solid was washed with hot benzene. The filtrate was evaporated to small volume under reduced pressure and the product then was isolated with chloroform (with benzene, intractable emulsions were formed). The resulting product (2.5 g.) (only weak band at 3.02 μ) was chromatographed on 250 g. of alumina. The only crystalline material was eluted with pentane–ether (1:1). Trituration of this product with methanol yielded 45 mg. (1.5%) of the cyclic trimer V, the infrared and ultraviolet spectra of which were identical with those of the previously obtained substance.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Acid-catalyzed Cleavage of π-Substituted Tricyclenes. Synthesis of 3,8-Cyclocamphor[1]

BY E. J. COREY, MASAJI OHNO, S. W. CHOW AND ROBERT A. SCHERRER

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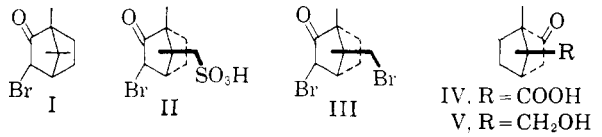
Syntheses of several *cis*-π-substituted camphor derivatives are described including *cis*-π-bromocamphor, *cis*-π-cyanocamphor, *cis*-isoketopinic acid and 3,8-cyclocamphor.

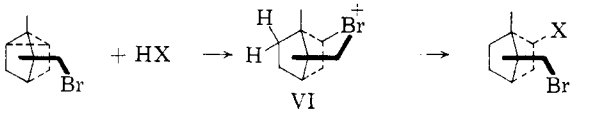
The introduction of substituents on one of the π-positions (C_8 or C_9) of camphor by reaction with certain electrophiles in strongly acidic media is one of the most interesting aspects of camphor chemistry. Exemplary of this process are the sulfonation and bromination of α-bromocamphor (I) to the corresponding π-substituted derivatives II and III.[2–4] These reactions are now understood to involve multi-stage rearrangement *via*



cations rather than direct substitution[3] and it is clear from data in the literature[5–7] that the substituent is located exclusively at the π-position which is distal (*trans*) to the carbonyl group.

Consequently, most of the studies with π-substituted camphors have been concerned with the *trans* rather than the *cis* derivatives. Indeed, the only *cis*-π-substituted camphors previously described in the literature are *cis*-isoketopinic acid (IV),[6] and *cis*-π-hydroxycamphor (V) which has been prepared from IV by reduction.[3]

Since *cis*-π-substituted camphors are of considerable chemical interest and are potentially useful intermediates in terpene synthesis, we have investigated the preparation of these compounds from the readily available *trans*-π-substituted camphors. The present paper describes some of our findings on the utility of *tricyclene* intermediates in the *trans*-π → *cis*-π conversion (see ref. 6 for a previous example). An efficient preparation has already been described[8] for π-bromotricyclene from *trans*-π-bromocamphor and this seemed a good starting point because of the replaceability of bromine by other groups. In addition the presence of bromine creates the possibility of directing acid-catalyzed ring cleavage specifically to the desired *cis*-substituted system. Participation by bromine in the ring-cleavage step to form the intermediate VI, a plausible pathway, would provide such direction.



Despite considerable experimentation on acid-catalyzed ring opening of π-bromotricyclene, no indication of selectivity was discernible. Two acids were employed for ring cleavage, formic and trifluoroacetic. In the former case *ca.* 20 hours at 60° was required for completion of the reaction, whereas with the latter acid cleavage was complete after only *ca.* 15 minutes at room temperature. Since the extent of participation by bromine should be greater with the less reactive acid, most of the data obtained relate to the formic acid system.

Formolysis of π-bromotricyclene at 50–60° yielded after distillation *ca.* 90% yield of a mixture of formate esters which was converted to bromoketone directly by oxidation with chromic acid–acetic acid–water in excellent yield. The direct oxidation procedure circumvents serious difficulties which are encountered with the two-step hydrolysis-oxidation sequence and is highly recommended.[9] The product of oxidation was shown by vapor phase chromatography (v.p.c.) to be a mixture of essentially equal amounts of *cis*-π-bromocamphor and *trans*-π-bromocamphor. The *trans* isomer was identified by comparison of infrared and v.p.c. measurements on the mixture with data on authentic material and by actual isolation from the mixture. The *cis* isomer, which could not be separated readily from the mixture, was obtained in pure form and characterized *via* 3,8-cyclocamphor as described below. It was shown

(1) We are indebted to the Alfred P. Sloan Foundation for generous financial support.

(2) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. II, 2nd ed., Cambridge University Press, Cambridge, 1949, pp. 386–432.

(3) D. H. R. Barton and S. W. Harper in Rodd, "Chemistry of Carbon Compounds," Vol. IIB, Elsevier Publishing Corp., Houston, Tex., 1953, Chapter XIII, pp. 602–618.

(4) H. Nishimitsu, M. Nishikawa and M. Hagiwara, *Proc. Japan Acad.*, **27**, 285 (1951).

(5) E. Wedekind and R. Stüsser, *Ber.*, **56**, 1557 (1923).

(6) T. Hasselström, THIS JOURNAL, **53**, 1097 (1931).

(7) Y. Sahashi and T. Iki, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **25**, 54 (1934).

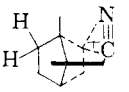
(8) E. J. Corey, S. W. Chow and R. A. Scherrer, THIS JOURNAL, **79**, 5773 (1957).

(9) The oxidation of the formate of a secondary alcohol to a ketone may occur directly without prior hydrolysis in two stages: (1) oxidation of the formyl group *via* the chromate ester formed by carbonyl addition and (2) oxidation of the resulting secondary alcohol.

by a control experiment that this mixture probably is not a result of equilibration of the π-bromoformates. Treatment of *trans*-π-bromoisoborneol with formic acid at 60–70° for 21 hours followed by oxidation of the resulting formate esters with chromic acid afforded a mixture of *trans*- and *cis*-π-bromocamphors in a ratio of 2.5 to 1. These data suggest that participation by bromine in the tricyclene cleavage, *via* a 1,4-bromonium ion, is not of much importance.

A study was made of the formolysis of π-iodotricyclene also and, although participation by halogen should be even more favorable in this case, the results obtained were similar to those with π-bromotricyclene. Formolysis and subsequent oxidation of π-iodotricyclene, which was prepared by reaction of π-bromotricyclene with sodium iodide, produced a mixture of *cis*- and *trans*-π-iodocamphors in the ratio of *ca.* 3 to 7.

It also seemed of interest to explore the possibility of participation by a π-cyano substituent during tricyclene ring cleavage with formation of a cation of type VII. The required π-cyanotri-



VII

cyclene was prepared in 90% yield from π-bromotricyclene with sodium cyanide in dimethyl sulfoxide[10] and solvolysis was effected both with formic acid and with trifluoroacetic acid. The formate mixture was oxidized directly using chromic acid to a mixture of *cis*- and *trans*-π-cyanocamphor containing approximately equal amounts of each. The two cyanoketones were separated readily by chromatography on alumina. Hydrolysis of the trifluoroacetate esters, followed by oxidation of the resulting cyanoalcohols also afforded a mixture of *cis*- and *trans*-π-cyanocamphor in approximately equal amounts. The *trans*-cyano ketone was identified by synthesis from *trans*-π-bromocamphor and sodium cyanide and from spectral data (see Experimental). The infrared spectrum of the *cis* isomer showed the absorption expected for cyano, carbonyl, α-methylene and methyl groups. The nuclear magnetic resonance spectra were fully compatible with the structures assigned to these cyano ketones. The formation of *cis* and *trans* isomers in about equal amounts from ring cleavage of π-cyanotricyclene argues against the intervention of the ion VII.

Hasselström[6] succeeded in obtaining the lactone IX by heating methyl teresantalate (VIII) with formic acid, a reaction which may proceed with π-substituent participation in contrast to the cases described above. This is by no means certain, however, since the predominance of IX may be a matter of thermodynamic control. Indeed, we have been able to utilize the stabilization imparted by the lactone ring to prepare IX, without the intermediate synthesis of the tricyclene VIII, by what amounts to an equilibration procedure. This transformation has practical value since it establishes access to *cis*-isoketopinic acid (XIII) by an efficient synthetic route which is outlined in Fig. 1.

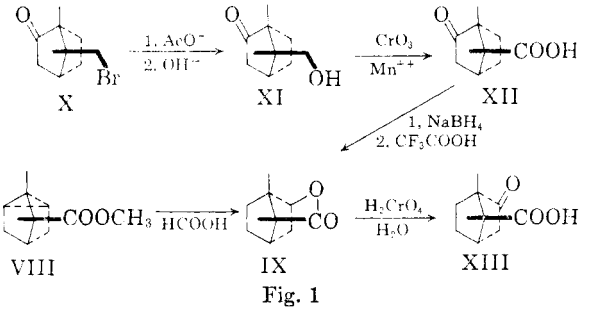
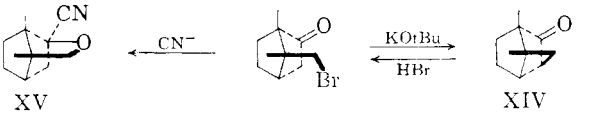


Fig. 1

trans-π-Bromocamphor[8] (X) was converted to the known *trans*-π-hydroxycamphor (XI) *via* the acetate in good yield. Oxidation of the keto alcohol XI with chromic acid–acetic acid consistently gave poor results and a mixture of acid and neutral products invariably was obtained. The occurrence of oxidative cleavage was suspected and consequently the oxidation was attempted in the presence of manganous ion as suggested by the findings of Westheimer.[11] This simple modification indeed proved to be effective and yields of 75% or better of *trans*-isoketopinic acid (XII) could be obtained consistently. Reduction of XII with sodium borohydride afforded a solid hydroxy acid which was converted without purification to the lactone IX by heating with trifluoroacetic acid–sulfuric acid (66% yield from XII). Oxidation of the lactone IX by means of chromic acid in aqueous acetic acid–sulfuric acid yielded *cis*-isoketopinic acid (XIII).

cis-π-Bromocamphor is a reactive and useful synthetic intermediate and, although it is not readily isolated from the mixture described above, it is sufficiently unique chemically to allow utilization of the *cis–trans* mixture in synthetic work. One such application is the synthesis of 3,8-cyclocamphor (XIV) by treatment of the π-bromocamphor mixture with potassium *t*-butoxide. 3,8-Cyclocamphor, a crystalline solid, could be separated from *trans*-π-bromocamphor by subli-



mation and was obtained in pure condition by vapor phase chromatography. The ultraviolet spectrum exhibits carbonyl absorption, λ_{max} 280 mμ (ε 61) (ethanol), which is slightly different from that of camphor, λ_{max} 289.5 mμ (ε 322) (ethanol). The infrared spectrum manifests carbonyl absorption at 1755 cm.$^{-1}$ (camphor, 1750 cm.$^{-1}$) and lacks the α-methylene absorption at 1420 cm.$^{-1}$ which is characteristic of camphor and its derivatives which possess the $-CH_2-CO-$ grouping. The nuclear magnetic resonance spectrum shows the presence of two methyl groups attached to hydrogen-free carbons [sharp peaks at 175 and 177.5

(10) These conditions were far superior to several others which were studied including the use of ethanol, carbitol or dimethylformamide as solvent.

(11) F. H. Westheimer, Abstracts 14th National Organic Symposium, American Chemical Society, Lafayette, Ind., June, 1955, p. 13.

c.p.s. (relative to CH_2Cl_2 at 40 mc.)] and the absence of olefinic protons. The proton alpha to the carbonyl group accounts for a triplet at 106 c.p.s.[12] 3,8-Cyclocamphor forms a nicely crystalline semicarbazone and is converted smoothly by treatment with hydrogen bromide–methylene chloride into pure *cis*-π-bromocamphor.

Reaction of the π-bromocamphor mixture with sodium cyanide converts the *cis* isomer into the volatile cyano ether XV which is purified readily by sublimation.

Experimental[13]

***cis*- and *trans*-π-Bromoisobornyl Formates.**—π-Bromotricyclene (20.52 g., 0.095 mole) was stirred vigorously with 35 ml. (42.7 g., 0.93 mole) of formic acid at 50° for 22 hours and 57° for 23 hours. The formic acid phase became violet in color shortly after heating was begun. The reaction mixture was diluted with about 300 ml. of ether–pentane (3:1) and washed with saturated salt solution several times and then several times with water. The acid remaining in the ether solution was neutralized with 10% sodium bicarbonate, and the solution washed, dried and concentrated to give 26 g. of crude formate. Distillation through a 30-cm. Holzmann column gave 21.57 g. of ester (89% correcting for 0.64 g. of recovered bromotricyclene–bromocamphene), b.p. 68° (0.03 mm.) to 64° (0.02 mm.), $n^{25.5}D$ 1.5139–1.5142. The infrared spectrum determined in carbon tetrachloride has characteristic absorption at 1730 and 1175 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{17}BrO_2$: C, 50.59; H, 6.56. Found: C, 51.03; H, 6.69.

Oxidation of *cis*- and *trans*-π-Bromoisobornyl Formates.—To a solution of sodium dichromate hydrate (67 g., 0.225 mole) and manganous sulfate hydrate (13 g., 0.077 mole) in 25 ml. of water was added 200 ml. of acetic acid followed by a cooled solution of 35 ml. of concentrated sulfuric acid and 10 ml. of water. This solution was cooled to below 5° in an ice-bath, and 21.35 g. (0.0816 mole) of *cis*- and *trans*-π-bromoisobornyl formates was added in a third 100-ml. portion of acetic acid. The reaction mixture was stirred in an ice-bath for 9 hours, and then for an additional 1.5 hours as it was allowed to come to room temperature. It was diluted with 300 ml. of 50% saturated sodium chloride solution, extracted with 700 ml. of pentane in 8 portions, and the pentane solution was washed with water, 5% sodium carbonate solution and water, dried and concentrated. The crude product was distilled over a T right angle tube at 105° bath temperature (0.5 mm.) to give 17.45 g. (92.5%) of mixed bromocamphors, $[\alpha]^{32}D$ + 11.5° (*c* 2 in chloroform).

By gas chromatography the mixture consisted of 51.5% *cis*- and 48.5% *trans*-π-bromocamphor (Perkin–Elmer column A, 175°, helium flow 75 cc./min.; elution times 89 and 101 minutes, respectively); or 50.5% *cis* and 49.5% *trans* isomers (column K, 200°, helium flow 75 cc./min.; elution times 5.6 and 6.4 minutes). On column K a component having an elution time of 8.0 minutes and amounting to about 2% of the total was detected.

The π-bromocamphor mixture (1.59 g.) was recrystallized from hexane to give 500 mg. of first crop, m.p. 88–90.5°, $[\alpha]^{29}D$ −11°, and a second crop of 244 mg., $[\alpha]^{27}D$ +7°. The first crop was partially sublimed to give a waxy solid, m.p. 90.5–91°, soft 83°, $[\alpha]^{27}D$ −6.5° (*c* 2.5, chloroform). By gas chromatography on column K it was shown to consist of 64.5% *cis* and 34.5% *trans* isomers.

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 51.96; H, 6.54; Br, 34.57. Found: C, 52.20; H, 6.59; Br, 34.72.

(12) The *endo*-α-hydrogen is split by the 8-methylene group but not by the bridgehead hydrogen at C_4 thus giving rise to the observed triplet. W. D. Kumler, J. N. Shoolery and F. V. Brutcher, THIS JOURNAL, **80**, 2533 (1958), have reported the absence of splitting ($J \cong 0$) between the *endo*-α-hydrogen and the bridgehead hydrogen at C_4 in α-halocamphors. Dr. J. C. Martin of these laboratories has made similar observations with norcamphor derivatives (private communication). In addition the Karplus equation [M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959)] predicts a coupling constant of *ca.* 0 for this case.

(13) We are indebted to Mr. J. Nemeth and associates for microanalyses, to Mr. P. McMahon for infrared spectra and Mr. Ben Shoulders for nuclear magnetic resonance measurements.

***trans*-π-Bromoisoborneol.**—To a solution of 1.96 g. (0.0516 mole) of lithium aluminum hydride and 7.23 g. (0.0541 mole) of aluminum chloride in 75 ml. of ether was added 9.58 g. (0.0415 mole) *trans*-π-bromocamphor and the solution was refluxed for 2.5 hours. After the cautious addition of water to decompose the excess hydride, more water and a little 6 *N* hydrochloric acid were added to give two clear phases. Further work-up in the usual manner followed by atmospheric distillation of the ether solution gave 8.95 g. (93%) of *trans*-π-bromoisoborneol and *trans*-π-bromoborneol, m.p. 99–115°. Repeated recrystallization from hexane gave an analytical sample, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{10}H_{17}BrO$: C, 51.51; H, 7.35; Br, 34.28. Found: C, 51.69; H, 7.50; Br, 34.17.

Preparation of *cis*- and *trans*-π-Bromoisobornyl Formates from *trans*-π-Bromoisoborneol.—The crude *trans*-π-bromoisoborneol (7.89 g., 0.0388 mole), was dissolved in 40 ml. (49 g., 1.06 moles) of 98–100% formic acid and warmed under nitrogen for 10 hours at 70° and 11 hours at 60°. The deep violet solution was diluted with 300 ml. of ether–pentane (2:1) and washed four times with water followed by 10% sodium bicarbonate solution and saturated sodium chloride solution. There was obtained 8.09 g. of crude formate as a dark brown liquid. Distillation through a 30-cm. Holzmann column gave 5.70 g. (63.5%) of *cis*- and *trans*-π-bromoisobornyl formates, b.p. 83–85° (0.30 mm.), $n^{26}D$ 1.5099–1.5128. The pot residue, a dark brown tar, weighed 1.54 g. and accounted for 17% of the starting material (calculated as formate ester).

Oxidation of *cis*- and *trans*-π-Bromobornyl Formates from *trans*-π-Bromoisoborneol.—The total formate from above (5.70 g., 0.0216 mole) in 25 ml. of acetic acid was added to a cold solution of 17.3 g. (0.058 mole) of sodium dichromate hydrate and 3.4 g. (0.020 mole) of manganous sulfate hydrate in 7.8 ml. of water, 50 ml. of acetic acid and 9 ml. of concentrated sulfuric acid. The reaction mixture was stirred in an ice-bath for 12 hours after which 75 ml. of saturated sodium chloride solution was added and the solution extracted ten times with pentane (350 ml.). The pentane was washed twice with water, quickly with 10% sodium bicarbonate solution, again with water, and dried. Removal of the solvent at atmospheric pressure and sublimation of the residue gave 3.58 g. of a slightly wet solid. By gas chromatography this consisted of 53% *trans*- and 21% *cis*-π-bromocamphors, the latter representing a 9% yield from *trans*-π-bromocamphor. The remaining components chromatographed as two broad peaks, one having an elution time earlier and one later than the bromocamphors. The latter component chromatographed as expected for a hydroxy bromocamphane and may be the tertiary alcohol.

π-Iodotricyclene.—A solution of 7.00 g. of π-bromotricyclene in 250 ml. of dimethyl sulfoxide containing 120 g. of sodium iodide was heated to 105° under nitrogen for two days. The reaction mixture was extracted with pentane after adding water enough to dissolve the sodium iodide. Removal of the solvent gave 8.10 g. of a crude material which was distilled using a 30-cm. Holzmann column at 0.5 mm. to give a fraction, b.p. 50–55°, 1.0 g. of which solidified, m.p. 116–117°, and proved to be π-hydroxytricyclene by mixed melting point with an authentic sample. A higher fraction, b.p. 55°, gave 5.75 g. (67%) of pure iodotricyclene as shown by v.p.c. The infrared spectrum has an absorption at 3050(w) cm.$^{-1}$ characteristic for cyclopropane and no absorption in the double bond region.

Anal. Calcd. for $C_{10}H_{15}I$: C, 45.82; H, 5.77. Found: C, 46.08; H, 6.06.

***cis*- and *trans*-π-Iodoisobornyl Formates.**—A solution of π-iodotricyclene, 5.10 g., in 3 ml. of chloroform was stirred vigorously with 30 ml. of formic acid at 45–50° for 24 hours under nitrogen. The formic acid phase became violet in color shortly after heating was begun. The reaction mixture was diluted with water and extracted with ether. Removal of the solvent and distillation through a Holzmann column gave 5.21 g. (89%) of ester, b.p. 107–110° (0.65 mm.). The infrared spectrum determined in carbon tetrachloride showed characteristic absorptions at 1725(s) and 1160(s) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{17}IO_2$: C, 42.90; H, 5.57. Found: C, 43.10; H, 5.65.

***cis*- and *trans*-π-Iodocamphors.**—Oxidation of *cis*- and *trans*-π-iodoisobornyl formates was carried out in the same

manner as for the bromo analogs except that a nitrogen atmosphere was used. A semisolid material (1.74 g.) was obtained from 2.50 g. of the formates. The infrared spectrum (10% chf. solution) exhibited strong carbonyl absorption at 1748 cm.$^{-1}$, and vapor phase chromatography indicated that the crude product was a mixture of two similar compounds in the ratio 70:30. The major product was purified by treatment of the total mixture with potassium *t*-butoxide, and then recrystallization, and proved to be *trans*-π-iodocamphor, m.p. 64–66°, identical with an authentic sample. The minor component must then be the *cis* isomer.

π-Cyanotricyclene.—π-Bromotricyclene (5.4 g., 0.025 mole) and sodium cyanide (9.7 g., 0.2 mole) in 75 ml. of dimethyl sulfoxide were heated at 90° with stirring for 18 hours. The sodium cyanide soon dissolved; the mass solidified on cooling and was diluted with water, then extracted with three 100-ml. portions of pentane. The pentane solution was dried over sodium sulfate and evaporated. The crude nitrile (3.94 g., 98%) was dissolved in 10 ml. of pentane and cooled in a Dry Ice–acetone-bath. The nitrile crystallized readily. The solvent was removed by decantation and the process was repeated. The nitrile so obtained then was sublimed at 60° (0.1 mm.), a cold finger being used to collect the product. There was obtained 3.06 g. (75%) of the cyanotricyclene as waxy solid, m.p. 45–48°; infrared absorption at 2240, 858 cm.$^{-1}$ (carbon tetrachloride), $[\alpha]^{26}D$ −25.2° (absolute ethanol).

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.58; H, 9.05; N, 8.91.

π-Cyanobornyl Trifluoroacetate.—π-Cyanotricyclene (13.8 g., 0.086 mole) was dissolved in 50 ml. of trifluoroacetic acid at ice-bath temperature. The mixture, which became homogeneous after 15 minutes, was allowed to stand for 3 hours at ice-bath temperature and then for 16 hours at room temperature. The excess trifluoroacetic acid was removed under reduced pressure and the product was dissolved in ether, washed successively with water, 5% sodium carbonate and water. Removal of solvent yielded a brown viscous oil which was distilled.

Fractions 2–5 contained 15.9 g. (65%), infrared absorption at 1788, 1228, 1175–1152 (double peak) cm.$^{-1}$ (carbon tetrachloride), b.p. 84–91° (0.25 mm.), $n^{22.5}D$ 1.4424–1.4430.

(B) π-Cyanotricyclene (1.8 g., 0.011 mole) was treated with 5 ml. of pentane and 5 ml. of trifluoroacetic acid at 0–15° for 15 hours. Work up in the usual manner yielded 1.94 g. (crude) of product, which contained only 10–20% of the trifluoroacetate (estimated by infrared absorption spectrum) and largely unreacted cyanotricyclene.

(C) π-Cyanotricyclene (0.9 g., 0.0055 mole) was treated with 3 ml. of trifluoroacetic acid at 0–20° for 3 hours. There was obtained 1.1 g. of oil which contained about 50% of the trifluoroacetate as estimated by the infrared spectrum.

π-Cyanobornyl Acetate.—A mixture of π-cyanotricyclene (1.6 g., 0.01 mole) and *p*-toluenesulfonic acid (9.5 g., 0.05 mole) in 35 ml. of glacial acetic acid was stirred at room temperature for 25 hours. Complete solution occurred after about 20 minutes and the solution, which darkened gradually, became violet in color. The solution was diluted with water and extracted with ether. The ether solution was washed with water, 5% ice-cold sodium hydroxide and dried over sodium sulfate. The bornyl acetate (1.82 g., 82.5%) obtained after removal of ether had absorption at 1742, 1240 cm.$^{-1}$ (carbon tetrachloride).

π-Cyanobornyl Formate.—π-Cyanotricyclene (2.0 g., 0.0124 mole) was heated at 60–70° in 5 ml. of formic acid for 26 hours. The mixture was poured into ice-water and extracted with ether. The ether solution was washed with 5% sodium carbonate and with saturated salt solution. Removal of ether yielded 1.6 g. of oil, infrared absorption at 1730, 1170, 858 cm.$^{-1}$ (carbon tetrachloride). The crude product still contained unreacted tricyclene (by infrared spectrum and oxidation of the formate described later).

π-Cyanoborneol.—(A) The trifluoroacetate of cyanoborneol was saponified with 5% alcoholic potassium hydroxide at room temperature for 24 hours.

(B) The π-cyanobornyl acetate (1.82 g., 0.0082 mole) was saponified with 15% ethanolic potassium hydroxide at room temperature for 40 hours. The crude cyanoborneol (1.4 g., 95%) was obtained as crystalline material, infrared absorption at 3620, 3480 cm.$^{-1}$ (carbon tetrachloride).

π-Cyanocamphor.—Crude cyanoborneol was oxidized to a mixture of π-cyanocamphors with chromic acid–sulfuric acid–acetic acid for 6 hours at 25°. The mixture was diluted with water, extracted with ether and washed successively with water, 5% sodium carbonate and water. The crude product was dissolved in pentane–benzene and chromatographed on alumina. The first fraction eluted with pentane was unreacted cyanotricyclene. The *trans*-π-cyanocamphor was eluted with benzene and *cis*-π-cyanocamphor was eluted with benzene and ether mixture (4:1).

The *trans*-π-cyanocamphor obtained in this way was identical with authentic material prepared from *trans*-π-bromocamphor as described below and had m.p. 167–169°, $[\alpha]^{26}D$ +68.4° (ethanol); infrared maxima at 2240, 1750, 1420–1430, 1296, 962 and 764 cm.$^{-1}$.

cis-π-Cyanocamphor had m.p. 160–161°, $[\alpha]^{26}D$ −44.50 (ethanol); infrared maxima at 2240, 1750, 1420–1430, 945, 770(w) and 670(w) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 75.54; H, 8.53; N, 7.90. Found: C, 74.52; H, 8.74; N, 8.20.

The yield of the mixture of *cis*- and *trans*-π-cyanocamphors ranged from 63 to 90% and the ratio of *cis*/*trans* as determined by optical rotation of the mixture and by isolation from the chromatogram varied from 1.3 to 1.1, with very little dependence on the acid used for tricyclene cleavage; results with formate, trifluoroacetate and acetate esters were comparable. In the case of the formate the mixture of *cis*- and *trans*-π-cyanocamphors was obtained directly from the ester by oxidation with chromic acid–acetic acid–sulfuric acid at 40° for 17 hours.

***trans*-π-Cyano-*d*-camphor.**—A mixture of *trans*-π-bromo-*d*-camphor (4.6 g., 0.02 mole) and sodium cyanide (9.8 g., 0.2 mole) in 50 ml. of dimethyl sulfoxide was heated at 100° overnight. The mixture was diluted with water and extracted with ether–pentane mixture. The organic layer was washed with water, dried over sodium sulfate and evaporated. The dark residue was dissolved in ether and filtered through a column of alumina. The eluate was recrystallized from hexane to give 1.25 g. (39%) of the cyanocamphor, m.p. 167–169°, which was further recrystallized from methanol–water to yield 1 g. of the product, m.p. 167–168.5°, $[\alpha]^{26}D$ +56.7°. Sublimation of which gave pure *trans*-π-cyanocamphor, $[\alpha]^{26}D$ +68.4°, m.p. 168–169°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.74; H, 8.55; N, 8.17

3,8-Cyclocamphor.—Six grams of potassium was added to 180 ml. of dry *t*-butyl alcohol with stirring at room temperature. After the potassium had dissolved 18.0 g. of *cis* and *trans*-π-bromocamphor in 200 ml. of ether was added gradually. The reaction mixture was heated to reflux for 18 hours under nitrogen during which time a white precipitate formed gradually. The ethereal solution was concentrated under reduced pressure at room temperature, diluted with 200 ml. of water and extracted with 1 l. of pentane in 5 portions. The pentane solution was washed, dried over magnesium sulfate and concentrated very carefully to give 14.2 g. of semi-solid product. The crude material was distilled at a pressure of 1.2 mm. affording a fraction b.p. 50–60°, which solidified affording 5.2 g., m.p. 110–130°. Vapor phase chromatography showed it to be a mixture of 60% 3,8-cyclocamphor, 20% unidentified material and 20% *trans*-π-bromocamphor. A later fraction, b.p. 101–105°, gave 6.1 g. of *trans*-π-bromocamphor. The first fraction was sublimed at 80° at atmospheric pressure to give a solid, m.p. 142–145°. Vapor phase chromatography showed that this material consisted of 70% 3,8-cyclocamphor, 25% unidentified component and a small amount of *trans*-π-bromocamphor. An analytical sample of 3,8-cyclocamphor was prepared using vapor phase chromatography and showed m.p. 151–152.5°, $[\alpha]^{26}D$ −232° (in chloroform), negative Beilstein test, ν_{max} 1755 cm.$^{-1}$, no α-methylene band at 1420 cm.$^{-1}$, λ_{max} 280 mμ (ε, 61) in ethanol. The nuclear magnetic resonance spectrum is described in the discussion.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.61; H, 9.65.

Semicarbazone of 3,8-Cyclocamphor.—Fifty mg. of 3,8-cyclocamphor was treated with 37.5 mg. of semicarbazide hydrochloride and 19 mg. of potassium hydroxide over a

steam-bath for 8 hours; 38 mg. of a precipitate was formed. It was recrystallized from aqueous ethanol and then sublimed under 0.01–0.02 mm. at 130°. The analytical sample showed m.p. 218–220° dec.

Anal. Calcd. for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27. Found: C, 63.78; H, 8.27.

cis-π-**Bromocamphor.**—Seventy ml. of methylene chloride in a 200-ml. round-bottom flask was saturated with hydrogen bromide gas at 0° and 104 mg. of 3,8-cyclocamphor was added in 10 ml. of methylene chloride. After 30 minutes at 0°, the mixture was stored at room temperature for 10 hours. The reaction mixture was washed with 5% sodium carbonate, sodium chloride saturated solution and distilled water and the aqueous fraction was extracted with ether. The ethereal and methylene chloride solutions were combined, dried over magnesium sulfate and evaporated completely under aspirator pressure yielding 96 mg. of crude product. Recrystallization and sublimation under 0.01–0.02 mm. at 70° gave *cis*-π-bromocamphor, m.p. 121.5–122.5°, $[\alpha]^{26}D$ −95°, ν_{max} 1740 and 1420 cm.$^{-1}$, and λ_{max} 296 mμ (ε, 54).

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 51.95; H, 6.54; Br, 34.60. Found: C, 52.31; H, 6.72; Br, 34.97.

trans-π-**Hydroxycamphor.**—A solution of *trans*-π-acetoxycamphor[14] (49 g., 0.23 mole) in 500 ml. of 10% ethanolic potassium hydroxide was heated at reflux for one hour and then concentrated to 200 ml. and diluted with saturated salt solution. Extraction with several portions of ether, evaporation of the ether and recrystallization of the residual solid from hexane–benzene afforded 31.2 g. (85%) of hydroxy ketone, m.p. 238–240°.

trans-**Isoketopinic Acid (XII).**—To a solution of 40 g. of chromic anhydride, 67.5 g. of manganous sulfate hydrate and 12 ml. of concentrated sulfuric acid in 100 ml. of water was added slowly a solution of 16.8 g. of *trans*-π-hydroxycamphor in 300 ml. of water. After completion of the addition (*ca.* 1 hour addition time) the mixture was stirred and heated at 40–45° for 16 hours. Dilution with saturated salt solution and extraction with ether (three 150-ml. portions) removed the acid which then was purified by extraction with aqueous base, acidification, re-extraction and recrystallization from aqueous methanol. The yield of *trans*-isoketopinic acid, m.p. 248–251°, was 14 g. (77%).

d-cis-π-**Apoborneol-7-carboxylic Acid Lactone (IX).**—Isoketopinic acid (1.82 g., 0.01 mole) was dissolved in 50 ml. of reagent grade methanol and neutralized with 10% potassium hydroxide in methanol until just alkaline to phenolphthalein. Sodium borohydride (4 g., 0.104 mole) then was added portionwise, and the solution was stirred overnight at room temperature. The solvent was evaporated under aspirator pressure and the residue was taken up in water, acidified with dilute hydrochloric acid, saturated with salt and extracted with ether. The ether solution was dried over sodium sulfate and evaporated. The hydroxy acid (obtained as a colorless, crystalline solid) was dissolved in 20 ml. of trifluoroacetic acid and 5 ml. of concentrated sulfuric acid, and heated at reflux for 2.5 hours. Most of the trifluoroacetic acid was recovered by distillation (continued as long as the distillate formed easily; no attempt was made to remove all the trifluoroacetic acid). The product was dissolved in ether, washed with water, cold 5% sodium carbonate, and again with water, then dried over sodium sulfate and evaporated. The product was recrystallized from hexane and then sublimed at 150–170° (12 mm.). There was obtained 1.1 g. (66%) of the lactone, m.p. 190–196° (lit.[4] 190–191°), infrared absorption at 1765 cm.$^{-1}$ (chloroform). Other preparations gave yields ranging from 40–70%.

cis-**Isoketopinic Acid (XIII).**—The lactone IX (1.0 g., 0.06 mole) was oxidized by chromium trioxide (1.35 g., 0.0135 mole) in acetic acid (5 ml.) containing sulfuric acid (1.0 ml.) and water (2.5 ml.) at 40–45°. The reaction mixture was stirred at 40–45° for 30 hours, diluted with water and extracted with ether. The crude keto-acid (0.988 g.) obtained after evaporation of ether and acetic acid was recrystallized from aqueous methanol to yield 530 mg. (49%) of colorless crystals (as plates), m.p. 273–276°. Concentrating the mother liquor gave an additional 60 mg. of the keto acid, infrared absorption at 3460, 1740, 1695 cm.$^{-1}$ (chloroform). In other experiments, ethyl acetate–hexane proved to be a superior solvent for recrystallization.

Methyl *cis*-**Isoketopinate.**—To the *cis*-keto-acid dissolved in ether was added an ethereal solution of diazomethane until a pale yellow color persisted. The solution was allowed to stand for 30 minutes, then treated with dilute hydrochloric acid, washed with water and dried over sodium sulfate. There was obtained 180 mg. (92%) of the methyl ester which was recrystallized from aqueous methanol. The methyl ester (126 mg., 65%) had m.p. 73–75°; infrared absorption at 1750, 1728 cm.$^{-1}$ (carbon tetrachloride).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.30; H, 8.22. Found: C, 67.56; H, 8.34.

URBANA, ILL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, TEXAS TECHNOLOGICAL COLLEGE]

The Oxidation of Hydrocarbons. III. The Decomposition of Acetyl Peroxide in Cyclohexene Solutions

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The thermal decomposition of acetyl peroxide in cyclohexene solution at 80° and at reflux temperature has been studied. The decomposition does not give the approximately quantitative yield of carbon dioxide that is usually associated with decomposition of this peroxide in solution. Instead, only 65–75% of the expected carbon dioxide is obtained. At the same time there are obtained 1,1′-bi-2-cyclohexenyl and an approximately 20% yield of a mixture of 3-cyclohexenyl acetate and cyclohexyl acetate. Thus, these two esters account, approximately, for the missing carbon dioxide. The predominant component of the ester mixture is the saturated ester. This unique result from a decomposition of acetyl peroxide is most simply explained by the reactions of acetoxy radicals. That is, contrary to the general belief regarding acetoxy radicals, it appears that they are not necessarily so unstable that they must decompose either prior to or during reaction with another entity.

It was found by Shine and Snyder[1] that, in the oxidation of cyclohexene in acetic anhydride solution under free-radical initiation, one of the products formed was cyclohexyl acetate. Although it is stated that small amounts of cyclohexyl acetate are formed by boiling cyclohexene in acetic anhydride solution,[2] it was felt that the large amount of cyclohexyl acetate obtained under the relatively gentle conditions of the free-radical work, and that the marked influence of acetic anhydride on the rate of oxidation of cyclohexene, were best interpreted as being due to reactions involving free acetoxy

(1) H. J. Shine and R. H. Snyder, THIS JOURNAL, **80**, 3064 (1958).

(2) H. Friese and D. Djiang, *Ber.*, **71B**, 667 (1938).