Oxidation of 3.—A 75% aqueous acetone solution containing 5.3 mmole (900 mg.) of **3** was refluxed with excess potassium permanganate (12 mmole) for 5 hr. The manganese dioxide was filtered and leached with 10% sodium bicarbonate solution and ether. Layers of the filtrate were separated. Acidification of the aqueous layer gave 5.1 mmole (840 mg., 95% yield) of tricyclenic acid, identified by its infrared spectrum. Characterization of the neutral components isolated from the ether extracts is in progress.

Camphene Hydrochloride (2).—The compound, prepared by the method of Nevell,[21] showed a distinctive set of infrared absorption peaks at 9.02, 9.23, 9.41, and 9.72 μ.

Acknowledgment.—Part of this work was accomplished through the combined and dedicated efforts of the following undergraduates: Edward Sun, Phillip Engel, Virginia Hooper, Kenneth Kenyon, Steven Dolberg, Nina Stein, Petty Brown, William Quinn, Frank Anderson, Benjamin Graeme Fincke, Carol Stone, and Donna Stevenson. We wish to thank M. Z. Naser and J. M. Lehn for their help in the interpretation of n.m.r. spectra and to acknowledge with gratitude financial support from the National Science Foundation (Undergraduate Research Participation) and the Petroleum Research Fund of the American Chemical Society.

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[21] T. Nevell, E. deSalas, and C. Wilson, *J. Chem. Soc.*, 1188 (1939).

Chlorination Products of Camphene[1]

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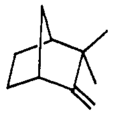
Reaction of camphene and chlorine in carbon tetrachloride containing sodium bicarbonate according to the procedure of Tishchenko gave a small monochloride product of which 10-chlorotricyclene (**3**) was the major component. *exo*-2,10-Dichlorobornane (**16**) was the largest reaction product.

Reaction of camphene (**1**) and chlorine in organic solvents leads to product mixtures that contain monochlorides and trichlorides as well as dichlorides.[3] Two surprising reports have appeared of the composition of the monochloride portion of the product obtained from such a reaction.[5,6]

Tishchenko added chlorine to a solution of camphene in carbon tetrachloride containing suspended sodium bicarbonate.[5] Distillation gave a monochloride fraction that on the basis of its reactions he concluded must consist of **2** (*cis* and *trans*), **3**, and **4**. This monochloride mixture was treated with potassium acetate under conditions that caused only partial reaction yielding a chloride fraction, said to contain recovered **2** and **3**, and an acetate fraction. Saponification of the acetate fraction gave camphenol which was assigned structure **5** on the basis of oxidation and rearrangement reactions; it was assumed that its chloride and acetate precursors had structures **4** and **6**.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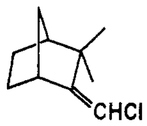

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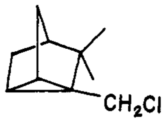

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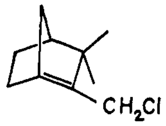

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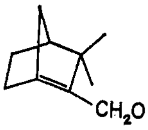

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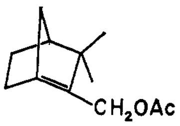

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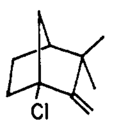
Chiurdoglu, Goldenberg, and Geeraerts concluded, principally on the basis of infrared spectra, that the monochloride fraction prepared in the same manner as by Tishchenko consisted of **2**, **3**, and **7**, that reaction with potassium acetate gave a mixture of **8** and **9**, and that saponification of the acetate mixture gave a mixture of **10** and **11**.[6] They prepared the known chloride **7**[7] and claimed that all bands of its infrared spectrum appeared in the spectrum of the monochloride fraction. Treatment of **7** with potassium acetate was said to lead to **8**, all bands in the infrared spectrum of which appeared also in the spectrum of the acetate mixture. Further publications by Tishchenko[8] and by Chiurdoglu, Goldenberg, and Geeraerts[9] discussed the discrepancies between their conclusions but did not report additional experimental information.



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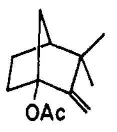

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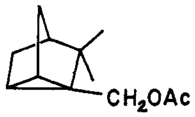

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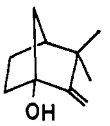

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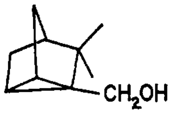

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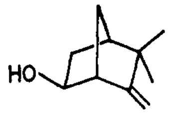

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Neither **4** nor **7** seem to be reasonable structures for a reactive component of the monochloride mixture.[10] Structure **4** violates Bredt's rule and **7**, having a bridgehead chlorine, would not be expected to react rapidly with potassium acetate. We have already demonstrated that camphenol is **12** rather than **5**, **10**, or **11**.[10] This paper describes a study of the composition of the chlorides obtained from camphene using

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[1] Some of this work is contained in the Senior Theses of T. J. G. (June 1962) and D. L. D. (June 1963), The Pennsylvania State University.

[2] Alfred P. Sloan Foundation Research Fellow.

[3] A summary of early work has been published.[4]

[4] J. L. Simonsen, "The Terpenes," 2nd Rev. Ed., Cambridge University Press, Cambridge, 1949.

[5] D. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **23**, 1051 (1953).

[6] G. Chiurdoglu, C. Goldenberg, and J. Geeraerts, *Bull. soc. chim. Belges*, **66**, 200 (1957).

[7] H. Meerwein and R. Wortmann, *Ann.*, **435**, 190 (1924).

[8] D. V. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **27**, 2943 (1957).

[9] G. Chiurdoglu, C. Goldenberg, and J. Geeraerts, *ibid.*, **28**, 1086 (1958).

[10] H. G. Richey, Jr., T. J. Garbacik, D. L. Dull, and J. E. Grant, *J. Org. Chem.*, **29**, 3095 (1964).

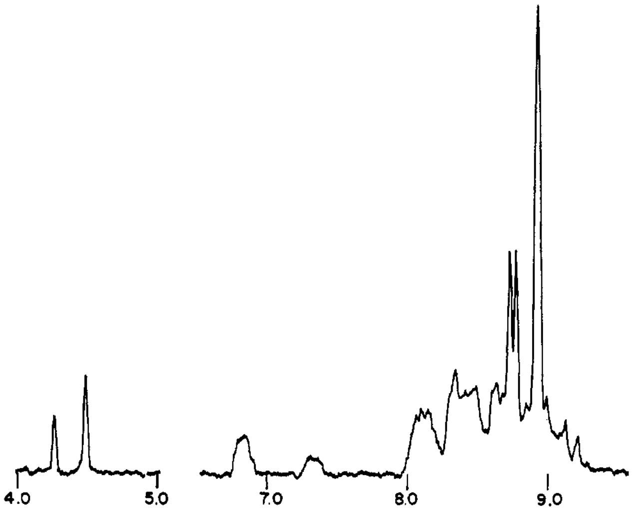


Figure 1.—The n.m.r. spectrum of a carbon tetrachloride solution of **2**.

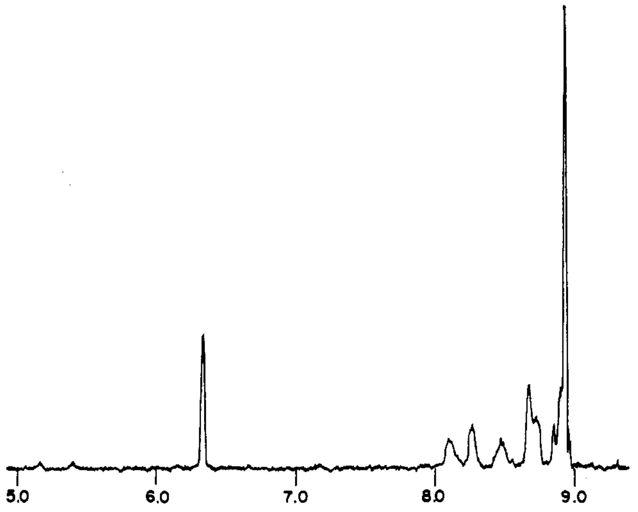
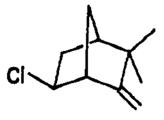


Figure 2.—The n.m.r. spectrum of a carbon tetrachloride solution of **3**.

Tishchenko's procedure. We were interested primarily in identifying the components in the monochloride fraction and, in particular, the reactive compound or compounds. Therefore, we ran the chlorination only as described by Tishchenko, adding chlorine (0.6 mole/mole of camphene) to very concentrated solutions of camphene in carbon tetrachloride containing suspended sodium bicarbonate. Jennings and Botyos have independently studied the chlorination of camphene under more varied conditions. In the preceding paper[11] they describe the composition of the reaction products obtained by adding varying amounts of chlorine to dilute solutions of camphene in carbon tetrachloride both in the presence and absence of sodium bicarbonate.

We conclude that **3** was the only monochloride present in significant amounts in the chlorination product. This conclusion is based on n.m.r. and infrared spectra of the chlorination product before distillation and of the monochloride fraction and individual components obtained from it by gas–liquid partition chromatography (g.l.p.c.). Samples of **2**, **3**, **7**, and **13** were prepared for comparison purposes. N.m.r. spectra (Figures 1–4) and infrared spectra were in accord with their assigned structures. The n.m.r. spectra were particularly characteristic, confirming the purity of these chlorides and greatly facilitating the identification of the composition of mixtures.



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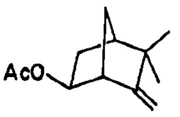

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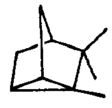

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Chloride **13** constituted as much as 87% of the monochloride distillates. However, it apparently was a secondary product that arose from isomerization of **3** after the initial chlorination. The n.m.r. spectrum of the chlorination product before distillation showed absorption due to **3** but none of the characteristic absorptions of **13**. In fact, samples of **3** rearranged slowly to **13** on standing (half-time about 6 months) at room temperature and much more rapidly at higher temperatures or in the presence of small amounts of added ferric chloride. Attempted g.l.p.c. of **3** gave only one peak which on collection proved to be due to **13**. Some monochloride distillates did contain substantial amounts of **3**, but this compound slowly disappeared and the amounts of **13** in the samples increased proportionately. Though **13** has not been described previously,[12] the ready isomerization of **3** to **13** suggests that some of the reported preparations[13–15] of **3** may have contained **13**. The preparation of this monochloride by rearrangement of **3** and in some attempted conversions of **11** to **3** suggested **13** as the most reasonable structure. The n.m.r. spectrum (Figure 4) was consistent with this structure, exhibiting sharp peaks at τ 5.08 and 5.34 ($=CH_2$), a multiplet at 6.20 (H—C—Cl), and a peak at 7.18 (allylic bridgehead H). The infrared spectrum had absorptions at 885, 1650, and 3090 cm.$^{-1}$ characteristic[16] of an exocyclic methylene group.

The monochloride distillates contained as little as 11% of **2**. Further heating of the higher boiling material left after distillation of the monochlorides produced considerable amounts of **2**. Therefore, the small amounts of **2** in the monochloride distillates may have formed from decomposition of higher boiling products. The samples of **2** obtained from the monochloride fraction and from a known preparation[17] of **2** were identical mixtures of *cis* and *trans* isomers in a ratio of about 1:2. In the n.m.r. spectrum (Figure 1) the bands at τ 4.50 ($=CH_2$), 6.83 (allylic bridgehead H), and 8.92 (methyl H's) are due to one isomer and those at τ 4.25 ($=CH_2$), 7.33 (allylic bridgehead H), and 8.73 and 8.78 (methyl H's) to the other isomer.[18]

Absorptions of **7** (Figure 3) were not detected in n.m.r. spectra of the crude reaction mixtures before distillation nor in the monochloride distillates. G.l.p.c. of monochloride distillates did not give a peak with the

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(11) B. H. Jennings and G. L. Botyos, *J. Org. Chem.*, **30**, 3902 (1965).

(12) A compound to which structure **13** once was assigned[7] later was shown to be 4-chlorocamphene.[4]

(13) M. Hanack and H. Eggensperger, *Ann.*, **648**, 3 (1961).

(14) G. Komppa, *Ber.*, **62**, 1366 (1929).

(15) P. Lipp, *ibid.*, **53**, 769 (1920).

(16) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, Chapter 3.

(17) G. Langlois, *Ann. chim.* (Paris), [IX] **12**, 193 (1919).

(18) The isomer present in larger amount probably has the chlorine *trans* to the *gem*-dimethyl group at C-3. The n.m.r. spectrum[19] of 8-bromocamphene (prepared in the same manner as authentic **2**) is reported to contain only one absorption in the vinyl hydrogen region and must be the *trans* isomer.

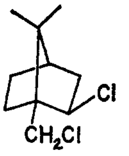
(19) J. Wolinsky, *J. Org. Chem.*, **26**, 704 (1961).

retention time of **7**. This chloride did not react significantly when treated with potassium acetate using Tishchenko's conditions,[5] and therefore could not have been a reactive component of the monochloride fraction. The previous report of conversion of **7** to **8** did not specify the reaction conditions.[6]

Products obtained from treating the monochloride distillates with potassium acetate were separated by distillation into monochloride and acetate fractions.[5,10] The acetate obtained from monochloride distillates containing only **2** and **13** was **14**; a monochloride fraction also containing **3** probably furnished acetate **9** in addition to **14**. The monochloride fractions contained only **2**.

The C-6 substituents of **13** and **14** (and therefore **12**) are presumably *exo* rather than *endo* because formation of the *exo* isomers is more reasonable mechanistically.[20] This assignment is confirmed by the n.m.r. absorptions of the allylic bridgehead H's of these compounds. These absorptions did not exhibit a splitting of about 4 c.p.s. that would be expected for coupling with an *exo* H[21] and therefore the C-6 substituents must have been *exo*.[22]

The monochloride fraction obtained from camphene and chlorine using Tishchenko's procedure accounted for less than 15% of the chlorine. The remainder of the product was a mixture of higher boiling materials; a dichloride to which Tishchenko[25] assigned the structure of **16** constituted more than one-half of this mixture. The n.m.r. spectrum had a multiplet at 5.88 (H–C–Cl) and sharp peaks at τ 8.83 and 9.05 (methyl H's). An AB pattern with $\delta_A = 6.11$ and $\delta_B = 6.54$ τ ($J_{AB} = 11$ c.p.s.) was assigned to the two hydrogens of the chloromethyl group; different chemical shifts are expected for these hydrogens since the methylene group is adjacent to an asymmetric carbon.[26] It is assumed that the chlorine at C-2 is *exo* as shown rather than *endo*[27] because of the mode of preparation of this dichloride.[20]



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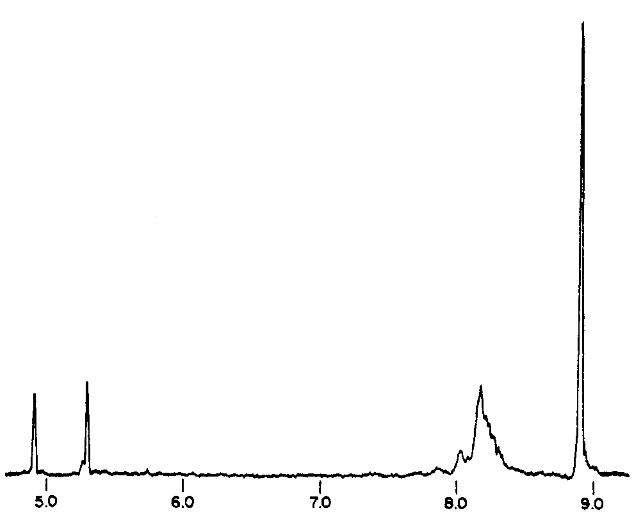

Figure 3.—The n.m.r. spectrum of a carbon tetrachloride solution of **7**.

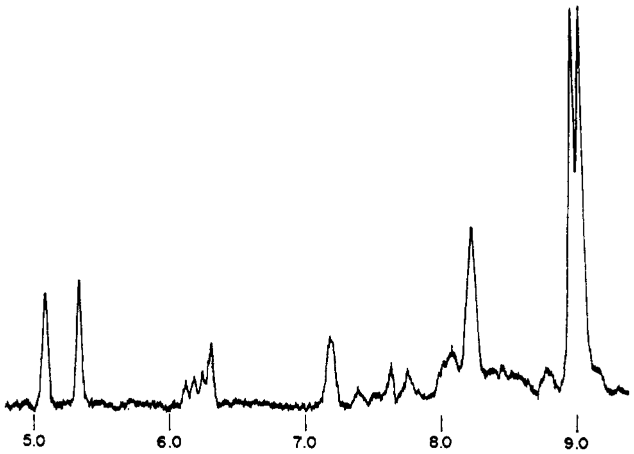

Figure 4.—The n.m.r. spectrum of a carbon tetrachloride solution of **13**.

The chlorination products of camphene therefore are unexceptional. The reactive components of the previously studied[5,6] monochloride distillates probably were mixtures of **3**, a primary product of the chlorination, and **13**, arising from isomerization of **3**.

Experimental Section

Spectra are of carbon tetrachloride solutions. N.m.r. spectra were taken at 60 Mc.; chemical shifts are given in parts per million relative to tetramethylsilane at 10.0. Distillations were done with a platinum, spinning-band column unless otherwise noted. An 8 ft. × 0.25 in. column packed with 21% silicone oil 550 (Dow Corning) on 60–80-mesh Chromosorb P (Johns-Manville) was used for g.l.p.c. separations. Melting points were taken in capillary tubes.

Reaction of Camphene (1) and Chlorine.—Camphene (Eastman) was distilled before use. G.l.p.c. analysis (105°, flow rate 30 ml./min.) showed a small peak with a retention time of 0.27 relative to camphene as 0.32. Infrared and n.m.r. spectra of collected samples of the material causing this additional absorption indicated that it was **15**. There was no evidence for other impurities in the camphene. Chlorine (about 0.6 mole/mole of camphene) was added to mixtures of camphene, sodium bicarbonate, and carbon tetrachloride of the same composition

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[20] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 126–133.

[21] P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964), and references cited therein.

[22] *exo* configurations have been assigned on the same basis[23] to 6-bromocamphene, prepared[23,24] from reaction of *n*-bromosuccinimide and tricyclene (**15**), and to **12**.

[23] N. Gaitonde, P. A. Vatakencherry, and S. Dev, *Tetrahedron Letters*, **No. 30**, 2007 (1964).

[24] A bromide, prepared from **11** and phosphorus tribromide using Lipp's procedure [P. Lipp, *Ber.*, **80**, 165 (1947)], even before distillation exhibited identical n.m.r. absorption confirming Lipp's assignment of 6-bromocamphene (rather than 10-bromotricyclene) as its structure. However, a quite similar preparation has recently been reported to give 10-bromotricyclene [F. Dallacker, K. Ulrichs, and M. Lipp, *Ann.*, **667**, 50 (1963)].

[25] D. Tishchenko and I. Uvarov, *J. Gen. Chem. USSR* (Eng. Transl.), **23**, 1473 (1953).

[26] The spectrum of 2,10-dibromobornane was reported to show a quartet for the hydrogens of the bromomethyl group.[19] We prepared this compound and found an AB pattern with $\delta_A = 6.27$ and $\delta_B = 6.57$ τ ($J_{AB} =$ 10 c.p.s.).

[27] A compound thought to be *endo*-2,10-dichlorobornane has been described[28]; its infrared spectrum is different from that of our compound. The 2,10-dichlorobornane structure has also been assigned to a compound prepared by treating **11** with hydrochloric acid. We prepared this compound and found in the n.m.r. spectrum a multiplet at τ 5.90 (H–C–Cl) and sharp peaks at 8.40, 8.78, and 9.05 (methyl H's). This compound may be the hydrochloride of **13**; it has been shown[28] not to be compound thought to be *endo*-2,10-dichlorobornane.

[28] C. T. Bothner-By, Ph.D. Thesis, New York University, 1950.

used by Tishchenko.[5] Distillation at reduced pressure of a typical reaction product gave a forerun, consisting principally of camphene, followed by the monochloride fraction in 12% yield (on the basis of chloride), b.p. 72–74° (4 mm.), lit. b.p. 60–61[5] (2 mm.) and 60–64[6] (0.6 mm.). The solid pot residue accounted for 74% of the chlorine (assuming that it consisted only of dichlorides). Absorptions of **16** accounted for more than one-half of the absorption in the n.m.r. spectrum of this solid.

N.m.r. and infrared spectra of the distilled monochloride fraction usually indicated that it consisted principally of **13**, though some preparations also contained considerable amounts of **3**. G.l.p.c. analysis (130°, flow rate 25 ml./min.) of the monochloride fraction above gave the peaks described in Table I.

TABLE I

Peak	Relative retention time	% of total[a]
1	0.32	<1
2	0.83	<2
3	1.00[b]	87
4	1.17	11

[a] It was assumed that peak areas were proportional to molar amounts. [b] This peak had a retention time of 43 min.

Peak 1 had the same retention time as camphene. The infrared spectrum of material collected from peak 2 exhibited a strong absorption in the infrared at 1740 cm.$^{-1}$; this material was not investigated further. Peak 3 had the same retention time as **13** and collected material had an infrared spectrum identical with that of the authentic material. The retention time of peak 4 and the infrared spectrum of collected material indicated that it was **2**.

A sample of **7** had a retention time of 0.97 (relative to 1.00 for **13**), but such a peak was not observed for the monochloride fractions. N.m.r. and infrared spectra of monochloride fractions also indicated the absence of **7**.

In one experiment, 58.8 g. of the solid pot residue remaining from distillation of the monochloride fraction was refluxed for 63 hr. at atmospheric pressure. Distillation yielded 16.3 g. of liquid at 66–68° (3.5 mm.). The n.m.r. and infrared spectra of the distillate were virtually identical with those of **2**.

In one chlorination experiment, n.m.r. and infrared spectra were taken of the filtered solution before distillation. The spectra indicated the presence of considerable amounts of camphene (and small amounts of tricyclene); the remainder of the absorption was consistent with that of a mixture containing about 10% of **3**, 50% of **16**, and 40% of unidentified materials. Absorptions due to **2**, **7**, and **13** were not apparent (though amounts of less than 1% would not have been detected).

Reaction of the Monochloride Fraction with Potassium Acetate.—We have already described this preparation[10] carried out according to the instructions of Tishchenko.[5] The n.m.r. and infrared spectra as well as g.l.p.c. of recovered chloride fractions showed that they consisted almost entirely of **2**. The n.m.r. spectrum of an acetate fraction obtained from a monochloride distillate containing only **2** and **13** indicated that it consisted mostly of **14**. The spectrum showed sharp singlets at τ 5.05 and 5.32 (=CH_2), a multiplet at 5.50 (H—C—O), a band at 7.28 (allylic bridgehead H), and sharp peaks at 8.05 (O=C—CH_3) and 8.93 (*gem*-dimethyl H's), all of the appropriate areas. The acetate fraction prepared from a monochloride distillate that contained **3** in addition to **2** and **13** probably also contained **9**; the n.m.r. spectrum showed additional singlets at τ 5.88 (CH_2O) and 9.08 (*gem*-dimethyl H's).

10-Chlorotricyclene (3).—Tricyclenol (**11**, 6.8 g., 0.045 mole) was dissolved in a solution of 125 ml. of ether containing 15 ml. (0.19 mole) of pyridine. Thionyl chloride (5.3 g., 0.045 mole) was added dropwise over several minutes to the stirred solution which was maintained at −10°. The solution was allowed to warm to room temperature for 2 hr. and then was refluxed for 20 min. The mixture was poured into 200 ml. of water and extracted with two 100-ml. portions of pentane. The pentane solution was dried over sodium sulfate. Distillation gave 3.1 g. (40%) boiling between 44 (1 mm.) and 37° (0.75); lit. b.p. 82[13] (11 mm.), 75–76[14] (6 mm.), and 81–82.5[15] (11 mm.). Figure 2 shows the n.m.r. spectrum of this compound. G.l.p.c. analysis of **3** gave a single peak with the same retention time as **13**; collected material had an infrared spectrum identical with that of **13**.

Preparation of **3** from **11** and phosphorus pentachloride[13] gave a product that contained significant amounts of **13** and a preparation using triphenylphosphine dichloride[29] gave a product that contained mostly **13**.

6-Chlorocamphene (13).—This chloride was obtained as the product of thermal isomerization of **3**; the isomerization was accelerated by traces of ferric chloride. The following procedure gave **13** uncontaminated by **3**.[30] Tricyclenol (**11**, 1.75 g., 0.012 mole) was dissolved in a solution of 25 ml. of anhydrous ether and 0.91 g. (0.012 mole) of pyridine. The solution was cooled to −10° and 0.68 g. of thionyl chloride (0.006 mole) was added dropwise over several minutes to the stirred solution. The mixture was allowed to warm to room temperature over 2 hr. The mixture was filtered and the solvent was removed at reduced pressure from the filtrate. Thionyl chloride (0.68 g., 0.006 mole) was added to the residue and the mixture was heated at 70° for 16 hr. Pentane (30 ml.) was added, the mixture was filtered, and the filtrate washed with dilute aqueous bicarbonate and dried over sodium sulfate. Distillation from a Claisen apparatus gave 0.53 g. (27%) of **13**, b.p. 43–46° (0.25 mm.). The n.m.r. spectrum is shown in Figure 4.

Anal. Calcd. for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.14; H, 8.82; Cl, 20.66.

8-Chlorocamphene (2).—This chloride was prepared according to the procedure of Langlois,[17] b.p. 82–84° (11 mm.), lit.[17] b.p. 95–98° (15 mm.). The n.m.r. spectrum is shown in Figure 1.

1-Chlorocamphene (7).—This chloride was prepared from 2,2-dichlorobornane,[7] b.p. 74–75° (3.5 mm.), lit. b.p. 193–197°[7] (1 atm.) and 72–73[31] (12 mm.). The n.m.r. spectrum is shown in Figure 3.

Attempted Reaction of 1-Chlorocamphene (7) and Potassium Acetate.—A sample of **7** was refluxed with a solution of potassium acetate in acetic acid using the procedure described by Tishchenko[5] for reaction with the monochloride fraction. The material, recovered in 94% yield, had n.m.r. and infrared spectra virtually identical with those of **7**.

***exo*-2,10-Dichlorobornane (16).**—The pot residue from the reaction of chlorine and camphene was distilled and a cut that solidified was collected at 93–95° (1 mm.). Recrystallizations from ethanol gave **16**, m.p. 132–134°, lit.[25] m.p. 133–134°. It was difficult to free this compound from other materials present in the distillate. The other compounds in the pot residue were not investigated.

Anal. Calcd. for $C_{10}H_{16}Cl_2$: C, 57.98; H, 7.79; Cl, 34.23. Found: C, 57.82; H, 7.59; Cl, 33.78.

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(29) The reaction was based on the procedure of G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

(30) The reaction was based on the procedure of M. J. Frazer, W. Gerrard, G. Machell, and B. D. Shepherd, *Chem. Ind.* (London), 931 (1954).

(31) J. Houben and E. Pfankuch, *Ann.*, **501**, 219 (1933).