2.—Five grams of V, was treated with 25 g. of concentrated sulfuric acid and warmed for 45 min. and finally worked up as in 1 gave 1.61 g. (35% VI and/or VII), m.p. 38–42°, semicarbazone, m.p. 230–240°.

3.—A mixture of 2.5 g. of V and 25 g. of concentrated sulfuric acid was left at room temperature for 1–1.5 hr. with frequent shaking. The fraction mixture was then worked up as in 1 and 2 and this gave 1.8 g. (39% VI and/or VII), m.p. 38–42°, which on recrystallization from petroleum ether melted at 45–48° (m.p. of VI,[7] 48°) and gave a semicarbazone, m.p. 245–254°.

The product, presumably a mixture of VI and VII, obtained in each of the five cyclization reactions described previously, was separately reduced by the Clemmensen method (68–85%) except that obtained in 3 which was reduced by Huang-Minlon reaction (94%).

Each material (VIII and/or IX) obtained by Clemmensen reduction including one obtained by Huang-Minlon reduction, was purified by alumina chromatography and directly aromatized by heating 500 mg. with 100 mg. of platinum black for 0.5 hr. at 265–270° under nitrogen atmosphere. The reaction product was taken up in petroleum ether (b.p. 40–60°). Evaporation of the solvent gave a mixture of X and XI in yields ranging from 62–80%. The mixture of X and XI obtained from each of the products of cyclization in A, B, and C was separated by alumina chromatography on elution in a number of fractions, using petroleum ether (b.p. 60–80°) as eluent. Careful fractionation and repeated chromatography of some of the fractions, gave pure phenanthrene and anthracene in different proportions. The per cent yields of X and XI obtained by this method are given in Table I and are based on the total recovering of pure samples of each from the aromatized product.

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The Stereospecific Fragmentation of 2-Dichloromethyl-2-methylcyclohexanone

MANFRED G. REINECKE

Department of Chemistry, University of California, Riverside, California

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Primarily because of its reported inertness to base,[1] 2-dichloromethyl-2-methylcyclohexanone (1) was selected as one of the substrates for a study of the catalytic hydrogenolysis of aliphatic halides in basic solution.[2] Hydrogenations which were carried out in methanolic potassium hydroxide led to a side reaction, however, one of whose products was 6-methylheptanoic acid (2). Evidence presented in this paper suggests that this acid is formed by reduction of 7-chloro-6-methyl-6-heptenoic acid (3) which arises from the dichloro ketone 1 by a stereospecific fragmentation reaction.[3]

Treatment of the dichloro ketone 1 with methanolic potassium hydroxide under conditions similar to those used for the dehalogenation studies,[2] except for the absence of hydrogen and a catalyst, produced a high-boiling acid 3 whose neutralization equivalent and analysis (as the amide) are consistent with the formula $C_8H_{13}O_2Cl$. In addition to the characteristic carboxylic acid absorption, the infrared spectrum of this acid has a weak, but sharp peak at 1655 cm.$^{-1}$ suggestive of a nonconjugated double bond.[4]

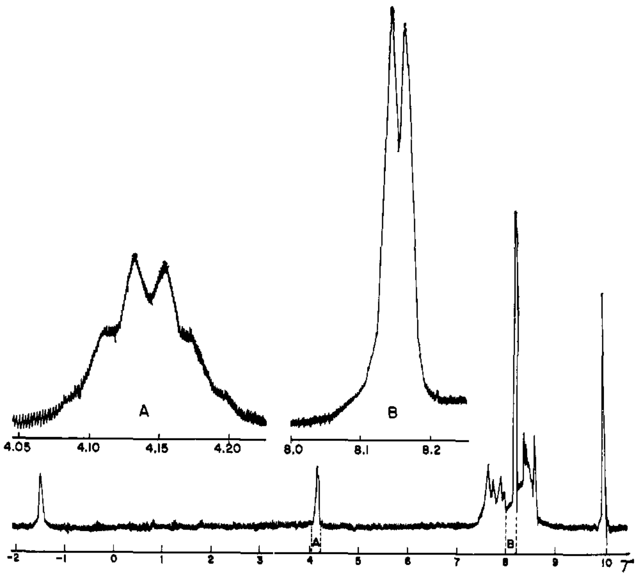

Fig. 1.—The n.m.r. spectrum of 7-chloro-6-methyl-6-heptenoic acid (3).

Reduction of the chloro acid 3 with palladium on charcoal in ethanol required two equivalents of hydrogen, one for the double bond and one for hydrogenolysis of the chlorine atom. This facile dehalogenation in neutral solution indicates that the chlorine atom of the unknown acid 3 is allylic or vinylic, since aliphatic chlorides without adjacent unsaturation are stable under these conditions.[5]

The reduction product was identified as 6-methylheptanoic acid (2) by comparing its infrared spectrum and retention time on vapor phase chromatography with those of an authentic sample. This establishes the carbon skeleton of the unknown chloro acid 3 and also demonstrates that it is a likely precursor of the 6-methylheptanoic acid found in the dehalogenation reaction.[2]

The structure of the unknown acid was eventually determined from its n.m.r. spectrum (Fig. 1). The sharp singlet at −1.48 was assigned to the carboxyl proton while the quartet at 4.14 (one proton, J = 1.2 c.p.s.) and the doublet at 8.15 τ (three protons, J = 1.2 c.p.s.) were allocated to the mutually spin-spin coupled protons of a double bond and an allylic methyl group, respectively.[6] No resonances which could be attributed to the α-protons of a chloroalkyl group were observed.[7]

Since the unknown acid 3 must contain two terminal carbon atoms, the presence of only one methyl group,

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[1] N. Kreutzkamp, H. Meerwein, and R. Stroh, "Methoden der Organischen Chemie" (Houben-Weyl), Vol. 5, part 4, Eugen Müller, Ed., Georg Theime Verlag, Stuttgart, 1960, p. 686.

[2] M. G. Reinecke, *J. Org. Chem.*, in press.

[3] (a) C. A. Grob in "Theoretical Organic Chemistry; Papers Presented at the Kekule Symposium," Butterworth, London, 1959, p. 117; (b) A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 34.

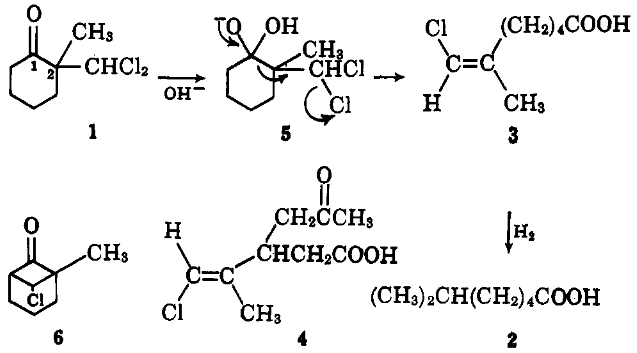
[5] R. Baltzly and A. Phillips, *J. Am. Chem. Soc.*, **68**, 261 (1946).

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp. 58, 61.

[7] Reference 6, p. 54.

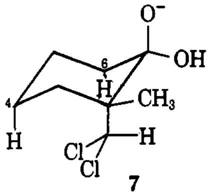
as well as the absence of a chloromethyl group, indicates that the other terminal carbon atom is part of the double bond. The existence of a single olefinic proton requires that the chlorine atom is attached to this double bond. The unknown acid is, therefore, 7-chloro-6-methyl-6-heptenoic acid (**3**).

That this acid consists predominantly of one geometrical isomer is indicated by the absence of two different olefinic and methyl proton resonances in its n.m.r. spectrum and also by the presence of a single peak in its vapor phase chromatogram. Since a study of the n.m.r. spectra of related geometrical isomers has shown that $J_{\mathrm{CH_3-H},\,cis} \geq J_{\mathrm{CH_3-H},\,trans}$,[8] it might be possible to determine the configuration of the acid **3** if its n.m.r. spectrum could be compared with that of the other possible isomer. Although this second isomer was not available, the n.m.r. spectrum of a structurally similar chloro acid **4** has been reported,[9] and both its olefinic and allylic methyl proton resonances described as singlets. If the reasonable assumption is made that the magnitude of $J_{\mathrm{CH_3-H}}$ is determined primarily by the configuration of the double bond and not by structural changes in more remote parts of the molecule, then the allylic methyl group and olefinic hydrogen atom are *cis* in the chloro acid **3** and *trans* in the chloro acid **4**, as shown.



A probable mechanism for the formation of the chloro acid **3** from the dichloroketone **1** involves addition of hydroxide ion to the carbonyl group to give the intermediate **5** which undergoes a 1,4-elimination of chloride ion accompanied by cleavage of the carbon–carbon bond. Fragmentation reactions of this type are quite general,[3] although in the case of β-halo ketones previous examples apparently have been restricted to rigid bicyclic molecules in the terpene series.[10]

The formation of a single geometrical isomer of the chloro acid **3** suggests that one conformation of the intermediate **5** is particularly prone to fragmentation.[11] There are two conformations, **7** and **8**, which possess the necessary stereochemical features for fragmentation[3a] and which would lead to the observed product. A choice between them based on conformational preference is difficult, however, since although **7** has a very favorable arrangement of the opposing dipoles it also has a severe steric interaction between the chlorine atom which is to be retained and the axial hydrogens at C-4 and C-6.



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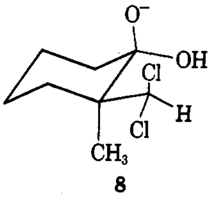

8

Experimental

Melting points were determined on a Kofler hot stage and are corrected. The proton magnetic resonance spectra were recorded on a Varian A-60 instrument in carbon tetrachloride solution with tetramethylsilane as an internal standard (τ 10). Infrared spectra were taken with a Perkin-Elmer Model 421 grating spectrophotometer. Analyses were carried out by Mr. C. F. Geiger, Ontario, Calif.

7-Chloro-6-methyl-6-heptenoic Acid (3).—A solution of 500 mg. of 2-dichloromethyl-2-methylcyclohexanone (**1**)[12] and 2 g. of potassium hydroxide pellets in 20 ml. of absolute methanol was stirred for 10 hr. in a stoppered flask at room temperature. After the methanol had been evaporated at reduced pressure, the remaining mixture was distributed between ether and water and the aqueous layer separated, acidified with sulfuric acid, and extracted with three 10-ml. portions of ether. The dried ether extracts (sodium sulfate) were evaporated at reduced pressure to give 30 mg. of a viscous, colorless, odorless oil, b.p. 109–110° (2 mm.), which solidified in an ice bath and turned pale yellow on exposure to air. The infrared spectrum of this material (neat) exhibited broad absorptions at 3050 and 2650 (OH) and sharp peaks at 1720 (C=O) and 1655 cm.$^{-1}$ (C=C). Titration with standard sodium hydroxide indicated that this acid had a neutralization equivalent of 176 ± 3. (Calcd. for $C_8H_{13}O_2Cl$: 176.5.)

Treatment of this acid with thionyl chloride on a steam bath for 45 min. followed by reaction with cold, concentrated ammonium hydroxide gave a white precipitate which after several crystallizations from ether–petroleum ether (b.p. 30–60°) melted at 65.5–66.5°.

Anal. Calcd. for $C_8H_{14}NOCl$: C, 54.70; H, 8.03. Found: C, 54.87; H, 8.05.

Catalytic Reduction of 3.—A solution of 106 mg. of 7-chloro-6-methyl-6-heptenoic acid (**3**) in 20 ml. of 95% ethanol containing 34 mg. of 10% palladium on charcoal was hydrogenated at room temperature and atmospheric pressure. After hydrogen absorption ceased (2.2 equivalents), the catalyst was removed by filtration. Titration of an aliquot of the filtrate with standard silver nitrate to a silver chromate end point indicated the presence of one equivalent of chloride ion. Upon treatment of the remaining filtrate with sodium hydroxide and evaporation of the ethanol at reduced pressure, a white solid was obtained which was dissolved in water and the resulting solution acidified with sulfuric acid and extracted with three 10-ml. portions of ether. The combined ether extracts were dried over calcium sulfate, and the ether removed by distillation through a micro Vigreux column. The residue consisted of 67 mg. (86%) of 6-methylheptanoic acid which was identified by a comparison of its infrared spectrum and retention time on vapor phase chromatography with those of an authentic sample.

Acknowledgment.—This research was supported by funds from the Research Committee of the University of California. The n.m.r. spectra were taken at Los Angeles State College through the courtesy of Dr. Thomas P. Onak of the Chemistry Department.

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[8] R. B. Bates, R. H. Carnighan, R. O. Rakutis, and J. H. Schauble, *Chem. Ind.* (London), 1020 (1962).

[9] E. E. van Tamelen, K. Kirk, and G. Brieger, *Tetrahedron Letters*, 939 (1962).

[10] J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. II, Cambridge University Press, New York, N. Y., 1949, pp. 388, 572.

[11] A similar stereospecificity has been reported in the formation of the cyclobutanone **6** from the dichloroketone **1** by an internal displacement of chloride ion [R. M. Dodson, J. R. Lewis, W. B. Webb, E. Wenkert, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **83**, 938 (1961)].

[12] K. Auwers and E. Lange, *Ann.*, **401**, 303 (1913).