furan was added to 50 ml. of methanol. One drop of N-ethylmorpholine was added as catalyst. After 20 hr. at room temperature, the solution was concentrated at a reduced pressure, treated with petroleum ether (b.p. 30–60°) and cooled at −20°. A small amount of a crystalline powder, m.p. 180–200°, was filtered. The mother liquors were further concentrated and gave a 38% yield of methyl carbamate melting at 54–56° (acetone–petroleum ether). There was no depression of the melting point on admixture with an authentic sample.

Anal. Calcd. for $C_2H_5NO_2$: C, 32.00; H, 6.71; N, 18.66. Found: C, 32.12 and 32.23; H, 6.84 and 6.78; N, 18.82.

Ethanolysis of Ethyl Phosphorodiisocyanatidite.—A solution of 1 g. of III (R = Et) in 150 ml. of ethanol was allowed to stand at room temperature for 2 hr. It was then concentrated to a few ml. and diluted with toluene. On standing at −18° for several hours, a crystalline material melting at 49.5–51° (methanol–toluene) was obtained. The melting point was undepressed on admixture with an authentic sample of ethyl carbamate.

Anal. Calcd. for $C_3H_7NO_2$: C, 40.44; H, 7.92; N, 15.72. Found: C, 40.16; H, 8.21; N, 15.41.

In both cases the quantitative isolation of the carbamates was impossible because of their low melting points, high solubility in alcohols, and the presence of the corresponding alkyl phosphites in the crude reaction mixtures.

Kinetic Studies of the Reactions of Organophosphorus Isocyanates with Alcohols.—Solutions of the isocyanates in anhydrous solvents (toluene or tetrahydrofuran) were titrated with dibutylamine and hydrochloric acid[10] to determine their normalities. Aliquots were placed in flasks protected with septums. Solutions of butanol or methanol in the same solvents were injected through the septums, while stirring magnetically, to give final solutions of known concentrations. Aliquots were withdrawn with a syringe at electrically timed intervals and added to excess dibutylamine in toluene. The excess of dibutylamine was titrated with aqueous 0.1 *N* HCl in the presence of bromophenol blue. Methanol or isopropyl alcohol was added to each sample before titration, to give a uniform solution without separation into layers. The initial concentration of the isocyanates was maintained at about 0.1 *N*, while the amount of alcohol varied from equivalent to a large excess.

Under essentially bimolecular conditions, using a 50% excess of the alcohol, the phosphorodiisocyanatidites (III, R = Me or Et) gave plots of

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)}$$

vs. time consisting of two intersecting straight lines. Under pseudo unimolecular conditions plots of ln $a/a - x$ *vs.* time were rectilinear but did not pass through the origin.

Gas Chromatographic Study of the Reaction of Phenyl Phosphorodiisocyanatidite with Methanol.—A Perkin-Elmer vapor fractometer equipped with a 2-m. 5% silicon grease–Haloport F (trademark of F & M Corp., Avondale, Pa.) column was calibrated at 180° and a He pressure of 5 p.s.i.g. The following emergence times were obtained: methanol, 0.22–2.24; methyl carbamate, 0.35–0.37; dimethyl phenyl phosphite, 0.64; phenyl phosphorodiisocyanatidite, 2.20 min.

Stoichiometric amounts of III (R = Ph) and methanol were mixed at 0°. Samples, 2-μl. each, were withdrawn from time to time and injected into the chromatographic column. An unknown peak with emergence time of 1.60–1.65 min. was observed immediately after mixing the reacting compounds. On the basis of its polarity and estimated boiling range, it was tentatively identified as VII (R = Ph, R′ = Me). The experiment was continued for 205 min. During that time the following changes in the relative amounts of the components in the mixture were observed: methanol and III (R = Ph) decreased from very high to very low values, methyl carbamate and V (R = Ph, R′ = Me) increased considerably, and the presumed VII (R = Ph, R′ = Me) decreased from a medium to a low value.

Acknowledgment.—The author wishes to thank Professor Glen A. Russell of Iowa State University for a helpful discussion.

---

[10] "Spielberger's Method" reported by W. Siefken, *Ann.*, **562**, 99 (1949).

Studies on Double Acylation of Aromatic Hydrocarbons. I. Synthesis of Phenanthrene (Anthracene) by Double Succinoylation of Benzene

AZIZ-UR RAHMAN, AIDA T. VAZQUEZ, AND AUSAT A. KHAN

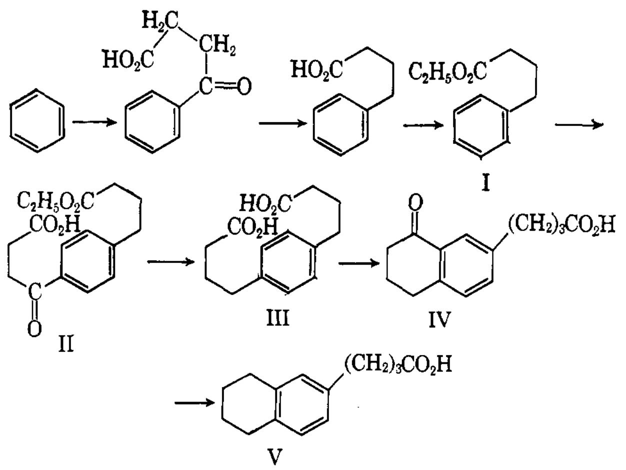
The Departamento de Quimica e Ingenieria Quimica, Universidad Nacional del Sur, Bahia Blanca, Argentina

Received February 8, 1962

The deactivating effect of *m*-directing substituents, such as a carbonyl group in the aromatic ring, in inter- and intramolecular acylation is well known. Thus the monosuccinoylated aromatic hydrocarbons generally cannot be subjected to further acylation. However, the reduction of the carbonyl function of the monoacylated product to a methylene group eliminates the deactivating effect of the former, and in the case of monosuccinoylated hydrocarbons separates the carbonyl group from the aromatic ring by three methylene groups, thus rendering the resulting γ-arylbutyric acid amenable to further acylation. Although the literature describes the succinoylation of ethyl β-phenylpropionate[1] and phthaloylation of γ-phenylbutyric acid[2] as isolated examples of Friedel–Crafts acylation, no systematic work seems to have been carried out on the intermolecular acylation of aromatic hydrocarbons containing a deactivating group, *e.g.* a carboxyl group, removed from the aromatic ring by a few methylene entities. The present work presents results of an attempt on double succinoylation of benzene.

It was considered that succinoylation of a γ-arylbutyric acid obtained by the reduction of the corresponding β-aroylpropionic acid, the latter containing a carbonyl group as the deactivating entity, would lead to a product which could serve as starting material for new routes to the syntheses of polynuclear hydrocarbons, through a series of steps including reduction, cyclization, and eventual dehydrogenation.

In the present work ethyl γ-phenylbutyrate[3] (I) obtained by succinoylation of benzene and subsequent reduction of the corresponding keto acid served as the starting material for a second succinoylation of benzene.



---

[1] W. Borsche and F. Sinn, *Ann.*, **553**, 260 (1942).

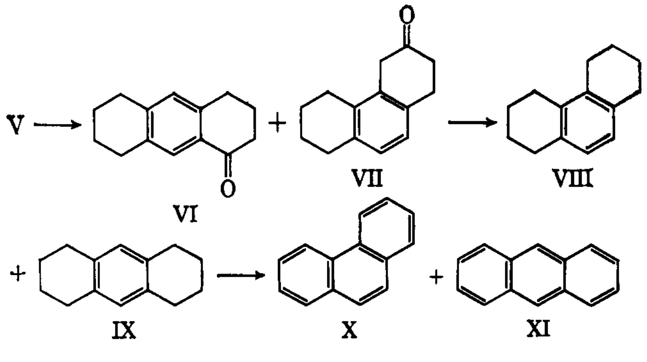
[2] L. F. Fieser and H. Heyman, *J. Am. Chem. Soc.*, **63**, 2333 (1941).

[3] J. von Braun, *Ber.*, **44**, 2871 (1911).

A study of the scope of double cyclization of the dicarboxylic acid of type III was considered as an additional point of interest.

Friedel–Crafts succinoylation of I in nitrobenzene, using three equivalents of aluminum chloride, gave γ-(*p*-succinylphenyl)butyric acid. This was isolated on direct hydrolysis of the reaction product because the latter was found to be a mixture of the half ester, II, and its ketodicarboxylic acid. Contrary to the findings of Fieser and Heyman[2] to the effect that γ-phenylbutyric acid, but not its ester, could be condensed satisfactorily with phthalic anhydride in tetrachloroethane, it was found that the said acid failed to enter into Friedel–Crafts succinoylation in nitrobenzene, tetrachloroethane, or in a mixture of these solvents. Huang-Minlon reduction of the ketodicarboxylic acid (corresponding to II) gave 1,4-di-γ-carboxypropylbenzene (III), m.p. 181–183° (Kofler hot stage), while Clemmensen reduction gave unsatisfactory results comparable with those reported by Butenandt, Dannenberg, and Rahman[4] with respect to γ-keto-γ-(4,5-benzindanyl-6)-butyric acid and its 1-methyl derivative, and by Fieser and Price[5] for β-2-(*t*-butylnaphthoyl-6)propionic acid. Cyclization of the dicarboxylic acid III with (1) phosphorus pentachloride and anhydrous stannic chloride, (2) thionyl chloride and aluminum chloride, and (3) concentrated sulfuric acid gave γ-(8-keto-2-tetralyl)-butyric acid (IV). An attempt to realize double cyclization of III in part or whole failed. Both Clemmensen as well as Huang-Minlon reduction of IV gave γ-2-tetralylbutyric acid (V) in excellent yields. The identity of V was confirmed by comparison (mixture melting point and infrared spectra) with an authentic sample prepared by succinoylation of tetralin and subsequent reduction of β-6-tetroylpropionic acid.[6]

Krollpfeiffer and Schaeffer[6] have reported the conversion of V by concentrated sulfuric acid exclusively to 1-keto-(1,2,3,4,5,6,7,8)-octahydroanthracene (VI) in 75% yield, b.p. 202° (13 mm.), m.p. 46–47°, and semicarbazone m.p. 252–253°. Schroeter,[7] on the other hand, described the formation of a mixture of VI and 4-keto(1,2,3,4,5,6,7,8-octahydro)phenanthrene (VII) by vacuum distillation of γ-2-tetralylbutyryl chloride without the use of any condensing agent.



The separation of VI and VII was achieved by Schroeter[7] by fractional crystallization of the mixture of their semicarbazones, m.p. 252–253° and m.m.p. 229–231°, respectively, with the resulting recovery of 43% of semicarbazones of VI as against 37% of that of VII from the mixture.

In the present work, the cyclization of γ-2-tetralylbutyric acid (V) was studied by three methods: (1) treatment with phosphorus pentachloride and anhydrous stannic chloride, (2) with phosphorus pentachloride and anhydrous aluminum chloride, and (3) treatment with concentrated sulfuric acid. The latter method was subjected to variation in as much as the acid V was heated with sulfuric acid for 4 hr. in one case, warmed for 45 min. in the second, and in the third one the treatment with sulfuric acid was limited to room temperature.

Table I summarizes the results on the relative yields of phenanthrene and anthracene obtained by different methods of cyclization. It is noteworthy that while phosphorus pentachloride used in conjunction with anhydrous stannic chloride favors the formation of anthracene, its use combined with aluminum chloride yields predominantly phenanthrene accompanied by only 2% anthracene.

TABLE I

YIELDS OF PHENANTHRENE AND ANTHRACENE

Method used for cyclization of	Yield of phenanthrene in the mixture, %	Yield of anthracene in the mixture, %
A. PCl_5 and $SnCl_4$	22	45
B. PCl_5 and $AlCl_3$ (heating 3 hr. at 100–120°)	58	2
C. Concd. H_2SO_4		
1. Heating for 4 hr.	20	2
2. Warming for 45 min.	25	25
3. Treatment at room temp. for 1–1.5 hr.	5	50

In the case of sulfuric acid used as the cyclizing agent, the angular ring closure of V is favored under more vigorous conditions (heating for 4 hr.) while the mild treatment with sulfuric acid maintaining the reaction at room temperature, produces the inverse effect resulting in linear cyclization to the extent of 50% as against only 5% in favor of the angular. Possibly, under the vigorous conditions of cyclization the ketone VI isomerizes to VII. Intermediate conditions consisting of warming the acid with five times its quantity of sulfuric acid on the water bath, on the other hand, offer equal possibilities of angular and linear closures. This result is contrary to that reported by Krollpfeiffer and Schaeffer[6] who claimed to have obtained VI as the exclusive product of cyclization.

In all the methods of cyclization the mixture of ketones VI and VII was purified by alumina chromatography without effecting their separation. The purified mixture was then reduced by Clemmensen reaction and finally dehydrogenated after purification by alumina chromatography. The final reaction product, presumably a mixture of phenanthrene and anthracene, was subjected to careful alumina chromatography using petroleum ether (b.p. 60–80°). Benzene was added to the product mixture in suitable proportions as eluent, resulting in the separation of phenanthrene and anthracene.

An attempted fractionation of the mixture of VI and VII, obtained by cyclization of V using phosphorus pentachloride and aluminum chloride, by alumina

(4) A. Butenandt, H. Dannenberg, and A. Rahman, *Ber.*, **88**, 1395 (1955).

(5) L. F. Fieser and C. C. Price, *J. Am. Chem. Soc.*, **58**, 1838 (1936).

(6) F. Krollpfeiffer and W. Schaeffer, *Ber.*, **56B**, 620 (1923).

(7) G. Schroeter, *ibid.*, **57**, 2003 (1924).

chromatography showed that the pure material obtained in 60% yield consisted of 58% of VII and only 2% of VI.

Experimental

All melting points were determined on Kofler hot stage and are uncorrected. Infrared spectra were measured on a Perkin-Elmer double beam spectrophotometer Model 21 (potassium bromide pellet) and Beckman spectrophotometer (Nujol) and ultraviolet spectra on a Beckman automatic recording spectrophotometer Model DK 2 in 95% ethanol.

γ-(*p*-Succinylphenyl)butyric Acid.—Powdered anhydrous aluminum chloride (80 g.) was added to nitrobenzene (60 ml.) with vigorous stirring to yield a solution. The reaction flask was then kept in a bath containing ice–water slurry, and powdered succinic anhydride (22 g.) was added all at once. Finally, ethyl γ-phenylbutyrate (34 g.) was added dropwise over a period of 45 min. maintaining the temperature at 10°, and the stirring was continued for a further period of 10 hr. The reaction mixture was then allowed to stand 48 hr. at 5° and then was decomposed with ice and hydrochloric acid. The treatment of the ethereal extract of the dark brown reaction product with 10% sodium bicarbonate, followed by acidification of the extract, afforded 32 g. of a product, possibly a mixture of II and the corresponding ketodicarboxylic acid, which melted at 135–150°. Hydrolysis with 25% potassium hydroxide in methanol and crystallization of the hydrolysate from dilute ethanol gave 27.5 g. (*ca.* 60%) of γ-(*p*-succinylphenyl)butyric acid, m.p. 162–163°.

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.69; H, 6.11. Found: C, 64.09; H, 6.35.

The infrared spectrum (KBr) showed 5.85–5.95 (doublet, COOH and CO); 11.6, 12.0, and 12.20 μ (γ_{CH}); ultraviolet spectrum (EtOH), λ_{max}^{EtOH} 251 mμ (ε 15,179).

The semicarbazone of II prepared in the usual way, and crystallized from 90% ethanol, gave m.p. 192–194°.

Anal. Calcd. for $C_{15}H_{19}O_5N_3$: C, 56.12; H, 5.97; N, 13.09. Found: C, 55.84; H, 5.91; N, 13.31.

1,4-Di-(γ-carboxypropyl)benzene (III).—A mixture of II (18 g.), potassium hydroxide (12 g.), diethylene glycol (90 ml.), and 85% hydrazine hydrate (9 ml.), was heated under reflux for 1 hr. at 140–145°. The temperature was then raised to 180–182° whereby the excess of hydrazine hydrate and the water formed in the reaction distilled. Finally, the reaction mixture was heated to 200–205° for 4 hr. On cooling, the reaction product was poured into water, acidified, extracted with ether, and washed. The dried ethereal solution (anhydrous magnesium sulfate), on evaporation of the solvent, gave 16.5 g. (94%) of III, m.p. 174–178°. Recrystallization from acetic acid gave 13.8 g. of III as colorless needles, m.p. 181–183°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.26; H, 7.26. Found: C, 67.05; H, 7.21.

The infrared spectrum (KBr) showed 3.45 (aromatic CH), ν_{CO} 5.9 (COOH), γ_{CH} 10.9, 11.9, and 13.0 μ; ultraviolet spectrum, λ_{max} mμ (ε), 259 (305), 264 (392), 267 (356), and 273 (388).

γ-(8-Keto-2-tetralyl)butyric Acid (IV). **A.**—Five grams of III was dissolved in 50 ml. of dry thiophene-free benzene and treated with 8.5 g. of phosphorus pentachloride. The reaction mixture was allowed to stand for 1 hr. at room temperature, cooled to 0°, and treated with a solution of 16 ml. of anhydrous stannic chloride in 25 ml. of benzene and left for 50 min. at 0°. The reaction mixture was then decomposed with ice and hydrochloric acid and finally extracted with solvent. The ether–benzene extract was shaken with 10% sodium hydrogen carbonate. The alkaline aqueous layer when treated with dilute hydrochloric acid gave a solid product whch was taken up in ether. On working up the ethereal solution, 4.2 g. (90%) of IV was obtained. Recrystallization from benzene–petroleum ether (60–80°) gave IV as colorless needles, m.p. 79–81°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.47; H, 6.95. Found: C, 72.73; H, 7.00.

The infrared spectrum (KBr) showed 3.4 (aromatic CH), ν_{CO} 5.9–5.95 (doublet, COOH and keto), 6.2 (CO conjugation with aromaticity); γ_{CH} 10.85, 12.2, and 13.15 μ; ultraviolet spectrum, λ_{max} mμ (ε), 211.5 (27,200), 250.5 (11,000), and 302 (2020).

B.—A solution of 2.5 g. of III in 20 ml. of absolute ether was treated with 5 drops of pyridine and 8 ml. of thionyl chloride. The mixture was allowed to stand at room temperature for 0.5 hr. and the ether and thionyl chloride were removed under reduced pressure. The ice-cold solution of the acid chloride so obtained in 20 ml. of benzene was treated with 8 g. of anhydrous aluminum chloride and the mixture heated for 0.5 hr. at 60–80°. The reaction complex was then hydrolyzed with ice and hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide, and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* and recrystallization of the residue from benzene–petroleum ether (60–80°) gave a product, melting point and mixture melting point with IV obtained in A, 79–81°, 1.7 g. (74%).

C.—Two and one-half grams of III was heated for 45 min. with 7 ml. of concentrated sulfuric acid on a water bath. On cooling the reaction product was poured on ice and worked up with ether and aqueous sodium hydrogen carbonate. The compound IV was obtained by this method in 79% yield and melted at 80–81°; the melting point did not depress on admixture with samples of IV obtained in B and A.

γ-2-Tetralylbutyric Acid (V).—A mixture of 5 g. IV, 20 g. of amalgamated zinc, 20 ml. of concentrated hydrochloric acid, and 25 ml. of toluene was refluxed for 24 hr. and concentrated hydrochloric acid (20 ml.) was added every 6 hr. over this period. The toluene layer was separated and the aqueous layer was extracted with ether. The ether–toluene solution was washed and dried over magnesium sulfate. Removal of the solvents gave 4.2 g. (88%) of V, m.p. 47–49°, the identity of which was confirmed by a mixture melting point determination with an authentic sample prepared by a direct succinoylation of tetralin and subsequent reduction of β-(6-tetroyl)propionic acid.[6]

Huang-Minlon reduction of 2.5 g. of IV, using 1.63 g. of potassium hydroxide, 13 ml. of diethylene glycol, and 1.2 ml. of 85% hydrazine hydrate, and working up the reaction mixture as usual gave γ-2-tetralylbutyric acid, m.p. 47–49°, 92%.

Cyclization of γ-2-Tetralylbutyric Acid (V). 4-Keto(1,2,3,4-5,6,7,8-octahydro)phenanthrene or 1-Keto(1,2,3,4,5,6,7,8-octahydro)anthracene. A. With Phosphorus Pentachloride and Stannic Chloride.—A solution of 5 g. of V in 40 ml. of dry thiophene-free benzene was treated with 8 g. of phosphorus pentachloride and the reaction mixture was allowed to stand for 1 hr. at room temperature. It was then cooled to 0° and a solution of 15 ml. of anhydrous stannic chloride in 20 ml. of benzene was added. The mixture was allowed to stand for 45 min. at 0° and then decomposed with ice and hydrochloric acid, extracted with ether, washed with water and 10% sodium bicarbonate solution, and finally dried over magnesium sulfate. Removal of the solvent gave a light yellow liquid which distilled at 165–180° (4 mm.) and which on purification by alumina chromatography gave 3.1 g. of a liquid which solidified on standing. This material presumably a mixture of VI and VII, yielding a semicarbazone, melting at 230–240° (semicarbazone of VII, m.p. 229–231°,[7] and that of VI, m.p. 250–251°[7]), was reserved for Clemmensen reduction and subsequent reactions.

B. With Phosphorus Pentachloride and Aluminum Chloride.—A solution of 2.5 g. of VI in 20 ml. of thiophene-free benzene was treated with 3.5 g. of phosphorus pentachloride and the mixture was left at room temperature for 1 hr. The reaction mixture was then treated with 4.5 g. of aluminum chloride and heated for 3 hr. at 100–120°. The resulting mixture, on removal of benzene, decomposition with ice and hydrochloric acid, and working up with ether gave a liquid (2.0 g., 87%) which was directly purified by alumina chromatography. The pure material obtained in 60% yield was collected in two fractions. The first fraction (38%) was converted to its semicarbazone (97%), m.p. 229–233°; on crystallization from ethanol it melted at 230–231°. This was hydrolyzed, purified by chromatography, subjected to Clemmensen reduction (80%), and finally dehydrogenated (52%) yielding pure phenanthrene obtained by chromatography. The second fraction (22%), subjected to the reactions as described, yielded phenanthrene and anthracene in 10:1 proportions thus showing that the purified mixture of VI and VII, obtained in 60% yield from V, consisted of 58% of VII and 2% of VI.

C. With Concentrated Sulfuric Acid. 1.—Five grams of V was treated with 40 ml. of concentrated sulfuric acid and the mixture was heated on the steam bath for 4 hr. The reaction mixture was then cooled and poured on ice and finally taken up in ether. The ethereal solution was washed with aqueous sodium bicarbonate and water and finally dried over magnesium sulfate. Evaporation of the solvent gave 1.13 g. (25% VI and/or VII), m.p. 39–44°, semicarbazone, m.p. 218–230°.

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.

Acknowledgment.—The authors wish to express their thanks to Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires for a research grant and to Professor Dr. Heinz Dannenberg for his help in connection with the absorption spectra.

The Stereospecific Fragmentation of 2-Dichloromethyl-2-methylcyclohexanone

MANFRED G. REINECKE

Department of Chemistry, University of California, Riverside, California

Received June 26, 1963

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]

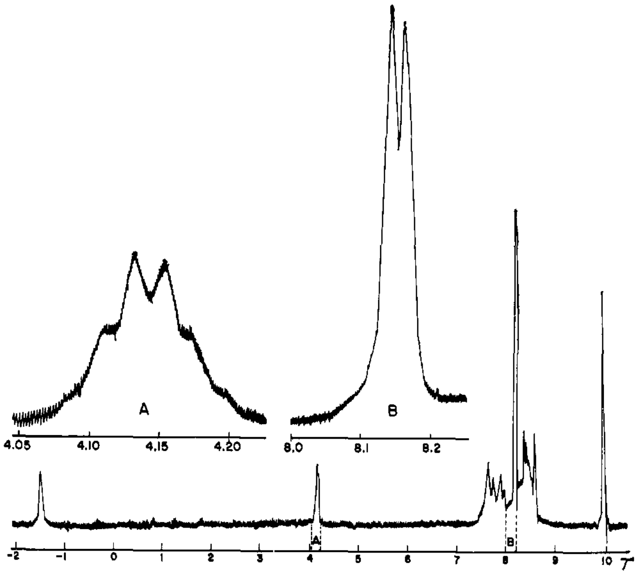


Fig. 1.—The n.m.r. spectrum of 7-chloro-6-methyl-6-heptenoic acid (**3**).

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,

---

(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.