tion of CD_2H_2 to the mass spectrometer pattern, it is safe to assume that the concentration did not exceed the calculated amount in Table III. These results do not eliminate the possibility that iron alkyls exist on the catalyst surface during synthesis but no evidence was found for their presence in the used catalyst samples.

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[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

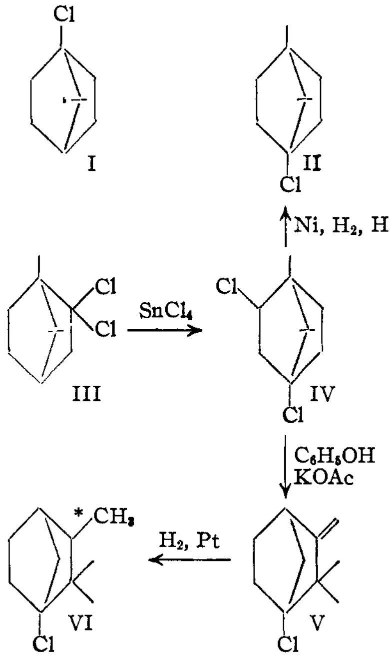
4-Chlorocamphane[1]

BY W. VON E. DOERING AND E. F. SCHOENEWALDT

The bridgehead chloride, 4-chlorocamphane, has been synthesized conveniently from camphor in three steps and has been found to lose chlorine and form an inseparable mixture of C_{10} hydrocarbons on treatment with the halophilic reagents, aluminum bromide, zinc chloride and silver ion. These results are interpreted as suggestive of a difficultly formed, transitory, bridgehead carbonium ion.

The significant and original investigation by Bartlett and Knox[2] of 1-chloroapocamphane (I), in demonstrating failure to obtain reaction with silver nitrate in refluxing aqueous ethanol, has aroused our curiosity concerning the limits of unreactivity of bridgehead chlorine under more strongly halophilic conditions. In this paper a partially satisfactory description of the behavior of the homologous and easily available 4-chlorocamphane (II) is presented.

D(−)2,2-Dichlorocamphane (III, α-dichlorocamphane), prepared by the action of phosphorus pentachloride on D(+)camphor,[3,4] rearranges in the presence of stannic chloride to β-dichlorocamphane (IV),[3,4] the structure of which Houben and Pfankuch have shown to be L(+)2,4-dichlorocamphane (IV).[5] Hydrogenation of IV with Raney nickel in the presence of alcoholic alkali gives optically inactive II, the yield from camphor being 15% of the theoretical. The structure of 4-chlorocamphane is assigned to II on the grounds of consistency (1) with the method of preparation and the structure of the starting material, IV, (2) with the reduction of II to camphane by sodium and alcohol, and (3) with the *meso* nature of II. This latter hypothesis is supported by the facts that *optically active* 4-chlorocamphene (V)[4] is hydrogenated under identical conditions to the *optically active* L(−)4-chlorodihydrocamphenes (VI)[6] and that L(+)2,4-dichlorocamphane (IV) is optically and chemically stable to ethanolic alkali.



Like 1-chloroapocamphane (I),[2] 4-chlorocamphane (II) and L(−)4-chlorodihydrocamphene (VI) are stable to potassium hydroxide in refluxing 90% ethanol for two days. More strikingly II is also unaffected by ethanolic sodium ethoxide at 205° for two days.

Whereas I is reported not to form a Grignard reagent,[2] VI, which also fails to react with magnesium, does react with sodium–potassium alloy (but not with sodium sand) to give a metallic derivative, carbonation of which leads to the mixture of isocamphane-4-carboxylic acids. This result indicates that there is no inhibition to the existence of a negative charge at a bridgehead, a conclusion that seems implicit in the reported reductions of bridgehead halogen with sodium and alcohol.[4]

With silver nitrate in 90% ethanol, 4-chlorocamphane (II) shows no detectable reaction on refluxing or on heating at 160° but the reaction is complicated by the complete reduction of the silver ion at the higher temperature. At 205° suspended in *aqueous* silver nitrate, II reacts to give 59% of the theoretical amount of silver chloride, some unreacted II, and an inseparable mixture of organic

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(1) Taken from a dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939).

(3) H. Meerwein and R. Wortmann, *Ann.*, **435**, 190 (1923).

(4) J. Houben and E. Pfankuch, *ibid.*, **501**, 219 (1933).

(5) There follows a brief outline of the evidence and interpretations on which the expression for IV rests. (a) β-Dichlorocamphane and β-chlorocamphene (from D camphor) are interconvertible in a manner completely analogous with the isobornyl chloride–camphene interconversion. (b) β-Chlorocamphene reacts under the Bertram–Wahlbaum conditions to give a chlorohydrin, the structure of which is clearly L-4-chloroisoborneol on the grounds that reduction gives L-isoborneol and oxidation gives a chloroketone which in turn by an unequivocal series of reactions is converted to the known α-chlorocamphoric anhydride. (c) On the highly reasonable assumption that the reaction of hydrogen chloride with β-chlorocamphene proceeds as does the hydration, IV is L(+)2,4-dichlorocamphane.

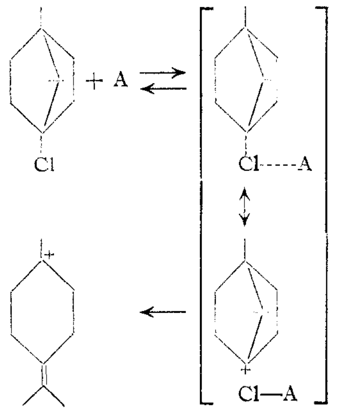
(6) Although the ease of preparation commends the 4-chloroisocamphanes (VI) as a source of bridgehead chloride, the fact that in our hands the substance is an inseparable mixture of *endo* and *exo* isomers detracts from its usefulness.

products. Water alone at 205° for 91 hours is without effect on II.

Initial efforts to attack II by the powerfully halophilic reagent, aluminum bromide, have been attempted in the non-reacting solvents, carbon disulfide and nitrobenzene, without effect, presumably because of the decreased catalytic activity of the aluminum bromide–solvent complex.[7] With refluxing cyclohexane as solvent, II reacts with aluminum bromide to give hydrogen bromide and a saturated $C_{10}H_{20}$ fraction, which is not obtained in similar reactions where cyclohexyl chloride or camphane replaces II. As no pure, identifiable products could be isolated from the C_{10} fraction, it must be assumed that extensive rearrangement and hydrogen transfer of the Bartlett, Condon and Schneider type[8] has followed the removal of bridgehead chlorine. The $C_{12}H_{22}$ cyclohexane dimers[9] appearing as complicating by-products suggest the source of hydrogen.

To minimize interference by the solvent, a 50% aqueous solution of the moderately active catalyst, zinc chloride, has been employed. With this catalyst 4-chlorocamphane is stable indefinitely at 185°, but reacts at 195° or above to give an oily product which is unsaturated and contains a small amount of chloride in the form of difficultly removable starting material. Likewise, with butyl ether as solvent, zinc chloride at 200° effectively removes chlorine from II giving a product corresponding to $C_{10}H_{20}$. Blank determinations with 50% aqueous zinc chloride and camphane, and zinc chloride, butyl ether and butyl bromide fail to produce the C_{10} fraction.

Unsatisfying as these experiments are in the sense that pure products have not been isolated, they nevertheless constitute the first evidence that bridgehead chlorine can be removed as chloride ion if sufficiently strong halophilic conditions are provided. Any interpretation which implies that a bridgehead carbonium ion has been produced is certainly premature, but there can be little doubt that at least in the transition state of the removal of chlorine an electron-deficiency at a bridgehead carbon is involved, even though the products may be derived by initial ring opening.



Experimental[10]

L(+)4-Chloroisobornyl Chloride (IV).—According to the method of Houben and Pfankuch,[4] IV was prepared from 425 g. of D-camphor, $[\alpha]^{25}\mathrm{D}$ +44.5° (*c*, 10 in ethanol), by halogenation with phosphorus trichloride and phosphorus pentachloride at −5 to 0° for one month, the resulting D(−)-2,2-dichlorocamphane (III) being rearranged to the desired product by the action of stannic chloride in toluene. Repeated crystallization of the crude material (300 g.) from methanol afforded 197 g. of colorless, fern-like needles, m.p. 164–166° (dec.) in a sealed tube and pre-heated bath, $[\alpha]^{25}\mathrm{D}$ +23.3° (*c*, 10 in ether).

Anal. Calcd. for $C_{10}H_{16}Cl_2$: C, 57.98; H, 7.79; Cl, 34.23. Found: C, 58.59; H, 7.64; Cl, 33.01.

In a similar manner, 425 g. of synthetic camphor (U.S.P., du Pont) yielded 190 g. of racemic IV, m.p. 177–178.5° (dec.) in a sealed tube and preheated bath.

Anal. Found: C, 57.52; H, 8.13; Cl, 33.32.

4-Chlorocamphane (II).—In a typical experiment, 20 g. of L(+) IV or *rac.* IV in 150 cc. of absolute ethanol containing one equiv. of potassium hydroxide was hydrogenated over Raney nickel at 3 atm. and room temperature, 0.95 equiv. of hydrogen being absorbed in five days. Addition of water to the filtrate precipitated a white solid which, after being treated with concentrated sulfuric acid at room temperature for one day, was crystallized from methanol and sublimed *in vacuo* to yield 7.7 g. (46%) of colorless, fern-like needles, m.p. 175–176° in a sealed tube, showing no optical activity.

Anal. Calcd. for $C_{10}H_{17}Cl$: C, 69.50; H, 9.94; Cl, 20.56. Found: C, 69.56; H, 10.12; Cl, 20.40.

A sample of L(+) IV was recovered unchanged after being treated with alcoholic potassium hydroxide under the conditions of the hydrogenation.

A solution of 1.4 g. of II and 4.5 g. of potassium hydroxide in 20 cc. of 90% aqueous ethanol was refluxed for 42 hours. The addition of water precipitated 1.4 g. of unchanged starting material (m.p. and mixed m.p.).

A solution of 0.9 g. of II and sodium ethoxide (from 0.6 g. of sodium) in 15 cc. of absolute ethanol was heated at 205° for 45 hours in a sealed tube. The precipitate, which formed upon addition of water to the reaction mixture, after sublimation afforded 0.6 g. of starting material, m.p. 169–173° (mixed m.p. gave no depression).

L(−)4-Chlorodihydrocamphene (V).—Refluxing 40.0 g. of L(+) IV with phenol and potassium acetate according to the procedure of Houben and Pfankuch[4] yielded 34 g. (77%) of L(−)4-chlorocamphene; m.p. 130–131.5°; $[\alpha]^{26}\mathrm{D}$ −74.3° (*c*, 9 in ethanol). Hydrogenation of 12.4 g. of this material in 100 cc. of absolute ethanol with Raney nickel at 3 atm. and room temperature resulted in the absorption of 0.82 equiv. of hydrogen in one hour. Precipitation by the addition of water, treatment with concentrated sulfuric acid for one day at room temperature, and sublimation yielded 9.9 g. (80%) of V; m.p. 148–150°; $[\alpha]^{25}\mathrm{D}$ −17.9°.

Anal. Calcd. for $C_{10}H_{17}Cl$: C, 69.50; H, 9.94; Cl, 20.56. Found: C, 69.38; H, 9.61; Cl, 20.74.

A solution of 5 g. of V and 15 g. of potassium hydroxide in 100 cc. of 90% ethanol was refluxed 40 hours, 3 g. of unchanged material being recovered by the usual procedure.

Reduction of 4-Chlorocamphane (II).—In small portions, 4.0 g. of sodium was added slowly to a well-stirred, refluxing solution of 1.3 g. of II in 25 cc. of absolute ethanol. Addition of water to the reaction mixture precipitated material, m.p. 135–145°, having a positive Beilstein test. The reduction was repeated on this material giving 0.5 g. (48%) of colorless product which was crystallized from ethanol and sublimed to give camphane, m.p. 150–152°. This material showed no depression of m.p. when mixed with authentic camphane, m.p. 152–153°, prepared from bornyl bromide by the method of Wallach.[11]

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 87.02; H, 13.10.

Dihydrocamphene-4-carboxylic Acid.—A solution of 3.0 g. of V in dry pentane was added to a vigorously stirred mixture of 3.8 g. of sodium–potassium alloy (1:4) and 200

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(7) *Cf.* N. V. Sidgwick, "Chemical Elements and their Compounds," Vol. I, Oxford University Press, London, England, 1950, pp. 432–433.

(8) P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1531 (1944).

(9) C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 189 (1931).

(10) All melting and boiling points are corrected.

(11) O. Wallach, *Ann.*, **239**, 1 (1887).

cc. of dry pentane under a nitrogen atmosphere. The solution, refluxed with stirring for three hours, became bright green and deposited a reddish-brown precipitate. Following the addition of a large excess of solid carbon dioxide, ethanol was added to decompose any alloy remaining. The reaction mixture was extracted with water, giving an aqueous solution acidification of which precipitated 1.06 g. (33%) of the stereoisomeric dihydrocamphene-4-carboxylic acids, m.p. 140–170°. Houben and Pfankuch[12] report m.p. 170° for one of these stereoisomers.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95; neut. equiv., 182.3. Found: C, 71.97; H, 9.91; neut. equiv., 181.

4-Chlorocamphane (II) and Silver Nitrate (a) Ethanol.—A solution of 2.0 g. of II and 3.0 g. of silver nitrate in 50 cc. of 90% ethanol was refluxed 44 hours without causing any turbidity. A portion of this solution (30 cc.) was then heated at 160° for 21 hours in a sealed tube. There was considerable pressure in the cooled tube and some white crystals. Addition of water precipitated unchanged II, m.p. 171–174°. No chloride ion was present in the solution nor extractable from the precipitate with ammonia. The crystalline material fused to a lump of silver without loss in weight.

(b) **Water.**—After being heated for 19.5 hours at 205° in a sealed tube, 1.1 g. of II and 3 g. of silver nitrate in 10 cc. of water had evolved considerable gas and produced a copious precipitate. The ether extract of the aqueous solution consisted of a very small amount of acidic material. The water-insoluble residue was leached with three 15-cc. portions of hot ethanol, and after being combined the latter were diluted with water precipitating a tan solid. Sublimation afforded 0.4 g. of recovered II, m.p. 172–174°. Acidification with nitric acid of the concentrated ammonia extract of the ethanol-insoluble residue produced 0.54 g. of silver chloride, corresponding to 0.65 g. of II. The ammonia-insoluble material (1.46 g.) was metallic silver.

4-Chlorocamphane (II) and Aluminum Bromide.—In a typical experiment, 11 g. of anhydrous aluminum bromide (Eimer and Amend, Tested Purity) was dissolved in 400 cc. of dry, purified cyclohexane by stirring in a 1-l., 3-neck flask equipped with dropping funnel, reflux condenser and stirrer. As a solution of 7.0 g. of II in 100 cc. of cyclohexane was slowly added at room temperature, the solution first became bright yellow and opaque, then cleared to a bright green solution and a dark red lower phase. The reaction mixture was heated at 50° for one hour (vigorous evolution of hydrogen bromide) and at reflux for an additional half hour. Decomposed with hydrochloric acid, washed with water and concd. sulfuric acid and dried over calcium chloride, the reaction mixture was distilled in a short Vigreux column at atmospheric pressure giving the following fractions: (a) 1.8 g., b.p. 148–162°; (b) 1.5 g., b.p. 164–165°, $n^{20}\text{D}$ 1.4370, $d^{25}{}_4$ 0.7946; (c) 0.2 g., b.p. 168–171°, $n^{20}\text{D}$ 1.4400; (d) 1.5 g., b.p. 175–177°, $n^{20}\text{D}$ 1.4450, $d^{25}{}_4$ 0.8125; (e) 3.0 g., b.p. 190–216°; (f) 2.1 g., b.p. 216–220°, $n^{20}\text{D}$ 1.4641; (g) 3.0 g. of residue. Fractions (b), (c) and (d) gave negative Beilstein tests and negative bromine test for unsaturation. Fraction (d) was analyzed.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.81; H, 14.63.

Fraction (f) is apparently the dicyclic naphthene shown by Nenitzescu and Ionescu[9] to be a mixture of dimethyldicyclopentyl and dicyclohexyl.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.48; H, 13.22.

This fraction deposited crystals when cooled in solid carbon dioxide and acetone. Recrystallized twice from methanol it melted at 45–45.5°, whereas dimethyldicyclopentyl is reported[9] to melt at 46.5°.

Cyclohexyl Chloride, Cyclohexane and Aluminum Bromide.—This reaction was carried out in the same way as the preceding one adding 4.8 g. of cyclohexyl chloride (b.p. 141–141.5°, $n^{20}\text{D}$ 1.4260) in 39 g. of cyclohexane to 11.0 g. of aluminum bromide in 200 g. of cyclohexane. Distillation gave 213 g., b.p. 79.2–81.0°, $n^{20}\text{D}$ 1.4231 corresponding on the assumption of linearity of the index of refraction curve of cyclohexane–methylcyclopentane mixtures to 82% cyclohexane and 12% methylcyclopentane. The residue was distilled as before giving 5.0 g., b.p. 80–81.3°; 0.2 g., b.p. 81–213°; 3.4 g., b.p. 215–219°; and 1.5 g. of residue. The fraction, b.p. 215–219°, on cooling gave crystals, m.p. 44.5–45.5°.

Camphane, Cyclohexane and Aluminum Bromide.—In a similar experiment in which 3.4 g. of camphane in 40 cc. of cyclohexane was added to 6.7 g. of aluminum bromide in 163 g. of cyclohexane, no gas was evolved nor was a lower layer formed. Only cyclohexane and camphane (2.7 g., m.p. 152–153°; 80%) were recovered.

4-Chlorocamphane (II) and Aqueous Zinc Chloride.—Two sealed tubes, each containing 2.64 g. of II, 8 cc. of 50% aqueous zinc chloride and one drop of concentrated hydrochloric acid were heated to 205° for 90 hours. (At 185°, there was no detectable reaction; at 195°, only partial reaction.) A 3.0-g. portion of the oily reaction product was hydrogenated over platinum oxide in glacial acetic acid at 31° and 1 atm. After six hours, 12.8% of one equiv. of hydrogen had been absorbed. The addition of water precipitated an organic layer which was shaken with concentrated sulfuric acid, washed with water and steam-distilled. On cooling 4-chlorocamphane crystallized. The filtrate was distilled from sodium in a molecular still giving 0.3 g. of colorless oil, b.p. 206–207° in a Siwoloboff tube; $n^{28}\text{D}$ 1.4728; Cl, 2.24. A product completely free of chlorine could not be obtained.

Under these same conditions camphane (0.3 g.) was completely stable to zinc chloride, 0.3 g., m.p. 151–153°, being recovered.

Furthermore unchanged 4-chlorocamphane was recovered when 0.2 g. of II was heated for 91 hours at 205° in 5 cc. of water.

4-Chlorocamphane, *n*-Butyl Ether and Zinc Chloride.—After being heated at 200° in a sealed tube for 40 hours, a mixture of 5.2 g. of II, 5.6 g. of anhydrous zinc chloride and 20 g. of *n*-butyl ether (purified by washing successively with ferrous sulfate solution, water, aqueous sodium carbonate and water, drying over anydrous sodium sulfate and distilling, b.p. 140–141°) had separated into a colorless upper layer and a dark red lower phase (*ca.* 5 cc.). The reaction mixture, washed repeatedly with water, then with aqueous ferric chloride and finally with water, was hydrogenated over platinum oxide at atmospheric pressure and room temperature, 13.4% of 1 equiv. of hydrogen being absorbed. The reaction product, freed of solvent *in vacuo*, was steam distilled giving 6.85 g. of material which was hydrogenated once again (4.1% of an equiv. being absorbed). The product was repeatedly extracted with concentrated sulfuric acid, washed with water, dried over sodium sulfate and dissolved in 50 cc. of hexane. The hexane solution was added dropwise to a vigorously stirred mixture of 4 g. of sodium–potassium alloy (1:4) in 150 cc. of dry hexane contained in a 500-cc. 3-necked flask equipped with a vacuum-tight stirrer, reflux condenser and dropping funnel and having an outlet closed with a stop-cock leading from the bottom of the flask. The reaction mixture was stirred and heated under reflux for 11 hours during which time a white precipitate appeared. The mixture was filtered under vacuum through a fine fritted glass filter attached to the bottom outlet. The treatment with sodium–potassium alloy was then repeated. Removal of solvent left an oil containing no chlorine which was washed with concentrated sulfuric acid and water, and distilled at atmospheric pressure to give the following fractions: (a) 0.13 g., b.p. 73–153°; (b) 0.33 g., b.p. 153–161°, $n^{23}\text{D}$ 1.4342; (c) 0.56 g., b.p. 180–183°, $n^{23}\text{D}$ 1.4410, $d^{25}{}_4$ 0.797; (d) 0.44 g., b.p. 130–140° at 14 mm., $n^{23}\text{D}$ 1.4602, $d^{25}{}_4$ 0.833. Fraction (c) was analyzed.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.51; H, 14.35.

***n*-Butyl Bromide, *n*-Butyl Ether and Zinc Chloride.**—A mixture of 3 g. of *n*-butyl bromide, 5 g. of anhydrous zinc chloride and 20 g. of *n*-butyl ether in a sealed tube was heated at 200° for 40 hours. Washed with water, the product was dried over sodium sulfate and distilled at 18 mm., material boiling below 145° being collected and a residue (1.6 g.) being undistilled. The distillate was hydrogenated with platinum oxide catalyst and redistilled at atmospheric pressure. The fore-run, b.p. 120–145°, was rejected. The residue (6.5 g.) was extracted with concentrated sulfuric acid (most of the material dissolved), washed with water, diluted with 3 cc. of hexane, dried and distilled to give hexane and 0.31 g. of material boiling above 240° in a Siwoloboff tube.

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[12] J. Houben and E. Pfankuch, *Ber.*, **59**, 2285 (1926).