ −765°; $[\phi]_{313}$ −1095°; $[\phi]_{250}$ −2930°.

(b) A mixture of 4α,10-dibromo-10α-pinan-3-one (900 mg), $Br_2$ (510 mg) and acetic acid (8 ml) containing HBr in acetic acid (0·2 ml; 45%) was kept at 60° for 15 min. Isolation by means of ether gave a solid (1·15 g) which on crystallization from light petroleum gave the tribromoketone, m.p. and m.m.p. 82–83°, $[\alpha]_D$ −92° (*c* 1·01), $\nu_{max}$ ($CCl_4$) 1728 $cm^{-1}$ (C=O).

(c) Bromine (73 mg) in $CCl_4$ (0·5 ml) was added to a suspension of anhydrous $Na_2CO_3$ (100 mg) in a solution of 4α-bromopinocarvone (100 mg) in $CCl_4$ (2 ml) and the mixture kept at 35° for 10 min. Isolation by means of ether gave a solid (165 mg) and crystallization from light petroleum gave the tribromoketone (115 mg) m.p. and m.m.p. 82–83°.

*Rearrangement of* 2α,4α-*dibromo*-10β-*pinan*-3-*one* (III)

(a) The bromoketone (1·0 g) was heated under reflux with a suspension of $Li_2CO_3$ (1·0 g) in N,N-dimethylformamide (15 ml) for 2 hr. Isolation by means of ether gave an oily solid (850 mg) which was adsorbed on silica gel (100 g). Elution with pentane–ether (100:1) gave 4α-bromopinocarvone (150 mg) which on crystallization from light petroleum gave needles, m.p. 62–63°, $[\alpha]_D$ −172° (*c* 0·98) $\nu_{max}$ 1716 $cm^{-1}$.

Elution with pentane–ether (100:3) afforded 3-endo-6-endo-*dibromocamphor* (400 mg), which on crystallization from light petroleum gave fine needles (290 mg) m.p. 113·5–114·5°, $[\alpha]_D$ −156° (*c* 0·95). (Found: C, 38·8; H, 4·7; Br, 51·8. $C_{10}H_{14}Br_2O$ requires: C, 38·7; H, 4·6; Br, 51·5%). $\nu_{max}$ ($CCl_4$) 1769 $cm^{-1}$, $\lambda_{max}$ 300 m$\mu$ ($\varepsilon$ 65), 308·5 m$\mu$ ($\varepsilon$ 75) 318 m$\mu$ ($\varepsilon$ 65). O.R.D. in MeOH: $[\phi]_{400}$ −1540°; $[\phi]_{327}$ −8250°; $[\phi]_{290}$ +6700; $[\phi]_{268}$ +2190°.

(b) The bromoketone (500 mg) was heated under reflux for 3 hr with 10% acetic acid aq. (22 ml). Isolation by means of ether gave a solid (440 mg) which was adsorbed on silica gel (50 g). Elution with pentane–ether (100:3) gave 3-*endo*-6-*endo*-dibromocamphor (340 mg) which on crystallization from light petroleum gave needles, m.p. and m.m.p. 113·5–114·5°, $[\alpha]_D$ −158° (*c* 1·02).

*Debromination of* 3-endo-6-endo-*dibromocamphor* (IV)

The dibromoketone (90 mg) was heated under reflux with Zn powder (200 mg) in acetic acid–water (5 ml:1 ml) for 1 hr. Isolation by means of ether gave camphor (41 mg), $[\alpha]_D$ −39° (*c* 0·94) $\nu_{max}$ ($CCl_4$) 1746 $vm^{-1}$. Identical retention time on GLC as authentic material.

*Rearrangement of* 2α,4α,10-*tribromo*-10β-*pinan*-3-*one* (XII)

The tribromoketone (600 mg) was heated under reflux for 3 hr in 20% acetic acid aq. (24 ml). The product isolated by means of ether was an oily solid (520 mg) which was adsorbed on silica gel (60 g). Elution with pentane–ether (100:3) gave a solid (210 mg) which on crystallization from light petroleum afforded 3-endo-6-endo-10-*tribromocamphor* as needles, m.p. 131–132°, $[\alpha]_D$ +87° (*c* 1·01). (Found: C, 31·4; H, 3·7; Br, 61·1. $C_{10}H_{13}Br_3O$ requires: C, 30·9; H, 3·4; Br, 61·65%). $\nu_{max}$ ($CCl_4$) 1759 $cm^{-1}$ $\lambda_{max}$ 299 m$\mu$ ($\varepsilon$ 50), 306 m$\mu$ ($\varepsilon$ 50), 317 m$\mu$ ($\varepsilon$ 45).

*Attempted rearrangement of* 2α,4α,10-*tribromo*-10β-*pinan*-3-*one* (XI)

The ketone (800 mg) was added to a boiling suspension of $Li_2CO_3$ (1·0 g) in N,N-dimethylformamide (10 ml) and the whole heated under reflux for 10 min. Isolation by means of ether gave a solid (660 mg) which was adsorbed on silica gel (50 g). Elution with pentane–ether (100:1) gave a solid (415 mg) which on crystallization from light petroleum gave 4α-bromopinocarvone as needles, m.p. 62–63°, $[\alpha]_D$ +146° (*c* 0·99), $\nu_{max}$ 1734 $cm^{-1}$.

*Attempted rearrangement of* 2α-10-*dibromo*-10β-*pinan*-3-*one* (IX).

The bromoketone (1·0 g) was added to a boiling suspension of $Li_2CO_3$ (1 g) in N,N-dimethylformamide (10 ml) and heated under reflux for 30 min. Isolation of the terpene by means of ether gave a liquid (530 mg), which was shown to be pinocarvone by its characteristic IR spectrum and by GLC comparison with an authentic sample.

*Attempted rearrangements of bromoketones with aqueous acetic acid*

(a) 2α-*Bromo*-10β-*pinan*-3-*one* (II). The bromoketone was heated under reflux for 3 hr in 10% acetic acid aq. The crude product isolated by means of ether could not be separated into its components by column chromatography. However, one component of the mixture (ca. 40%) was identified tentatively by GLC as 6-*endo*-bromocamphor.

(b) 2α,10-*Dibromo*-10β-*pinan*-3-*one* (IX). The crude product was not resolved into its components by column chromatography. The IR spectrum exhibited bands 1755 $cm^{-1}$ (C=O and 3280 $cm^{-1}$ (OH).

(c) 4α-10-*Dibromo*-10α-*pinan*-3-*one* (X). The crude product was adsorbed on silica gel. Elution with pentane–ether (100:1) gave 4α-bromopinocarvone (60%) as needles, m.p. and m.m.p. 62–63°, from light petroleum.

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