of racemic α-ionone. There was a distinct difference in odor between the *d*- and the *l*-form.

Experimental

The *dl*-α-ionone used had been purified by repeated recrystallization of its semicarbazone until the refractive index n^{23}_{D} = 1.4995.[8]

Preparation of *d*- and *l*-α-Ionone-*l*-menthydrazones.—Fifty-seven and six-tenths g. (0.3 mole) of *dl*-α-ionone was dissolved together with 64.2 g. (0.3 mole) of *l*-menthydrazide of $[\alpha]^{23}_{D}$ −76.7° in 240 cc. of 95% ethanol, containing 2% of sodium acetate and 1% of acetic acid. After refluxing for two and one-half hours, 113 g. of a mixture of the diastereomers crystallized on cooling. The specific rotation of the mixture was about −20°, its m. p. 163–65°. Repeated fractional recrystallizations led to a product of $[\alpha]^{22}_{D}$ −320° (in EtOH), m. p. 185°, and a more soluble fraction of $[\alpha]^{22}_{D}$ +230° (in EtOH), m. p. 176° (calcd. for $C_{24}H_{40}O_2N_2$: N, 7.21. Found: N, 7.37).

Preparation of β-Ionone-*l*-menthydrazone.—The *l*-menthydrazone of β-ionone was prepared for comparison from a sample of β-ionone of n^{22}_{D} 1.5183. The specific rotation of the recrystallized product was −35°, m. p. 178°. As this value represents the contribution of the *l*-menthydrazone moiety to the specific rotation, a 1:1 mixture of *d*- and *l*-α-ionone-*l*-menthydrazone should approximate this value. Hence, the value of +230° for the dextrorotatory diastereomer is presumably *ca.* 20° too low in comparison with −320° for the levorotatory form. The higher purity of the *l*-compound accounts for the higher numerical value of the specific rotation for the resulting free *l*-α-ionone as compared with the *d*-enantiomer (see below).

Hydrolysis of Menthydrazones.—2.0 g. of purest *l*-α-ionone-*l*-menthydrazone was suspended with 4.5 g. of phthalic anhydride in 35 cc. of water and subjected to steam distillation for two and one-half hours. The distillate was thoroughly extracted with ether and 0.6 g. of an oil was obtained. Its $[\alpha]^{27}_{D}$ showed the high value of −406°, its refractive index was n^{25}_{D} 1.5000. By the same procedure a dextrorotatory α-ionone was obtained from *d*-α-ionone-*l*-menthydrazone; its specific rotation $[\alpha]^{23}_{D}$ was +347°, its n^{22}_{D} 1.5021.

2,4-Dinitrophenylhydrazones and *p*-Chlorobenzoylhydrazones of *l*- and *d*-α-Ionone.—Both optically active α-ionones were characterized by the preparation of the two derivatives. Their melting points are summarized below; N of dinitrophenylhydrazones of *d*-and *l*-α-ionone; Found: 15.3 and 15.2; calcd. 15.1.

TABLE I

Melting points, °C., of	*l*-α-Ionone	*d*-α-Ionone	*dl*-α-Ionone
2,4-Dinitrophenylhydrazone	133	129	143
p-Chlorobenzoylhydrazone	200–201	196–198	214

Summary

The resolution of *dl*-α-ionone was accomplished by means of *l*-menthydrazone. The use of optically active α-ionone as an indicator for the stability of the double bond system in ionone and its derivatives is discussed.

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[8] We are greatly indebted to Dr. Ernest Theimer, Director of Research, Van Ameringen-Haebler Inc., Elizabeth, N. J., for supplying us with highly purified α-ionone and β-ionone.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Synthesis of 16,17- and 17,18-Octadecenoic Acids[1,2]

BY ROLAND KAPP[3] AND ALEXANDER KNOLL[4]

Although several isomeric octadecenoic acids are known, the group is incomplete. The following reports the synthesis of two new members of this important group, and in addition two new keto-octadecenoic acids.

Three methods have been used in the preparation of long chain monoethenoid acids: the malonic ester synthesis, the Grignard synthesis and the acetoacetic ester synthesis.

The syntheses of the 16,17- and 17,18-octadecenoic acids were achieved by preparing the unsaturated keto acids by means of the acetoacetic ester method, followed by reduction of the keto acids by means of the Wolff–Kishner method to the respective olefinic acids.

The 17,18-octadecenoic acid was synthesized by the following procedure: 10,11-undecenoyl chloride was condensed with sodio-diethyl-acetyl suberate, whereupon α-acetyl-α-10,11-undecenoyl-diethyl suberate was formed. G. M. Robinson and R. Robinson[5] have pointed out that when two acyl groups occur in a compound such as (III), the acyl group derived from the stronger acid is preferentially removed by hydrolysis. Therefore, (III) was hydrolyzed by means of the stepwise procedure used by the Robinsons and their associates yielding (VI) 8-keto-17,18-octadecenoic acid. The keto acid (VI) was then reduced using the Wolff–Kishner method to (VII), 17,18-octadecenoic acid.

The synthesis of the 16,17-octadecenoic acid was achieved in the same general way using 9,10-undecenoyl chloride.

The position of the double bond in the 16,17- and 17,18-octadecenoic acids was proved by oxidation to the expected dicarboxylic acids, 1,14-tetradecamethylene dicarboxylic acid and 1,15-pentadecamethylenedicarboxylic acid. Both unsaturated acids absorbed two gram atoms of hydrogen and were converted thereby into stearic acid. The following diagram outlines the preparation of 17,-18-octadecenoic acid.

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[1] From a dissertation submitted by R. Kapp to the Faculty of Pure Science, Columbia University, N. Y. C., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The authors are deeply indebted to Professor J. M. Nelson, Columbia University, for his encouragement and advice.

[3] Address: National Oil Products Co., Harrison, N. J.

[4] Address: Metals Disintegrating Co., Elizabeth, N. J.

[5] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **127**, 175 (1925).

$\mathrm{CH_3COCH_2COOC_2H_5 + NaOC_2H_5 + BrCH_2(CH_2)_4COOC_2H_5}$

Anhydrous $\downarrow$ ethanol

(I) $\mathrm{CH_3COCH[(CH_2)_5COOC_2H_5]COOC_2H_5}$

Na anhydrous $\downarrow$ ethyl ether

(II) $\mathrm{CH_3COCNa[(CH_2)_5COOC_2H_5]COOC_2H_5}$

$\downarrow$ $\mathrm{CH_2{=}CH(CH_2)_8COCl}$

(III) $\mathrm{CH_2{=}CH(CH_2)_8COC(COCH_3)[(CH_2)_5COOC_2H_5]COOC_2H_5}$

Dilute aqueous $\downarrow$ potassium hydroxide

(IV) $\mathrm{CH_2{=}CH(CH_2)_8COCH_2[(CH_2)_5COOC_2H_5]COOC_2H_5}$ (not isolated)

Dilute aqueous $\downarrow$ sulfuric acid

(V) $\mathrm{CH_2{=}CH(CH_2)_8CO(CH_2)_6COOC_2H_5}$

Dilute aqueous sodium hydroxide followed by acidification with hydrochloric $\downarrow$ acid

(VI) $\mathrm{CH_2{=}CH(CH_2)_8CO(CH_2)_6COOH}$

Sodium ethoxide $\downarrow$ hydrazine hydrochloride

(VII) $\mathrm{CH_2{=}CH(CH_2)_{15}COOH}$

Experimental

6-Bromoethyl-hexoate.—The method of Robinson and associates[6,7] was followed; b. p. 117–118° (10 mm.).[8]

Di-ethyl-α-acetyl Suberate.—The method of Gaubert and associates[9] was followed; b. p. 164–165° (4.5 mm.).

10,11-Undecenoyl Chloride.—Undecenoic acid[10] was recrystallized from heptane; m. p. 24.5–25°. 31.3 grams of the acid was added to 21.2 g. of thionyl chloride over a period of forty-five minutes. The mixture was allowed to stand for two hours, and then heated on the water-bath for fifteen minutes to remove the excess thionyl chloride. The undecenoyl chloride was distilled under reduced pressure in a stream of dry nitrogen; b. p. 127.5–128° (13 mm.), bath at 157°; yield, 26.3 g. (76%).

8-Keto-17,18-octadecenoic Acid (VI).—To a suspension of 2.7 g. of sodium sand in 120 cc. of absolute ether, 32.7 g. of di-ethyl-α-acetyl suberate was added over a period of eight and a half hours. The mixture was then heated on the steam-bath for forty-five minutes, cooled to room temperature, and a solution of 26.3 g. of 10,11-undecenoyl chloride in 30 cc. of absolute ether was added. The resulting gel, after standing overnight, was refluxed for forty-five minutes on the steam-bath, the salt extracted from the ethereal solution, the ether distilled, and the residue shaken for twenty-four hours with 750 cc. of a 4% potassium hydroxide solution. After this solution had been acidified with dilute acetic acid, extracted with ether, and the ether distilled, the residue was refluxed for twenty-four hours with 375 g. of a 5% sulfuric acid solution, cooled, and again extracted with ether. After removal of the ether the residue was boiled for five hours with 375 g. of a 5% sodium hydroxide solution; the resulting clear solution, after cooling overnight, solidified to a crystalline mass of the sodium salt. This, after acidification with hydrochloric acid, was extracted with ether. The ethereal solution, after standing in a refrigerator overnight, deposited 7.4 g. of white glistening plates of the keto acid, which were filtered off. The ether was removed from the filtrate by distillation and the residue extracted with petroleum ether, yielding 2.6 g. of keto acid, making a total yield of 28%, m. p. 68–69°. Decolorization with activated charcoal (Darco G-60) and three further recrystallizations from petroleum ether gave fine white plates with a constant melting point of 72.2–73°. *Anal.*[11] Calcd. for $\mathrm{C_{18}H_{32}O_3}$: C, 72.91; H, 10.89. Found: C, 73.04; H, 10.98.

The semicarbazone, recrystallized twice from ethyl alcohol, melted at 102.5–103°. *Anal.* Calcd. for $\mathrm{C_{19}H_{35}O_3N_3}$: N, 11.89. Found: N, 12.15.

17,18-Octadecenoic Acid (VII).—To a freshly prepared solution of sodium ethoxide, made by adding 1.42 g. of sodium to 20 cc. of absolute ethanol in a glass bomb-tube, were added 3 g. of the keto acid (VI) dissolved in 10 cc. of absolute ethanol; 1.45 g. of hydrazine hydrochloride was then washed into the tube using 10 cc. of absolute ethanol. The bomb tube was sealed and heated at 185–200° for sixty hours. The contents of the tube were next dissolved in 20 cc. of hot water, acidified with hydrochloric acid, heated to boiling, cooled and extracted with ether. The crude 17,18-octadecenoic acid (VII) obtained from the ether weighed 1.65 g. (65% yield), m. p. 48–50°. It was recrystallized from aqueous methanol as fine plates, m. p. 55–55.5°.

Anal. Calcd. for $\mathrm{C_{18}H_{34}O_2}$: C, 76.52; H, 12.14. Found: C, 76.67; H, 12.39.

9,10-Undecenoyl Chloride.—Fifty-two grams of 9,10-undecenoic acid[12] was converted to the acid chloride by reaction with 35.9 g. of thionyl chloride in the same manner as for 10,11-undecenoyl chloride; b. p. 112–113° (4 mm.) (bath 143°); yield 45 g. or 80%.

8-Keto-16,17-octadecenoic Acid.—This was prepared in the same manner as VII, using 4.86 g. of sodium sand in 350 cc. of absolute ethyl ether, 57.14 g. of ethyl α-acetyl suberate, and 45.00 g. of 9,10-undecenoyl chloride; yield, 16 g. (23%) of the acid, m. p. 75–76°. The acid after two recrystallizations from petroleum ether melted at 78.4–78.9°. *Anal.* Calcd. for $\mathrm{C_{18}H_{32}O_3}$: C, 72.91; H, 10.89. Found: C, 73.19; H, 11.15. The semicarbazone after being recrystallized twice from ethyl alcohol melted at 112.8–113.5°. *Anal.* Calcd. for $\mathrm{C_{19}H_{35}O_3N_3}$: N, 11.89. Found: N, 11.60.

16,17-Octadecenoic Acid.—This was prepared[13] in the same manner as the 17,18-octadecenoic acid (VII). The acid was recrystallized twice from methanol; m. p. 62.8–63.5°. *Anal.* Calcd. for $\mathrm{C_{18}H_{34}O_2}$: C, 76.52; H, 12.14. Found: C, 76.38; H, 12.12.

Proof of Structure.—About 100 mg. of 16,17-octadecenoic acid in 25 cc. of acetone was oxidized by refluxing with about 0.3 g. of potassium permanganate. After evaporation of the acetone and destruction of the excess permanganate with a little hydrochloric acid and sodium meta-bisulfite, the solution was extracted with ether. The ether extract yielded a residue which was recrystallized twice from ethylene dichloride, and then from glacial acetic acid, m. p. 123.6–124.0°. 1,14-Tetradecamethylene dicarboxylic acid is reported to melt at 124–124.2°.[14] *Anal.* Calcd. for $\mathrm{C_{16}H_{30}O_4}$: C, 67.08; H, 10.56. Found: C, 66.89; H, 10.50.

Similarly 17,18-octadecenoic acid on oxidation yielded an acid which after two recrystallizations from ethylene dichloride, two from acetone and three from aqueous acetic acid, melted at 113–114°. Two more recrystallizations from glacial acetic acid brought the melting point to 117.0–117.4°. 1,15-Pentadecamethylene dicarboxylic acid is reported to melt at 118°.[14] *Anal.* Calcd. for $\mathrm{C_{17}H_{32}O_4}$:

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[6] Robinson and Smith, *J. Chem. Soc.*, 371 (1937).

[7] Barger, Robinson and Smith, *ibid.*, 718 (1937).

[8] All boiling points are uncorrected. All melting points are corrected.

[9] Gaubert, Linstead and Rydon, *J. Chem. Soc.*, 1977 (1937).

[10] We are indebted to Mr. Wm. Valentine of the Naugatuck Chemical Co. for a gift of this acid.

[11] All analyses were done by Mr. Saul Gottlieb, Organic microanalyst of the Department of Chemistry, Columbia University.

[12] Harris and Smith, *J. Chem. Soc.*, 1109 (1935).

[13] The keto acids reported here did not respond to reduction by the Clemmensen method.

[14] Chuit, *Helv. Chim. Acta*, **9**, 271 (1926).

C, 67.94; H, 10.74. Found: C, 67.83; H, 10.98.

Both octadecenoic acids were subjected to catalytic hydrogenation using Adams catalyst[15]: 0.356 millimole of the 16,17-octadecenoic acid required 0.352 millimole of hydrogen for complete reduction, and 0.500 millimole of the 17,18-octadecenoic acid required 0.505 millimole of hydrogen. The stearic acid obtained from both reductions, after recrystallization from glacial acetic acid, melted at 69.5–70.2°; reported for stearic acid, 69–70.2°.[16]

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(15) "Organic Syntheses," Coll. Vol. I, 2d. ed., John Wiley and Sons, Inc., New York, N. Y., p. 463.

(16) Kass and Kayser, This Journal, 62, 230 (1940).

Summary

8-Keto-16,17- and 8-keto-17,18-octadecenoic acids have been prepared by the acetoacetic ester synthesis. These acids have been reduced to the respective octadecenoic acids by the Wolff–Kishner method. Proof of structure of the octadecenoic acids rests on their reduction to stearic acid, on their oxidation to the expected dibasic acids, and on the method of synthesis.

Harrison, New Jersey Received June 3, 1943

[Contribution from the School of Chemistry and Physics of the Pennsylvania State College]

Fluorine Derivatives of Acetophenone and Ethylbenzene

By J. H. Simons and D. F. Herman

In a previous paper[1] the synthesis of 1,1,1,2,2-pentafluoro-2-phenylethane was suggested. This has now been accomplished and a number of fluorine derivatives of both acetophenone and ethylbenzene synthesized. In this work a variety of methods of fluorination were used. In some cases the replacement of chlorine with fluorine was accomplished by the use of antimony fluoride in the Swarts reaction. In other cases hydrogen fluoride was used following the method employed by Simons and Lewis[2] and Simons and Ramler.[1] A highly active silver fluoride made by the use of elementary fluorine and containing an excess of fluorine atoms over silver atoms was used for some of the more difficult replacements of chlorine. This was done in a liquid hydrogen fluoride solution. By using liquid anhydrous hydrogen fluoride as a solvent, a direct fluorination of acetophenone with elementary fluorine was accomplished.

Experimental

Preparation of ω,ω-Difluoroacetophenone from Dibromoacetophenone.—Into a 350-cc. steel bomb connected by a forged steel fitting to a steel water-cooled condenser fitted with an exhaust valve was placed 67 g. (0.24 mole) of ω,ω-dibromoacetophenone, 80 g. (0.63 mole) of silver fluoride and 100 g. (5 mole) of anhydrous hydrogen fluoride. The silver fluoride was prepared by passing elementary fluorine through a copper tube packed with silver which had been precipitated by the reduction of ammoniacal silver solution with hydroxylamine hydrochloride. The increase in weight of the silver is accounted for by the formula $AgF_{1.6}$. The formula $AgF_{1.8}$ has been reported.[3] The steel bomb was placed into a shaker and heated to 75° for twelve hours. The reaction products were poured over ice and extracted with ether. This extract was washed with water and then with several 50-cc. portions of 5% sodium bicarbonate solution. It was dried with anhydrous sodium sulfate. After the removal of the ether the products were fractionated in columns of 8 to 12 theoretical plates. There was obtained 15.2 g. (40% yield) of difluoroacetophenone b. p. 83–85° (29 mm.). There was no indication of the formation of the mixed fluorobromoacetophenone. Difluoroacetophenone readily yielded a 2,4-dinitrophenylhydrazone of m. p. 221–223°. *Anal.* Calcd. for $C_8H_6OF_2$; F, 24.36. Found: F, 24.5, 23.8.

This compound was shown to be the ω-difluoroacetophenone by the following experiment. One gram was warmed for forty-eight hours with 30 cc. of 5% sodium hydroxide solution. When this solution was acidified and ether extracted, mandelic acid was found: m. p. of recrystallized acid and mixed m. p. with an authentic sample was 117–118°.[4] Mandelic acid is similarly prepared from dichloroacetophenone.[4]

Dibromoacetophenone failed to react with antimony trifluoride in the presence of antimony pentachloride to give difluoroacetophenone. Also a reaction with anhydrous hydrogen fluoride using antimony pentachloride as a catalyst and a reaction with silver fluoride in a petroleum ether medium were unsuccessful.

Liquid Phase Fluorination of Acetophenone.—The fluorine used in this work was produced by fluorine generators similar to the one described by Simons.[5] The fluorine produced by each of two generators was passed through one-fourth inch copper tubing into a brass T-tube where it was diluted with five times its volume of nitrogen. It then passed through a copper surge chamber and into the reaction chamber. Two $^1/_8''$ tube inlets were provided in the reaction chamber so that the fluorine from each generator entered at a different place. The generators were operated to yield approximately one-tenth mole of fluorine per hour. The nitrogen dilution was controlled by means of flowmeters. The copper reaction vessel was cylindrical, 5.8 cm. diameter and 26.2 cm. long. A copper condenser cooled with dry ice–acetone was provided. This condensed and returned most of the hydrogen fluoride carried out with the exit gases. From the top of the condenser the gases were led through a tube containing sodium fluoride and then through two traps cooled with liquid air.

The reaction vessel was charged with 60 g. (0.50 mole) of acetophenone, 2 g. of silver oxide and 200 g. of hydrogen fluoride. Approximately one mole of fluorine was passed in five hours. For the first two hours the reaction proceeded very smoothly at 0°. A slight odor of fluorine was then noticed in the exit gases. After five hours a large portion of the fluorine passed through unreacted. About 2 g. of carbon tetrafluoride contaminated with oxygen fluoride was found in the liquid air traps.

The contents of the reaction vessel were poured over ice,

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(1) J. H. Simons and E. O. Ramler, This Journal, 65, 389 (1943).

(2) J. H. Simons and C. J. Lewis, *ibid.*, 60, 492 (1938).

(3) H. Jockusch, *Naturwissenschaften*, 22, 561 (1934).

(4) J. Houben and W. Fischer, *Ber.*, 64B, 2644 (1931); J. G. Aston, J. D. Newkirk, D. M. Jenkins and J. Dorsky, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943.

(5) J. H. Simons, This Journal, 46, 2175 (1924); "Inorganic Syntheses," McGraw-Hill Book Company, Inc., New York, N. Y., 1939, Vol. VI, p. 142.