The pyrolysis products obtained at 800° were separated quantitatively on the v.p.c. column described above and were collected for analysis. FA, m.p. 71–72° (for biphenyl, lit.[25] m.p. 69–71°), 0.4 g., was identified as biphenyl by melting point of admixture with a synthetic sample, by infrared spectrum, and by elution behavior on a v.p.c. column.

Fraction B, 0.2 g., had a melting point, after recrystallization from methanol, of 119–120° (lit.,[24] for *p*-bitolyl, m.p. 121°). The melting point of this sample was not depressed upon admixture with *p*-bitolyl; its infrared spectrum and elution behavior from a v.p.c. column were identical with those of *p*-bitolyl.

FC was *p*-toluenesulfonic acid, m.p. 102 (lit.[26] m.p. 102). The sample was further identified by comparison of its infrared spectrum with that of a synthetic sample and by melting point of admixture.

B. **Pyrolysis of Solid *p*-Carbomethoxyphenyl Sulfone.**—Experimental arrangements were as in the previous experiment. The infrared spectra of the sample pyrolyzed at 750° indicated [total sample removed was 2.9 g. (wet), *ca.* 100%] that the $-SO_2-$ band at 7.80 μ decreased in relation to the $-CO_2CH_3$ band at 5.82 μ from a ratio of 0.97 to a ratio of 1.52. The reaction mixture was leached with 200 ml. of benzene for 2 days at 25°. The insoluble material was filtered and dried at 25° and 0.1 mm., yielding 30 mg., m.p. 230–232°. The infrared spectrum of this substance was identical with that of *p*-bibenzoic acid dimethyl ester, and the melting point of the sample was not depressed upon admixture with a reference sample.

Preparation of *p*-Carbomethoxyphenyl Sulfone.—The *p*-tolyl sulfone was oxidized according to the method of Bennett[27]: to 27.6 g. (0.1 mole) of *p*-tolyl sulfone was added 100 ml. of 35% nitric acid and the reaction mixture was heated in an autoclave with stirring for 3 hr. at 200° under an initial nitrogen pressure of 150 lb. The reaction mixture was cooled to room temperature, filtered, washed on the filter with water, and air dried: 35 g. (~100% conversion). Without further purification the solid was added to 300 ml. of methanol (absolute), 30 ml. of concentrated sulfuric acid was added, and the methanol–water mixture was gradually distilled off with intermittent addition of fresh absolute methanol. A total of 300 ml. of methanol was collected.

The reaction mixture was then cooled to room temperature and was filtered. The pinkish solid was extracted with benzene in a Soxhlet for 2 days and the benzene extracts were concentrated with nitrogen, cooled to 0°, and filtered, yielding 13.5 g. (0.040 mole) of the ester (after drying in a vacuum oven at 50° and 0.1 mm.), m.p. 192–196° (for the ester, lit.[27] m.p. 194°). The infrared spectrum exhibited a typical ester band at 5.79 μ.

Anal. Calcd. for $C_{16}H_{14}O_6S$: C, 57.48; H, 4.22. Found: C, 57.65; H, 4.53.

The benzene-insoluble material was treated with 0.2 mole of sodium bicarbonate in 200 ml. of water and the solution was filtered. The filtrates were acidified; the acid was filtered and was dried at 50° and 0.1 mm., giving 8.7 g. (0.026 mole) or 66% total conversion to both ester and acid.

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(25) F. J. Garrick, *Trans. Faraday Soc.*, **23**, 561 (1927).

(26) J. M. Crafts, *Ber.*, **34**, 1312 (1901).

(27) F. Bennett, unpublished results.

The Chlorination of Camphene

BOJAN H. JENNINGS AND GEORGENE B. HERSCHBACH

Departments of Chemistry, Wheaton College, Norton, Massachusetts, and
Harvard University, Cambridge, Massachusetts

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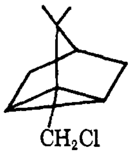
Chlorination of camphene with molecular chlorine in carbon tetrachloride at 0° gives a mixture of mono-, di- and polychlorides, the composition of which has been shown to vary systematically with the quantity of chlorine introduced. The main product found under all conditions studied is the Wagner–Meerwein related dichloride, *exo*-2,10-dichlorobornane (**5**). Primary monochloro products are camphene hydrochloride (**2**), 10-chlorotricyclene (**3**), and *cis*- and *trans*-8-chlorocamphene (**4**). An additional monochloride, *exo*-6-chlorocamphene (**6**), which is found in the liquid distillates of the product mixture, has been shown to result from thermal rearrangement of 10-chlorotricyclene. Details of the chlorination as well as physical and chemical properties of the products are discussed.

Work on the dark chlorination of camphene (**1**) dates back to 1919 when Langlois[1] reported that the main chlorination product is 8-chlorocamphene (**4**). Tishchenko[2] reinvestigated this system in 1953 and maintained that the liquid monochloro fraction reported by Langlois consisted of three compounds to which he assigned structures **3**, **4** and **9**. In addition he isolated a solid dichloride which he reported[3] as **5**. Tishchenko never obtained pure samples of the monochloro compounds but based his assignments on chemical conversions of mixtures of the three materials.



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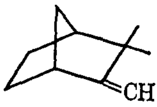

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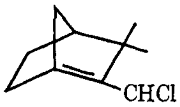

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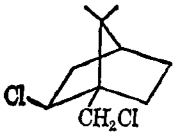

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In the case of **9**, for instance, he reported[2] having converted the chloride mixture to the corresponding alcohol, camphenol, from which he prepared a biphthalate derivative, which he subsequently oxidized to a diketo alcohol, $C_{10}H_{16}O_3$. That **9** was an allyl chloride was deduced from the observation that the product mixture contained very active chlorine.

In 1957 Chiurdoglu, *et al.*,[4] vigorously objected to Tishchenko's structure **9**, pointing out that it violated Bredt's rule. In the same publication these authors proposed the equally improbable structure **10** for Tishchenko's active chloride. They used infrared spectra as their main evidence.

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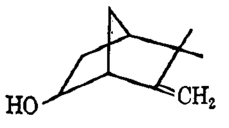
(1) G. Langlois, *Ann. chim.*, **12**, 193 (1919).

(2) D. Tishchenko, *Zh. Obshch. Khim.*, **23**, 1002 (1953); *J. Gen. Chem. USSR*, **23**, 1051 (1953).

(3) D. Tishchenko and I. Uvarov, *Zh. Obshch. Khim.*, **23**, 1407 (1953).

(4) G. Chiurdoglu, Ch. Goldenberg, and J. Gerraerts, *Bull. soc. chim. Belges*, **66**, 200 (1957).



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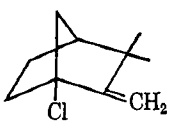

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Tishchenko[5] immediately vetoed the proposed Chiurodoglu structure. He pointed out that it did not fit his oxidation data; furthermore, as a bridgehead chloride, it would be inert toward substitution, a property quite contrary to the behavior exhibited by the monochloride. Tishchenko, however, neither put forward another structure nor withdrew his original suggestion.

The problem of the structures of camphene chlorination products thereupon lay dormant until recently when both we and Richey[6] independently reinvestigated it using modern physical methods. Richey has shown that Tishchenko's camphenol is in fact 6-hydroxycamphene (**7**) for which he assumed *exo* orientation of the hydroxyl group, an assignment confirmed by Gaitonde[7] from the n.m.r. spectrum of the alcohol. Our findings on camphenol as well as its parent chloride are in complete agreement with those of Richey; furthermore we have independently studied the entire chlorination reaction. Our results, which lead to the formulation shown in Figure 1, are discussed below.

Results and Discussion

The Chlorination Reaction.—Reactions were carried out at 0° in the dark by leading dry chlorine into 50 ml. of carbon tetrachloride containing 0.1 mole of camphene (**1**). The amount of gas was carefully measured (flow rate) and increased over a series of ten reactions from 0.03 mole (610 ml.) to 0.24 mole (5300 ml.). The course of the reaction was not affected by the rate at which the gas was added to the camphene solution, but both the nature and amounts of product were highly dependent on the quantity of chlorine introduced.

The infrared spectra of crude product solutions were examined for intensity changes in certain characteristic absorption bands found in the spectra of pure chloro derivatives previously isolated or prepared independently. Many of the runs were duplicated using carbon disulfide as solvent in order to study the critical infrared region, 12–14 μ. It was thus shown that camphene hydrochloride (**2**), 10-chlorotricyclene (**3**), and *exo*-2,10-dichlorobornane (**5**) were primary products. 8-Chlorocamphene (**4**) could not be detected directly by infrared analysis, for its characteristic absorption bands were masked by those of **2** and **5**. Another series of experiments described below established that **4** is also a primary product.

Distillation was accompanied by evolution of hydrogen chloride. Rapid distillation gave fractions boiling from 75 to 100° (12 mm.), whose infrared spectra showed the presence of **1**, **3**, and **4**. Residues of runs using up to 0.13 mole of chlorine to 0.1 mole of camphene consisted mainly of **5**; when more chlorine was used, distillation residues contained polychlorinated materials.

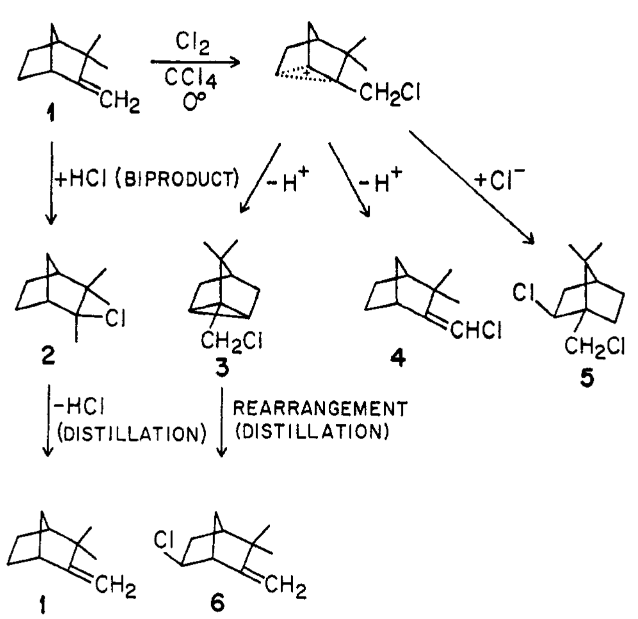

Figure 1.—General scheme of transformations leading to observed products.

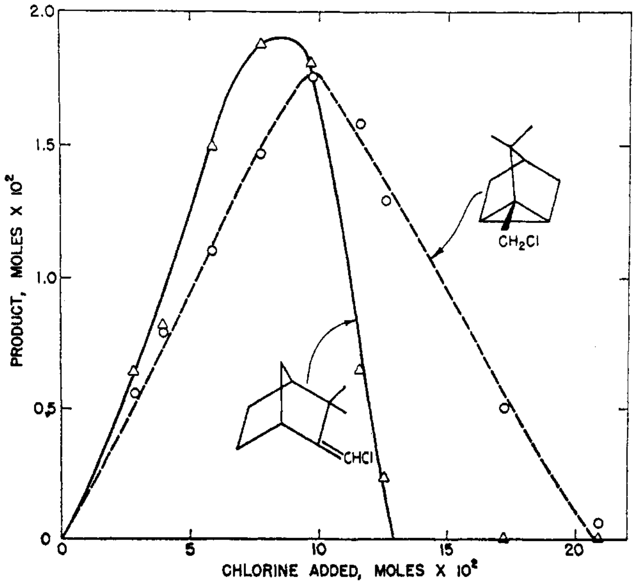

Figure 2.—Yield of products **3** and **4** as a function of chlorine introduced (0.1 mole of camphene).

Although *exo*-6-chlorocamphene (**6**) was not observed in crude product mixtures and was thus excluded as a primary product, it did appear in some monochloro distillates. A study of distillation conditions revealed that as the process was conducted more slowly (high reflux ratio) the amount of **3** decreased coincident with an increase in the amount of **6**. Independent experiments using pure tricyclyl chloride confirmed that **3** slowly rearranges to the homoallylic compound (**6**) under these conditions.

Gas chromatograms of distillates consisted of three peaks, the first assignable to **1**, the second to **6**, and the third to **4** (*cis* and *trans*). Vapor phase chromatography studies showed that **3** rearranged completely to **6** during passage through the column; the peak for **6**, therefore, represented the amount of **3** formed on chlorination.

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(5) D. Tishchenko, *Zh. Obshch. Khim.*, **27**, 2907 (1957); *J. Gen. Chem. USSR*, **27**, 2943 (1957).

(6) H. G. Richey, Jr., T. J. Garbacik, D. L. Dull, and J. E. Grant, *J. Org. Chem.*, **29**, 3095 (1964); **30**, 3909 (1965).

(7) M. Gaitonde, P. A. Vatakencherry, and S. Dev, *Tetrahedron Letters*, 2007 (1964).

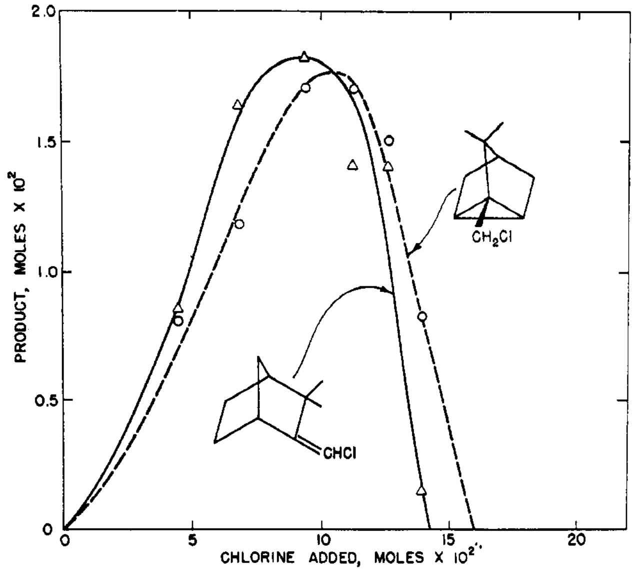

Figure 3.—Yield of products **3** and **4** as a function of chlorine added in the presence of sodium bicarbonate (0.1 mole of camphene).

Separate experiments excluded the possibility that 8-chlorocamphene (**4**) was produced in secondary rearrangement and/or dehydrohalogenation processes during work-up. It was demonstrated, for example, that neither **3** nor **5** gave the vinyl chloride (**4**) under the conditions of distillation. When the chlorinations were carried out in the presence of sodium bicarbonate to prevent the formation of camphene hydrochloride, distillation of products proceeded without evolution of hydrogen chloride. The yield patterns of the monochlorides **3** and **4** (see Figures 2 and 3) and of the dichlorobornane (**5**) were essentially the same as for runs without added bicarbonate.[8] Chloride ion determinations carried out on the bicarbonate reaction mixtures showed that the equivalents of chloride ion equalled the sum of the equivalents of **3** and **4**. Apparently the formation of these compounds was the only source of hydrogen chloride during the reaction.

The major product obtained in all chlorination reactions was *exo*-2,10-dichlorobornane, the maximum yield of which was 60–65%. The amount of **3** reached a maximum of 0.018 mole (18%) at *ca.* 0.10 mole of halogen and decreased slowly; it was absent after the addition of 0.23 mole of chlorine. The yield of **4** rose to a maximum of 0.019 mole (19%) at *ca.* 0.08 mole of chlorine (see Figure 2). As the reaction proceeded, polychlorinated compounds were formed; that products **3** and **4** undergo secondary reactions with excess chlorine was demonstrated by independent experiments with samples of the pure vinyl and tricyclyl chlorides.

The interpretation of the data on the chlorination of camphene is outlined in Figure 1.[9] Addition of a chloronium ion to the camphene double bond gives the carbonium ion intermediate which either loses a proton from C-6 or C-8 to give products **3** and **4**, respectively, or adds chloride ion to give the major product, *exo*-2,10-dichlorobornane. Camphene hydrochloride is produced by simple addition of hydrogen chloride to camphene.

The Products

***exo*-2,10-Dichlorobornane** (**5**).—The solid isolated from the distillation residue was shown to have the structure originally reported by Tishchenko[2] for the saturated dichloro product. The compound was recovered intact after treatment with zinc and acetic acid. The skeletal structure was confirmed by reduction to bornane with sodium and ethanol or lithium and *t*-butyl alcohol as well as by neutral hydrolysis of the Grignard reagent prepared from **5**.

Strong characteristic infrared absorption bands appeared at 10.40, 11.66 and 13.70 μ. The n.m.r. spectrum (see Table I) was consistent with the assigned structure. The coupling pattern due to the C-10 and C-2 protons, respectively, was a symmetrical AB quartet centered at τ 6.33 (J = 11 c.p.s.) and a triplet overlapping the quartet centered at τ 5.88 (J = 6 c.p.s.). The remaining ring protons appeared as complex and poorly resolved bands in the region τ 7.71–8.66. The methyl resonances are singlets at τ 9.07 and 8.84. The n.m.r. spectrum did not supply sufficient information for unambiguous assignment of the orientation of the C-2 proton. On mechanistic grounds, however, it is most reasonable that the chlorine be assigned the *exo* position.

The dichloride was converted to **4** in 23% yield on treatment with zinc and ethanol, or in 70% yield on treatment with dimethylaniline.[10] It was stable under the conditions used for distillation of the crude chlorinated mixture. The compound could not be eluted from any v.p.c. column at temperatures less than 110°, but on DC-11 at 150° it decomposed into a mixture of *cis* and *trans* isomers of **4** and an unidentified compound.

***cis*- and *trans*-8-chlorocamphene** (**4**) were eluted together from v.p.c. columns and were therefore collected and investigated as a mixture. Dehydrohalogenation of **5** was the most convenient route to the isomers (see above).

Langlois' assignment[1] of the vinyl chloride structure to one of the products of chlorination of camphene was based on the isolation of camphenilone from the neutral permanganate oxidation products of his monochloro fraction. As such, this evidence is ambiguous; camphene, which we always observed in this fraction, can itself give camphenilone under these conditions. An oxidation carried out in our laboratory using 95% pure chloride, however, also gave camphenilone and thus substantiated Langlois' evidence.

A strong broad infrared band at 12.42, with shoulders at 12.12, 12.60 and 12.80 μ, was useful for identification of **4** in a neat monochloro mixture. The n.m.r. spectrum (see Table I) was entirely consistent with the assigned structure and clearly showed that the sample was a 1:2 mixture of the *cis* and *trans* isomers. In addition to a complex multiplet similar to that of the camphene spectrum in the region τ 8.67–8.97, the n.m.r. spectrum of **4** contained two vinyl resonances (τ 4.27 and 4.50)

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[8] This result provides evidence that the dichloro product did not arise from reaction of either **3** or **4** with hydrogen chloride.

[9] Although we are aware that the mechanism of halogen addition in a nonpolar solvent such as carbon tetrachloride is probably more complex [see J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 218; M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965)], we have chosen for simplicity to include only known types of cationic species in this outline.

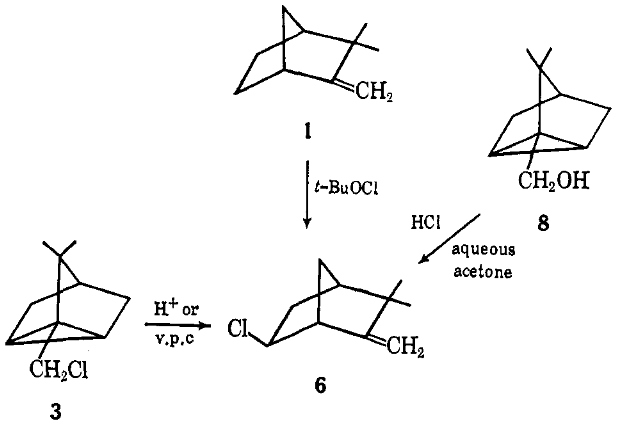
[10] Langlois[1] observed an analogous dehydrohalogenation of 2,10-dibromobornane.

TABLE I

N.M.R. SPECTRA[a] OF BICYCLIC COMPOUNDS

Compound	Chemical shift, τ value	Multiplicity[b] and coupling constant	Proton peak assignment
Camphene (1)	8.98	s	Methyl
	8.95	s	Methyl
	8.32–8.83	m	Methylene
	8.14	s, b	Bridgehead C-1
	7.38	s, b	Bridgehead C-4
	5.57	s	Vinyl
	5.37	s	Vinyl
8-Chlorocamphene (**4**, *cis*- and *trans*-)	8.94	s	Methyl (*trans*)[c]
	8.78	s	Methyl (*cis*)
	8.73	s	Methyl (*cis*)
	8.67–8.97	m	
	7.33	s, b	Bridgehead (C-1, *cis*)
	6.83	s, b	Bridgehead (C-1, *trans*)
	4.50	s	Vinyl (*trans*)
	4.27	s	Vinyl (*cis*)
exo-6-Chlorocamphene (6)	9.02	s	Methyl
	8.95	s	Methyl
	7.95–8.54	m	
	7.57	q (J = 7 c.p.s.)	
	7.19	s	Bridgehead (C-1)
	6.22	q (J = 3 c.p.s.)	C-6 proton
	5.34	s	Vinyl
	5.07	s	Vinyl
exo-2,10-Dichlorobornane (5)	9.07	s	Methyl
	8.84	s	Methyl
	7.71–8.66	m	
	6.33	q (J = 11 c.p.s.)	C-10 protons
	5.88	t (J = 6 c.p.s.)	C-2 proton

[a] All spectra were taken in carbon tetrachloride. Absorptions are given in τ units relative to tetramethylsilane internal standard (τ = 10). See G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958), for τ convention. [b] s = singlet; s, b = broad singlet; t = triplet; q = quartet; m = multiplet. [c] See text under 8-chlorocamphene (**4**) section.



in an intensity ratio of 1:2 and two C-1 bridgehead resonances (τ 6.83 and 7.33) in the ratio 2:1. The shift of one of the vinyl peaks to higher field is probably due to shielding by the *gem*-dimethyl group, for the same difference in chemical shift is observed for the two vinyl resonances in the spectrum of camphene. Accordingly, the *trans* isomer has been associated with the high-field, more intense vinyl peak. The C-1 bridgehead resonances are consistent with this assignment: the smaller bridgehead peak due to the *cis* isomer, expected to have approximately the same chemical shift as that of camphene (τ 7.38), appeared at τ 7.33.

***exo*-6-Chlorocamphene** (**6**) was isolated pure by preparative v.p.c. from the monochloro fraction of the camphene chlorination mixture. The most convenient independent preparation of **6** involved free-radical homoallylic substitution on camphene using *t*-butyl hypochlorite.[11] In this case it appeared as the sole detectable product. The *exo*-6-camphenyl system was also obtained readily by rearrangement of 10-substituted tricyclenes as indicated in col. 2.

The infrared spectrum of **6** contained absorption bands due to terminal methylene (5.61, 6.08 and 11.22 μ) and *gem*-dimethyl groups (an unsymmetrical doublet centered at 7.28 plus absorptions at 8.58 and 8.73 μ), as well as a characteristic unsymmetrical doublet centered at 10.03 μ and strong bands at 12.95 and 14.33 μ. The n.m.r. spectrum (see Table I) was essentially identical with that reported for *exo*-6-bromocamphene.[7] Since there was no spin–spin interaction between the C-6 and C-1 bridgehead protons, it is evident that H-6 is *endo* and therefore the chlorine atom must be in the *exo* position.

Treatment of **6** with silver nitrate solution resulted in immediate precipitation of silver chloride. The compound was converted to **7** by hydrolysis, a reaction shown to proceed with retention of configuration in the case of the bromo derivative.[7] 10-Hydroxytricyclene (**8**) was also observed as a by-product of this reaction in yields up to 10%. Neutral permanganate oxidation of pure **6** led to two unidentified compounds and about 5% tricyclenic acid.

exo-6-Chlorocamphene was historically the most baffling and controversial compound among the camphene chlorination products. The fact that the chlorine atom was so labile led earlier workers to confine

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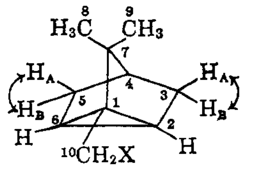
[11] C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

TABLE II

N.M.R. SPECTRA OF TRICYCLIC COMPOUNDS[a,b]

Compound	AB Quartet (C-3 and C-5)				Bridgehead (C-4)	Cyclopropyls (C-2 and C-6)	*gem*-Dimethyl (C-8 and C-9)	Functional group (C-10)
Tricyclenic acid	. . .[c]	8.16	8.75	. . .[d]	8.54	8.10	8.93	
Tricyclenic acid[e]	8.13	8.30	. . .[d]	9.02	8.61	8.04	8.77	
10-Hydroxytricyclene (**8**)	8.22	8.41	8.87	. . .[d]	8.63	8.94	9.07	7.07 (OH) 6.36 (CH_2O)
p-Nitrobenzoate of **8**	8.13	8.32	. . .[c]	. . .[d]	8.53	8.76	9.02	5.52
10-Chlorotricyclene	8.15	8.32	8.81	. . .[d]	8.55	8.76	9.02	6.29

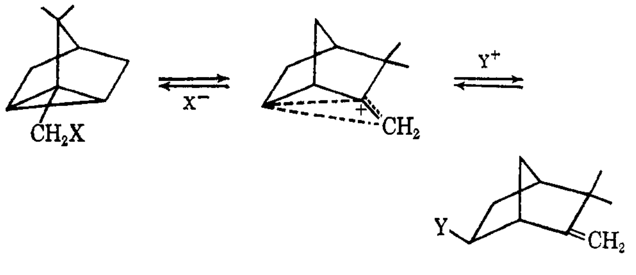
[a] The solvent used was carbon tetrachloride unless otherwise noted. All absorptions are given in τ units relative to tetramethylsilane internal standard (τ = 10). [b] In general the n.m.r. spectra of these tricyclic compounds show an AB quartet (J = 10–12 c.p.s.) due to the C-3 and C-5 protons and a very broad band due to the lone bridgehead protons (half-band width, 4–5 c.p.s.). The



(J_{AB} = 10 – 12 c.p.s.)

cyclopropyl hydrogens appear as a singlet with chemical shift largely a function of solvent and substituent at C-10 (see, for example, tricyclenic acid spectra in carbon tetrachloride and pyridine; 10-hydroxytricyclene and its *n*-nitrobenzoate derivative). R. A. Finnegan and R. S. McNees [*J. Org. Chem.*, **29**, 3234 (1964)] have reported a similar absorption pattern in the spectrum of tricyclene. [c] An exact τ value cannot be assigned to this peak because the cyclopropyl proton resonance is superimposed on this part of the quartet. [d] An exact τ value cannot be assigned to this peak because the *gem*-dimethyl resonance is superimposed on this part of the quartet. [e] Pyridine was used as solvent.

themselves to allylic halides in their structural proposals.[2,4] Also, **6** was always considered a primary chlorination product. It is clear now that the reactive chloride has the 6-camphenyl structure and that it is formed on thermal isomerization of the cyclopropylcarbinyl system.[12] Rearrangement of 10-chlorotricyclene to *exo*-6-chlorocamphene, the high chlorine activity of **6**, the stereospecificity of its hydrolysis, and isolation of tricyclenic derivatives can all be explained by the intervention of a stabilized homoallyl cation as shown below.



10-Chlorotricyclene (**3**), long suspected as a product of chorination of camphene, was prepared independently from 10-hydroxytricyclene (**8**) and phosphorus pentachloride by Komppa's method[13,14]; the product was always contaminated with **6**. Thionyl chloride in dry dioxane was a more satisfactory chlorinating agent.

The tricyclyl chloride (**3**) was the only monochloro product obtained from the chlorination of camphene under certain conditions (1:1.4 molar ratio of camphene to chlorine; see above). Rapid distillation minimized rearrangement of **3** to **6**; contamination by **1** was eliminated by redistillation.

Infrared absorption provided evidence for the *gem*-dimethyl groups (7.22 and 7.32 μ) and tricyclenic structure (12.30 μ[15]). Strong bands at 14.12 and 14.52 μ are uniquely characteristic of **3** and were used for its identification in chloride mixtures.

An n.m.r. spectrum of pure **3** was never obtained; however, the only contaminant in the sample was a small amount of **6** and bands due to this isomer were readily subtracted from the spectrum. The remaining peaks are consistent with the 10-chlorotricyclene structure (see Table II and particularly footnote *b*).

Hydrolysis of **3** gave erratic yields of **8**; oxidation yielded tricyclenic acid as well as unidentified neutral products. These reactions are being studied further.

Experimental Section

Gas chromatographic analyses were carried out on an Aerograph Model A-90-P (Wilkens Instrument and Research, Inc.). Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer, Model 137-B. A Varian Model A-60 spectrometer was used for the n.m.r. spectra. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y.

Chlorination of Camphene.—Starting material for most chlorinations was camphene-90 (Glidden Co., Jacksonville, Fla.), shown by v.p.c. to be contaminated with small amounts of tricyclene and other impurities. No difference in composition of

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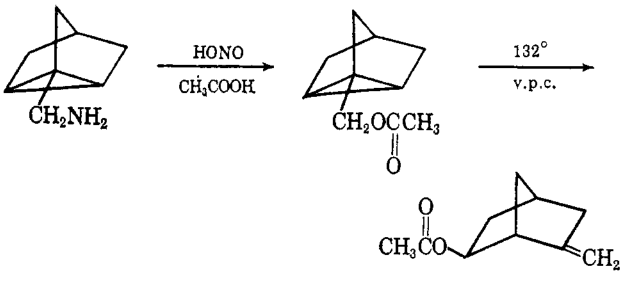
(12) H. Hart and R. Martin observed very similar behavior in a nortricyclyl system [*J. Am. Chem. Soc.*, **82**, 6362 (1960)], reporting that deamination of 1-aminomethylnortricyclene in acetic acid gave exclusively the cyclopropylcarbinyl acetate. V.p.c. at 132°, however, resulted in conversion to the homoallylic isomer.



(13) (a) G. Komppa, *Ber.*, **62**, 1366 (1929).

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

(15) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

the product mixtures was observed in micro reactions using pure camphene obtained by preparative v.p.c.

Chlorine (Matheson Co.) was led into 50 ml. of carbon tetrachloride or carbon disulfide solutions containing 0.1 mole (13.6 g.) of camphene-90 at 0–5°. The rate at which halogen was added, as measured with a bubble flow meter, varied from 41 ml. to 83 ml./min. with no change in product composition. The total amount of chlorine introduced was increased from 0.03 mole (610 ml.) to 0.24 mole (5300 ml.) in ten successive reactions. The product dependence on chlorine input is shown in Figure 2.

The course of the chlorination was followed by examining intensity changes of infrared bands characteristic of reactant and certain products. The absorptions used to identify these compounds were shown to be unique to the given substance by comparison of infrared spectra of pure materials: camphene (**1**), 11.36; camphene hydrochloride (**2**), 9.41 and 9.72; 10-chlorotricyclene (**3**), 14.12 and 14.52; and *exo*-2,10-dichlorobornane (**5**), 10.40, 11.66, 13.10, and 13.70 μ. 8-Chlorocamphene (**4**) could not be detected in the crude mixtures by infrared spectroscopy because its strong bands (9.00, 10.47, 11.20, 11.79, and 12.42 μ) were masked by absorptions of **2** and **5**. The spectra were examined for absorptions due to *exo*-6-chlorocamphene (**6**) (9.98, 10.08, 12.95, and 14.33 μ), but in no case were they observed.

All runs were distilled and the colorless effluent gases were led through silver nitrate solution. Voluminous precipitates of silver chloride were observed. Fractions were collected between 75 and 100° (12 mm.) with most of the liquid distilling in the range 82–92° (12 mm.). Distillations carried out using a high reflux ratio resulted in extensive rearrangement of **3** to its homoallylic isomer **6**; thus, to obtain **3** the monochloro product was distilled as rapidly as possible.

Each distillate was analyzed by v.p.c. using a 0.25 × 60 in. copper column packed with DC-11 on Chromosorb W, DMCS, 60–80-mesh, at 110°; detector temp., 139°; injector temp., 141°; and helium flow rate, 51 ml./min. Eluted materials, identified by infrared spectra, were **1**, **6**, and **4** (*cis* and *trans*). It was shown in independent experiments that **6** arose from quantitative rearrangement of **3** on the v.p.c. column; accordingly the peak due to **6** represented the amount of **3** originally formed in the chlorination. Peak areas, measured with a planimeter (Gelman Instrument Co.), were used for estimation of the amounts of the three components present.

Weights of the residues increased linearly with the amount of chlorine added. Unidentified products, presumably polyhalogenated compounds (11.21, 12.12 and 12.91 μ), began to appear in residues of runs in which 0.04 mole of chlorine had been added to 0.1 mole of camphene. It was thus difficult to determine the maximum yield of dichlorobornane, but a reasonable estimate, based on infrared analysis and total weight of residue (13.7 g.; 0.13 mole of chlorine added), is 60–65%.

Chlorination of Camphene in the Presence of Sodium Bicarbonate.—In a series of six chlorinations sodium bicarbonate was added to the camphene solutions in amounts equivalent to the chlorine introduced. The mixtures were stirred vigorously during reaction. Product analyses were carried out as described above. No camphene hydrochloride (**2**) was observed; the yield pattern for **3**, **4**, and **5** was nearly the same as that in runs with no added bicarbonate (see Figure 3).

A standard solution of sodium hydroxide was used to trap any hydrogen chloride produced on distillation. Titration with standard acid showed no change in base titer. Samples of inorganic salts from each run were analyzed for chloride using standard 0.02 *N* mercuric nitrate solution with diphenylcarbazone–bromophenol blue mixed indicator.[16] For runs using less than 0.1 mole of chlorine (maximum yields of **3** and **4**), the equivalents of chloride ion equalled the sum of the equivalents of **3** and **4**. When more chlorine was used the concentration of chloride ion increased, but yields of **3** and **4** decreased.

Chlorination of 10-Chlorotricyclene (3) and 8-Chlorocamphene (4).—**3** (0.04 mole, 0.6 g.), prepared by chlorination of camphene using a chlorine–camphene ratio in excess of 1.4:1, was treated with chlorine at 0° in both carbon tetrachloride and carbon disulfide solutions (3 ml.). Absorption peaks at 14.12 and 14.52 μ, due to **3**, disappeared after the addition of *ca.* 0.13 mole of chlorine.

4 (0.04 mole, 0.6 g.), prepared from **5** (see below), was dissolved in 3 ml. of carbon tetrachloride and treated with chlorine at 0° in the dark. The infrared spectrum of an aliquot withdrawn after the addition of 0.04 mole (880 ml.) of chlorine showed no unsaturation and an absorption pattern entirely different from that of **4**.

***exo*-2,10-Dichlorobornane (5).**—The dichloro compound was obtained pure by distillation, b.p. 122° (12 mm.), or recrystallization from ethanol of the residue remaining after distillation of the monochloro fraction, m.p. 139.5–140.5° (lit.[2] m.p. 134.5–135°). The infrared spectrum showed intense bands at 10.40, 11.66, 12.48, 13.10, and 13.70 μ; see Table I for n.m.r. absorptions.

Anal. Calcd. for $C_{10}H_{16}Cl_2$: Cl, 34.23. Found: Cl, 34.22.

Refluxing **5** at 12-mm. pressure, bath temperature 130–142°, for 70 min. and then at 140–180° for 50 min. produced no change in the compound. Gas chromatography using a DC-11 column at 150° (detector, 148°; injector, 168°), however, resulted in partial decomposition to **4** and an unidentified compound.

Reduction of 5. A. Sodium and Ethanol.—Sodium shavings (0.04 g.-atom, 1 g.) were added to 0.0097 mole (2.0 g.) of **5** dissolved in dry tetrahydrofuran. Absolute ethanol (20 ml.) was introduced dropwise. After reaction, water and ether were added. Work-up of the organic layer involved losses of the volatile product. The ether concentrate contained a single product (v.p.c.: DC-11, 118°) having the same retention time as authentic bornane prepared by Wolff–Kishner reduction of camphor.

B. Lithium and *t*-Butyl Alcohol.—Finely cut lithium (0.3 g.-atom, 2 g.) was added to 0.092 mole (19.2 g.) of **5** dissolved in 150 ml. of anhydrous tetrahyrofuran. *t*-Butyl alcohol (90 ml.) was admitted dropwise to the stirred solution and reflux was continued for 2.5 hr. Water and ether were added; the organic layer was separated, washed with water, and dried. Gas chromatograms (DC-11) of the concentrated ether extract showed one product having the same retention time and infrared spectrum as authentic bornane.

C. Grignard Hydrolysis.—A Grignard reagent was prepared with difficulty under nitrogen from 0.048 mole (9.9 g.) of **5** and 0.13 g.-atom (3.0 g.) of magnesium in anhydrous ether. After hydrolysis with saturated ammonium chloride solution, v.p.c. analysis (DC-11) of the ether layer showed the presence of a compound having the same retention time as bornane.

Dehydrohalogenation of 5. A. Zinc and Ethanol.—**5** (0.029 mole, 6.0 g.), dissolved in 20 ml. of ethanol, was added dropwise to 0.077 g.-atom (5.0 g.) of zinc in 30 ml. of refluxing ethanol. After 20 hr. the reaction mixture was filtered and distilled to yield 1.3 g. of material, b.p. 94–98° (18 mm.). V.p.c. analysis showed the distillate to be 95% **4** (23% yield).

B. Dimethylaniline.—**5** (0.019 mole, 4.0 g.) was refluxed 19 hr. in 4.0 ml. of freshly distilled dimethylaniline (b.p. 194°). Hydrochloric acid (10%) and ether were added; the organic layer was separated, washed and dried. Vacuum distillation gave 2.4 g. of a fraction, b.p. 87–89° (18 mm.), shown by v.p.c. (DC-11, 118°) and infrared spectrum, to be 95% pure **4** (70% yield).

***cis*- and *trans*-8-Chlorocamphene (4).**—A 1:2 mixture of *cis* and *trans* **4** was isolated from the monochloro distillate by preparative v.p.c. using either a DC-11 or Bentone column (see details above and below). The same isomeric mixture was readily prepared by dehydrohalogenation of **5** in refluxing dimethylaniline (see above). Characteristic infrared bands appeared at 6.04, 9.00, 10.47, 11.20, 11.79, and 12.42 μ. The n.m.r. absorptions are shown in Table I.

Anal. Calcd. for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.12; H, 9.02; Cl, 20.67.

The chloride did not react with 5% alcoholic silver nitrate, magnesium in refluxing ether, or zinc in refluxing ethanol. It was also inert to potassium cyanide in refluxing alcohol (12 hr.).

Oxidation of 4 to camphenilone.—**4** (95% pure; 0.024 mole, 4.0 g.), prepared from **5**, was refluxed with 0.15 mole (24 g.) of potassium permanganate in 100 ml. of 75% aqueous acetone to which zinc sulfate had been added. During distillation of an ether extract much of the volatile product was lost; 1.5 g. of material was isolated, b.p. 76° (18 mm.), lit.[17] b.p. 76° (16 mm.) and 75° (10 mm.). Preparative v.p.c. (DC-11, 125°; helium flow rate, 46 ml./min.; retention time, 23 min.) furnished a white solid, m.p. 36–38° (lit.[17] m.p. 38°), having an infrared

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(16) F. E. Clark, *Anal. Chem.*, **22**, 553 (1950).

(17) I. Heilbron and H. M. Banbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

spectrum identical with that of authentic camphenilone. The semicarbazone melted at 222–223° (lit.[17] m.p. 224°).

exo-**6-Chlorocamphene** (**6**).—The compound was isolated from distilled products of camphene chlorination by preparative v.p.c. (see details under Chlorination of Camphene). Addition of 1 drop of 10% alcoholic silver nitrate solution to 1 drop of pure **6** produced an immediate precipitate of silver chloride.

The infrared spectrum showed bands at 5.61, 6.08, 7.28 (center of doublet), 8.58, 8.73, 9.98, 10.08, 10.67, 11.22, 12.95, and 14.33 μ. A list of the n.m.r. peaks is given in Table I.

Anal. Calcd. for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.47; H, 9.00; Cl, 20.68.

Preparation of 6. A. Chlorination of Camphene with *t*-Butyl Hypochlorite.[11]—Equimolar (0.007) portions of camphene and *t*-butyl hypochlorite, prepared by the method of Teeter and Bell,[18] were placed in a Pyrex tube which was swept free of air, filled with argon, and sealed. The tube was placed in an ice bath and the mixture irradiated with visible light (100-w. G.E. bulb) for 8 hr. Gas chromatograms (DC-11) of the reaction mixture showed one product peak due to **6**. Microdistillation gave a few drops, b.p. 92° (24 mm.), having the infrared spectrum of **6**. Pure material was obtained for n.m.r. studies by preparative v.p.c.

B. Acid-Catalyzed Rearrangement of 10-Chlorotricyclene (**3**).—Hydrochloric acid (6 *N*, 1 ml.) was shaken with 0.5 g. of **3**, prepared free of **6** by rapid distillation of camphene chlorination products (see above). The mixture was allowed to stand at room temperature for 3 hr. and then extracted with ether. Solvent removal left an oil whose infrared spectrum showed bands due to **6** (see above) and no absorptions characteristic of **3**.

C. Reaction of 10-Hydroxytricyclene (**8**) **with Hydrochloric Acid.**—A few milligrams of **8**, prepared by lithium aluminum hydride reduction of tricyclenic acid, was dissolved in acetone to which a few drops of 6 *N* hydrochloric acid were added and left overnight at room temperature. Organic material was extracted and solvent was removed. The infrared spectrum of the remaining oil showed it to be mainly **6**.

Hydrolysis of 6.—A mixture of 0.66 mmole (113 mg.) of **6**, purified by preparative v.p.c. (10% Bentone; column temp., 98°; detector temp., 135°; injector temp., 123°; helium flow rate, 18 ml./min.), 0.78 mmole (58 mg.) of lithium carbonate, and 2 ml. of water was refluxed 12 hr. The product was extracted with ether, the combined extracts were dried, and the solvent was evaporated. Vapor phase chromatograms of the crude oil showed two product peaks (Carbowax 20M on Chromosorb W, 60–80 mesh at 62°; detector temp., 102°; injector temp., 106°; helium flow rate, 145 ml./min.) with retention times of 55 and 63 min., in the ratio 9:1. Both retention time and infrared spectrum (2.99, 5.62, 6.04, 11.23, and 14.62 μ) of eluted material verified that the major component was identical with *exo*-6-hydroxycamphene (**7**) prepared by water–lithium carbonate hydrolysis of *exo*-6-bromocamphene.[7] The minor product was identified by retention time and infrared spectrum as 10-hydroxytricyclene (**8**) (see below). It was demonstrated that under the v.p.c. conditions used neither alcohol rearranged.

Oxidation of 6.—An aqueous acetone solution of 3.4 mmole (536 mg.) of potassium permanganate and 0.62 mmole (114 mg.) of **6**, purified by preparative v.p.c. (Bentone, see above), was refluxed in the presence of 194 mg. of magnesium sulfate for 6 hr. Saturated sodium bicarbonate solution and ether were added, layers were separated, the organic layer was dried, and solvent was removed. The residual oil absorbed in the infrared at 2.86, 5.60 and 5.71 μ and gave two v.p.c. peaks (DC-11; column temp., 107°; detector temp., 147°; injector temp., 152°; helium flow rate, 19 ml./min.) with areas in 1:1.7 ratio. Eluate from the first, with a retention time of 35 min., was a semisolid showing no absorption at 2.86 μ but with a strong band at 5.71 and a shoulder at 5.81 μ. The second material, retention time of 110 min., was a solid absorbing at 2.86 and 5.60 μ. The sum of these two spectra gave all the peaks displayed by the spectrum of the injected oil.

Neutralization of the bicarbonate layer produced a precipitate which was centrifuged, washed with water, and extracted into ether. After solvent was removed there remained 0.03 mmole (5 mg., 5% yield) of solid which had an infrared spectrum identical with that of tricyclenic acid.

10-Hydroxytricyclene (**8**).—Tricyclenic acid was prepared from **1** either by nitration followed by treatment with sulfuric acid[13b] or by chlorination followed by oxidation with neutral permanganate (see below). A solution of 0.0067 mole (1.1 g.) of acid, m.p. 143–146°, in 20 ml. of anhydrous tetrahydrofuran, was added dropwise at reflux temperature to a stirred slurry of solvent and 0.025 mole (1.0 g.) of lithium aluminum hydride. After 7 hr. ether and 10% sodium hydroxide solution were added, metal hydroxide was removed by filtration, the organic layer and washings were dried, and the solvent was evaporated. Nearly pure alcohol (**8**), 0.0065 mole, 1.0 g., 98% yield) was obtained, m.p. 108–109°, lit.[14] m.p. 111–112°. Further purification was effected by preparative v.p.c. using a Carbowax 20M column at low operating temperatures to avoid rearrangement to **6** (conditions cited above). The eluate melted at 111–112° and showed a broad characteristic infrared absorption band centered at 9.83 μ with shoulders at 9.59 and 10.12 μ. The n.m.r. bands are listed in Table II. A *p*-nitrobenzoate derivative of the alcohol melted at 120.5–121.5°, lit.[19] m.p. 122–123°; its n.m.r. absorptions are also shown in Table II.

10-Chlorotricyclene (**3**).—The tricyclic chloride (**3**) could be isolated by rapid distillation of the camphene chlorination products. In a typical run 0.14 mole of chlorine was bubbled into a solution of 0.1 mole (13.6 g.) of camphene in 50 ml. of carbon tetrachloride maintained at 0–5°; 2.6 g. of distillate, b.p. 75–100° (12 mm.), was shown by infrared and v.p.c. analyses to consist of 30% **1** and 70% **3**. Redistillation provided a fraction, b.p. 86° (12 mm.), free of camphene. Infrared bands of structural significance appeared at 7.22 and 7.32 (*gem*-dimethyl) and 12.30 μ (tricyclenic structure[15]); strong absorptions at 14.12 and 14.52 μ were uniquely characteristic of **3**. See Table II for a list of n.m.r. peaks.

Preparation of 3. A. Chlorination of 10-Hydroxytricyclene (**8**) **with Phosphorus Pentachloride.**—Treatment of **8** with phosphorus pentachloride according to the procedure of Hanack and Eggensperger[14] gave a crude product always contaminated with **6** (6.08, 11.22, and 12.95 μ). Rapid short-path distillation gave cyclene (**3**), b.p. 86° (14 mm.), which still contained small amounts of **6**.

B. Chlorination of 10-Hydroxytricyclene (**8**) **with Thionyl Chloride.**—**8** (0.007 mole, 1.1 g.), dissolved in 10 ml. of freshly distilled anhydrous dioxane, was added dropwise to a stirred solution of 0.007 mole (0.5 ml.) of thionyl chloride in 10 ml. of dioxane precooled to −15°. The reaction temperature rose slowly to 0°. The mixture was maintained at this temperature for 2 hr. and then allowed to come to room temperature. Short-path distillation gave a fraction (0.037 mole, 0.063 g., 5% yield), b.p. 86° (16 mm.), containing **3** and trace amounts of **6** (infrared).

Stability of 3.—The chloro compound, prepared from **1**, was held under reflux at 12 mm. for several hours, bath temperature of 135–145°; an infrared spectrum of refluxed material showed the absorption pattern of **6** (see above). Rapid distillation at a bath temperature of 150–170° could be used, however, for purification of **3** without causing rearrangement of the tricyclic chloride (**3**) to its homoallylic isomer (**6**).

Pure **3** rearranged quantitatively into **6** on a wide variety of v.p.c. columns under a range of operating temperatures from 67 to 158°: Carbowax 400, Carbowax 20M, QF-1, 10% Bentone 34, and DC-11, all on Chromosorb W, 60–80 mesh, packed in copper tubing; DC-11, DMSC, 60–80 mesh in steel tubing and in copper tubing specially treated to remove active acid sites.[20]

Hydrolysis of 3.—**3** (0.009 mole, 1.6 g.) was heated at reflux temperature for 24 hr. in 250 ml. of water to which 0.8 g. of lithium carbonate had been added. The organic product was extracted with ether, the combined extracts were dried, and the solvent was removed. The crude solid thus obtained had an infrared spectrum very similar to pure **7** (2.99, 5.62, 6.04, 9.50, 11.23, and 14.62 μ). Gas chromatography showed the major product to be **7** with a small amount of **8** as well as other unidentified materials. The v.p.c. profile of another hydrolyzed mixture, refluxed for only 2 hr., showed unreacted chloro compound and both alcohols **7** and **8** in the ratio 2:1. Pure **8**, prepared by reduction of tricyclenic acid, was shown to be stable under conditions of hydrolysis.

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[18] H. M. Teeter and E. W. Bell, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 125.

[19] P. Lipp, *Ber.*, **80**, 165 (1947).

[20] H. P. Burchfield and E. E. Storrs, "Biochemical Applications of Gas Chromatography," Academic Press Inc., New York, N. Y., 1962, pp. 468–472.

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]

HERMAN G. RICHEY, JR.,[2] JAMES E. GRANT, THEODORE J. GARBACIK, AND DAVID L. DULL

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania

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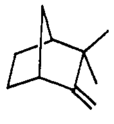
Reaction of camphene and chlorine in carbon tetrachloride containing sodium bicarbonate according to the procedure of Tishchenko gave a small monochloride product of which 10-chlorotricyclene (**3**) was the major component. *exo*-2,10-Dichlorobornane (**16**) was the largest reaction product.

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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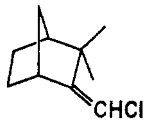

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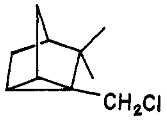

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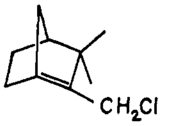

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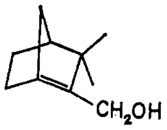

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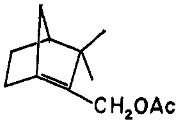

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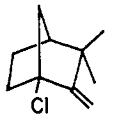
Chiurdoglu, Goldenberg, and Geeraerts concluded, principally on the basis of infrared spectra, that the monochloride fraction prepared in the same manner as by Tishchenko consisted of **2**, **3**, and **7**, that reaction with potassium acetate gave a mixture of **8** and **9**, and that saponification 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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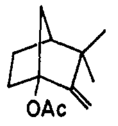

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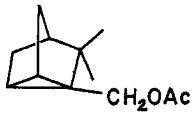

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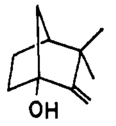

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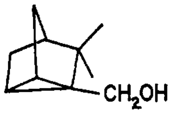

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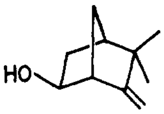

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Neither **4** nor **7** seem to be reasonable structures for a reactive component of the monochloride mixture.[10] Structure **4** violates Bredt's rule and **7**, having a bridgehead chlorine, would not be expected to react rapidly with potassium 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]

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