0.75 cc. of concentrated sulfuric acid was refluxed for two hours. After the addition of 1 cc. of water, solid sodium bicarbonate was added until the mixture was neutral to congo red. The filtered solution was concentrated to dryness under reduced pressure, and the residue was taken up in benzene which was distilled to remove water. The dried residue was extracted with absolute alcohol. The solution was filtered, evaporated to dryness, and the ethyl ester of *dl*-N-benzoylserine[4] was crystallized from benzene-petroleum ether; m. p. 79.5–80.5°; yield 3.7 g. (65%).

Ethyl Ester of *dl*-N-Benzoyl-β-chloroalanine, VIII.—A suspension of 1.3 g. of the ethyl ester of *dl*-N-benzoylserine in benzene was treated with 0.4 cc. of dry pyridine and with 0.6 cc. of thionyl chloride and was heated on a steam-bath for twenty minutes. After cooling, the solution was washed with water, dilute hydrochloric acid, saturated sodium bicarbonate solution, and again with water. The benzene was removed under reduced pressure and the ethyl ester of *dl*-N-benzoyl-β-chloroalanine was crystallized from ether–petroleum ether; m. p. 90.5–91.0°; yield, 0.9 g. (67%).

Anal. Calcd. for $C_{12}H_{14}O_3NCl$: C, 56.36; H, 5.52; N, 5.48. Found: C, 56.80; H, 5.15; N, 5.37.

Ethyl Ester of *dl*-N-Benzoyl-β-(carboethoxymethylmercapto)-alanine, V ($R = C_2H_5$).—A solution of 0.85 g. of ethyl thioglycolate in 4 cc. of 12% sodium ethoxide solution was added to a solution of 1.8 g. of the ethyl ester of *dl*-N-benzoyl-β-chloroalanine in a few cubic centimeters of absolute alcohol. After heating on the steam-bath for thirty minutes, the mixture was neutral to litmus. The precipitated sodium chloride was removed by filtering, and the alcohol was distilled under reduced pressure. The residue was taken up in ether. The solution was filtered to remove sodium chloride, and the ether was evaporated leaving the ester as an oil.

***dl*-4-Benzamido-3-ketotetrahydrothiophene.**—Ring closure of the crude ethyl ester from the preceding experiment with sodium ethoxide in ethyl alcohol gave 1.1 g. (50%) of the sodium salt of *dl*-4-benzamido-3-ketotetrahydro-2-thiophenecarboxylic acid ethyl ester. After hydrolysis and decarboxylation, the yield of *dl*-4-benzamido-3-ketotetrahydrothiophene was 0.5 g. (70%). This compound showed no depression of the melting point when mixed with ketone prepared from cysteine.

Acknowledgments.—The authors wish to thank Messrs. D. F. Hayman, R. N. Boos, W. R. Reiss and H. S. Clark for the microanalyses reported in this paper.

Summary

dl-4-Benzamido-3-ketotetrahydrothiophene, which is a key intermediate in the synthesis of biotin, has been synthesized from *l*-cysteine and chloroacetic acid, and from *dl*-serine and thioglycolic acid.

RAHWAY, NEW JERSEY RECEIVED SEPTEMBER 2, 1944

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[4] Erlenmeyer, *Ber.*, **35**, 3769 (1902).

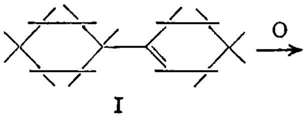
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Polymerization of Cyclohexene with Hydrogen Fluoride

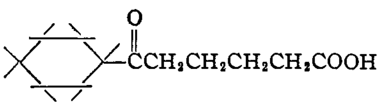
BY S. M. MCELVAIN AND JAMES W. LANGSTON[1]

In connection with a study of the action of hydrogen fluoride on various classes of organic compounds,[2] an investigation of the products formed from the polymerization of cyclohexene was undertaken. Of all of the olefins that can be polymerized by hydrogen fluoride, cyclohexene seemed especially suited to such an investigation because the characterization of its polymers might be facilitated by dehydrogenation to aromatic structures.

There are numerous reports of the polymerization of cyclohexane in the literature. Truffault[3] obtained the dimer (I) in high yields (80–90%) by the action of phosphorus pentoxide on the olefin. The dimer was characterized by oxidation to δ-hexahydrobenzoylvaleric acid (II). Hofmann[4] reported that boron fluoride, preferably mixed with some hydrogen fluoride, converted cyclohexene into di-, tri-, tetra- and higher polymers; the dimer was characterized by oxidation to the keto-acid II. Concentrated sulfuric acid was found by Nametkin[5] to convert cyclohexene at 5° to an oil (40%) which consisted of a *saturated* dimer and trimer, and an *unsaturated* tetramer. From the residue which remained after the distillation of this oil a tetracyclohexyl-cyclohexene, m. p. 83–85°, and a tetracyclohexyl-benzene, m. p. 265°, were isolated and identified. Aluminum chloride was reported[5] to give similar results.



I



II

Waterman, Leendertsa and ter Poorten[6] also studied the polymerization of cyclohexene with aluminum chloride; they found that this catalyst had no effect on the olefin at −78°, very little at 40°, but at 70° produced a considerable amount of polymers. These investigators made the interesting observation that a combination of aluminum chloride and hydrogen chloride caused polymerization of cyclohexene at −78° but that neither reagent alone had any effect on the olefin at this temperature, and, since they found that

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[1] Harshaw Chemical Company Fellow, 1942–1944.

[2] *Cf.* McElvain and Langston, THIS JOURNAL, **65**, 2239 (1943), for the trimerization of ketene acetal with hydrogen fluoride.

[3] Truffault, *Bull. soc. chim.*, [5] **3**, 442 (1936); *Compt. rend.*, **200**, 406 (1935).

[4] Hofmann, *Chem. Ztg.*, **57**, 5 (1933).

[5] Nametkin, *et al.*, *Ber.*, **66**, 358 (1933); *J. Gen. Chem. Soc.* (U. S. S. R.), **7**, 759, 763 (1937), *Chem. Abst.*, **31**, 5750 (1937).

[6] Waterman, Leendertsa and ter Poorten, *Rec. trav. chim.*, **54**, 245 (1935).

cyclohexyl chloride was unaffected by aluminum chloride at −78°, they concluded that the chloride was not an intermediate in the polymerization process. In this connection it should be noted that Swarts[7] obtained polymers of cyclohexene when cyclohexyl bromide was heated with mercuric bromide and because cyclohexene was not polymerized under similar conditions, he suggested that the polymerization of the olefin occurred only at the moment it is formed from the cyclohexyl bromide. Grosse and Linn[8] observed the formation of cyclohexene polymers in the preparation of cyclohexyl fluoride by the addition of hydrogen fluoride to cyclohexene. The nature of the polymeric material, however, was not investigated.

In the work which is now reported the polymerization of cyclohexene by hydrogen fluoride was studied at different temperatures between 0° and 100°, with varying times of reaction and ratios of reactants, and the results obtained lead to the conclusion that polymerization is associated with the olefins formed by the decomposition of cyclohexyl fluoride and polycyclohexyl-cyclohexyl fluorides. When cyclohexene and one equivalent of hydrogen fluoride were allowed to react at room temperature and the reaction product then steam distilled from an aqueous alkaline solution, the material recovered consisted of a mixture of cyclohexene and cyclohexyl fluoride from which the latter product could be obtained pure in 70% yield. However, if the reaction product were distilled directly without first destroying the unchanged hydrogen fluoride, the cyclohexyl fluoride decomposed at its boiling point (98–100°) into hydrogen fluoride and cyclohexene with the simultaneous formation of some polymeric material. Also it was found that pure cyclohexyl fluoride to which a small amount of hydrogen fluoride was added yielded the same type of polymeric material[9] as did cyclohexene when subjected to the conditions—100° for four hours—that caused complete polymerization of the olefin. Another indication that addition of hydrogen fluoride precedes the polymerization is the fact that one equivalent of hydrogen fluoride is required to completely convert cyclohexene to polymers; when 0.5 equivalent is used only 40% of the olefin is polymerized, the remainder being recovered unchanged or as cyclohexyl fluoride.

Cyclohexene is slowly polymerized at 25° by hydrogen fluoride but even after ninety-six hours a considerable amount of unchanged cyclohexyl fluoride remains. At 100°, however, the polymerization is very rapid and after four hours very little of the fluoride remains; after fifteen hours there is none. Presumably, the higher temperature is more effective because it produces a more rapid decomposition of the intermediate cyclohexyl fluoride and fluorinated polymers. While none of these fluorinated polymers were isolated, evidence for their presence was obtained in those experiments that were allowed to run for only a short time (one to four hours) at 100°; usually there was a sudden evolution of hydrogen fluoride when the polymeric material that remained, *after* the removal of the cyclohexyl fluoride and the dimer fraction, was heated further.

The products from the polymerization of cyclohexene with hydrogen fluoride were separated by fractional distillation into the fractions shown in Table I. Above the dimer the fractions collected had rather wide boiling ranges, as would be expected from the large number of isomeric higher polymers that could be formed. The fractions of the various polymers in Table I account for only 57% of the original cyclohexene; the remainder appeared as distillates that boiled between the boiling ranges of the listed fractions.

Table I

Polymer Fractions from the Reaction Cyclohexene with Hydrogen Fluoride

Polymer	Boiling range		Melting range,	Yield,	Mol. wt.	
	°C.	Mm.	°C.	%	Found	Calcd.
Dimer	93–95	8	...	17		
Trimer	120–140	0.1	...	6	245	246
Tetramer	165–180	.1	...	8	326	328
Pentamer	215–230	.1	50–56	6	411	410
Hexamer	255–275	.1	70–80	6	518	492
Heptamer	275–300	.1	85–95	6	602	574
Residue	.....	...	...	8	771	...

The dimer fraction was composed of about 20% cyclohexyl-Δ^1-cyclohexene (I) and 80% of bicyclohexyl. The olefin could be removed readily from the saturated hydrocarbon by extraction with concentrated or fuming sulfuric acid. Ozonolysis of the dimer fraction converted the unsaturated portion to the keto-acid (II) and thereby established the structure of the olefin. Dehydrogenation of the dimer fraction over reduced nickel chromite in the presence of benzene[10] converted it to biphenyl in approximately 90% yield. The presence of so much bicyclohexyl in the dimer fraction indicates that one or all of the cyclohexylcyclohexenes (I, III and IV) are capable of dehydrogenating some of the higher polymers under the conditions of the polymerization.

The trimer fraction was a pale yellow, viscous liquid which was dehydrogenated in benzene solution over reduced nickel chromite to a viscous colorless oil from which small amounts (about 3%) of *m*-terphenyl, m. p. 86–87°, and *p*-terphenyl, m. p. 211–212°, were isolated. The main portion of the dehydrogenated trimer fraction from which the solid terphenyls were isolated

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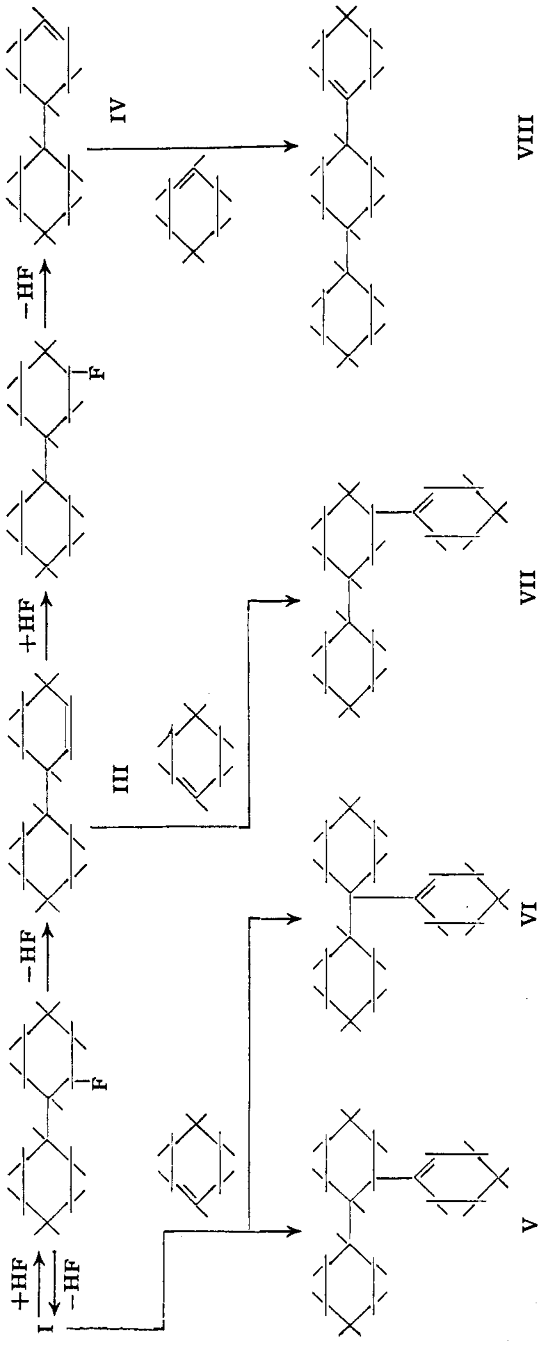
[7] Swarts, *Bull. classe sci., Acad. roy. Belg.*, **22**, 784 (1936), *Chem. Abst.*, **31**, 5333 (1937).

[8] Grosse and Linn, *J. Org. Chem.*, **3**, 26 (1938).

[9] Swarts, ref. 7, p. 105, *Chem. Abst.*, **30**, 4153 (1936), observed that hydrogen fluoride catalyzes the decomposition of cyclohexyl fluoride.

[10] Adkins, Richards and Davis, This Journal, **63**, 1320 (1941).

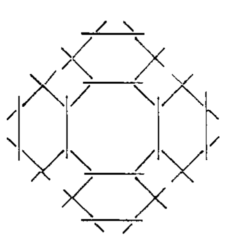
could not be caused to crystallize although it undoubtedly contained relatively large amounts of *o*-terphenyl, m. p. 56–57°. It is not improbable that dehydrogenation products of 1-cyclohexyl-1-cyclohexenyl-cyclohexane (VI) are mixed with the *o*-terphenyl in this fraction and prevent the latter compound from crystallizing. The presence in the polymer mixture of cyclohexene trimers that yield *m*- and *p*-terphenyl on dehydrogenation suggests the intermediate formation of the isomeric Δ^2- and Δ^3-cyclohexylcyclohexenes (III) and (IV) through successive hydrofluorinations and dehydrofluorinations of cyclohexyl-Δ^1-cyclohexene (I). The cyclohexenylation of the olefins I, III and IV would produce the four isomeric trimers V, VI, VII and VIII, the latter two of which yield *m*- and *p*-terphenyl on dehydrogenation.

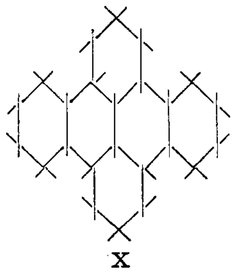


The trimer fraction, in contrast to the dimer, appeared to be mainly olefinic in nature; at least, it absorbed 90% of the theoretical amount of bromine required for a mixture of the olefinic isomers V–VIII.

The tetramer fraction shown in Table I could be further separated into two fractions (a) a yellow viscous oil (about 60% of the original fraction), b. p. 165–170° (0.1 mm.), mol. wt. 323, and (b) a yellow, sticky semi-solid, b. p. 170–180° (0.1 mm.); mol. wt. 330. When these fractions, separately or together, were dissolved in ether a small amount (2–3% of the original tetramer fraction) of hard, white, prismatic crystals remained as an insoluble residue. This material was quite insoluble in ether and only slightly soluble in benzene. After sublimation it melted at 269–271°. Molecular weight determinations indicated this compound to be a tetramer; analyses for carbon and hydrogen gave values that correspond more closely to the formula $C_{24}H_{38}$ than to the saturated tetramer $C_{24}H_{40}$. However, the compound gave no apparent reaction with bromine or potassium permanganate in acetone solution; nor was it soluble in hot, concentrated sulfuric acid.

The high melting point of this tetramer indicated that it must have a symmetrical structure. Considering its carbon and hydrogen content, its inertness and its formation from cyclohexene, the two most likely structures for this tetramer seemed to be a stereoisomeric form of perhydrotetraphenylene (IX) $C_{24}H_{40}$, or of perhydro-1,2,6,7-dibenzopyrene (X) $C_{24}H_{38}$. The symmetrical 1,3,5-tricyclohexylcyclohexane ($C_{24}H_{42}$) departs too far from the carbon and hydrogen content of the tetramer and one form of this hydrocarbon is reported[11] to melt at 157–159°.


IX


X

Both structures IX and X conform to the saturated behavior of the compound toward olefinic reagents; however, structure X, $C_{24}H_{38}$, corresponds more closely than IX, $C_{24}H_{40}$, to the carbon and hydrogen content.

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(11) Schneider and Keller, *Ber.*, **74**, 729 (1941).

It was thought that dehydrogenation of this high-melting tetramer might throw some light on its structure. The dehydrogenation product of IX, tetraphenylene, has recently been described[12] as melting at 233°; the dehydrogenation product of X, 1,2,6,7-dibenzopyrene, has been reported[13] to be a pale yellow compound that melts at 353–355°. The cyclohexene tetramer, however, was very difficult to dehydrogenate and no pure dehydrogenation product could be isolated. Heating with sulfur at 300° yielded hydrogen sulfide and a coke-like product that did not melt. Catalytic dehydrogenation in benzene solution at 300° for sixteen hours over a platinum–charcoal catalyst[10] gave only partial dehydrogenation; some of the original tetramer was recovered but the dehydrogenated material, m. p. 230–250°, was only partially aromatized. Under the same conditions for forty-eight hours none of the original tetramer remained and a nearly completely aromatized compound was isolated as a yellow powder in 65% yield. After sublimation this material melted at 390–410°; its carbon and hydrogen content approximated the formula $C_{24}H_{16}$. It appears from these results that dehydrogenation cannot be used to convert the high-melting cyclohexene tetramer to any known polycyclic aromatic structure.

Dehydrogenation of the tetramer fraction of Table I by the procedure used for the dimer and trimer fractions gave a pale yellow oil with a strong bluish fluorescence and with a boiling range approximately the same as that of the original tetramer fraction. Aromatization of the fraction was shown by the refractive index which was changed from 1.5270 to 1.5450 by the dehydrogenation. Only after several months of standing did any crystalline material appear in the dehydrogenated tetramer fraction. This material remained undissolved when the fraction was diluted with an equal volume of petroleum ether but, when separated, proved to be the same high-melting cyclohexene tetramer that was isolated from the original tetramer fraction.

No attempts were made to dehydrogenate the solid polymer fractions listed in Table I.

Experimental

Cyclohexyl Fluoride.—To 100 g. (1 mole) of cyclohexene, contained in a copper bomb-liner and cooled to approximately −78° by a dry-ice–ether bath, was added slowly and with stirring 35 g. (1.5 moles) of hydrogen fluoride, similarly cooled. The mixture, which became dark red in color, was allowed to warm up to room temperature and remain at this temperature for thirty minutes. It then was shaken with a 20% aqueous solution of sodium hydroxide to remove the excess of hydrogen fluoride. The resulting mixture was steam distilled until the volume of the aqueous distillate was approximately equal to that of the insoluble organic layer. The latter was separated from the water and treated with bromine to a faint but permanent coloration. The oil after washing with water containing a small amount of sodium bisulfite and drying over potassium carbonate was fractionated at 200 mm. through a modified Widmer column. The cyclohexyl fluoride, b. p. 60–63° (200 mm.), m. p. 12–13°, $n^{25}D$ 1.4130, collected amounted to 83 g. (70%). It is a colorless oil and quite stable at room temperature, but shows a slight tendency to decompose when distilled at atmospheric pressure (b. p. 98–100°). The dibromocyclohexane which remains after the removal of the cyclohexyl fluoride boils at 101° (13 mm.).

When the excess of hydrogen fluoride is not completely removed from the cyclohexyl fluoride before it is distilled, the fluoride decomposes during the distillation with the evolution of hydrogen fluoride and the formation of cyclohexene polymers. Pure cyclohexyl fluoride when treated with 5 mole per cent. of hydrogen fluoride and heated in a bomb at 100° for four hours is practically completely converted into polymers of cyclohexene.

Polymerization of Cyclohexene with Hydrogen Fluoride.—To 300 g. of cyclohexene, cooled at 0–5° in a copper bomb-liner of 1 liter capacity, was added, with stirring, 75 g. (1 mole) of hydrogen fluoride that had been cooled in a dry-ice–ether bath. The copper liner and its contents then were sealed (copper or lead gaskets) in a steel bomb and heated to 100° in an oil-bath for four hours. After this time the bomb was cooled in ice and opened. The black, tarry reaction mixture was dissolved in 3 volumes of ether and washed with a 10% aqueous sodium hydroxide solution until all of the free hydrogen fluoride was neutralized. The resulting red ether solution was washed with water and dried. After removal of the ether the reaction mixture was fractionated under diminished pressure through an 8-cm. modified Widmer column and with a cold trap between the receiving flask and the pump to collect low-boiling products.

The following fractions were collected: (a) 17 g., b. p. 93–95° (8 mm.); (b) 33 g., b. p. 58–72° (0.1 mm.); (c) 17 g., b. p. 120–140° (0.1 mm.); (d) residue, 180 g.; (e) cold trap material 5.4 g. The distillation usually was interrupted during the removal of fraction (a) by a sudden decomposition of the boiling liquid with the evolution of hydrogen fluoride. The temperature was lowered and the pump allowed to maintain a pressure of about 0.1 mm. within the system for about an hour. At the end of this time the evolution of hydrogen fluoride had stopped and the distillation could be resumed and completed without further signs of decomposition. This decomposition of fluorinated polymers during distillation was not encountered when the original polymerization reaction was allowed to run for fifteen hours at 100°.

The cold trap material (e), b. p. 80–100° (740 mm.), was chiefly cyclohexyl fluoride mixed with a small amount of unchanged cyclohexene. Fractions (a) and (b) both were the colorless dimer mixture. Fraction (c) was the yellow, viscous trimer fraction; its color remained after repeated distillations.

The residue, which solidified to a reddish-black, brittle resin on cooling, was distilled from a Claisen flask with a wide bore side arm which served as an air condenser and which was connected by a glass joint to a receiver. A glass rod, flattened at one end to a circular disk that just passed through the neck of the distilling flask, was suspended through a stopper in the neck of the flask so that the disk was just inside the bulb of the distilling flask. This disk served as a baffle to prevent the boiling liquid from splashing into the neck of the distilling flask.

The flask was heated in a metal bath and on the first distillation the material was separated into four fractions of 35–45 g. each, boiling over about 35° ranges between 170–315° (0.1 mm.). Approximately 25 g. of a black brittle solid remained as a residue from this distillation. Each of these fractions then was redistilled and the fractions listed in Table I collected. The molecular weights shown in this table were determined cryoscopically in benzene.

The Dimer Fraction.—A sample of this fraction, when titrated with a standard solution of bromine in carbon

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[12] Rapson, Shuttleworth and van Niekirk, *J. Chem. Soc.*, 326 (1943).

[13] Shin-ichi Sako, *Bull. Chem. Soc. Japan*, **9**, 55 (1935); *Chem. Zentr.*, **106**, 1241 (1935).

tetrachloride, absorbed only 20% of the bromine necessary for the saturation of cyclohexyl-Δ^1-cyclohexene (I).

Approximately 4 g. of a 5-g. sample of the dimer fraction remained undissolved when vigorously stirred for fifteen minutes with 10 g. of concentrated sulfuric acid; this insoluble material was unaffected by 20% fuming sulfuric acid.

A 10-g. sample of the dimer was hydrogenated over 1 g. of Raney nickel at 200° and 2000 lb. for one hour. The product from this hydrogenation boiled at 94–96° (8 mm.) and melted at −4° (m. p. of bicyclohexyl, +4°).

A 2.5-g. sample of the dimer in 20 ml. of benzene was heated with 1 g. of the reduced nickel chromite catalyst[10] at 250° for five hours. On cooling, filtering off the catalyst and evaporating the benzene, 2.1 g. (90%) of biphenyl, m. p. 67–69°, was obtained.

A solution of 10 g. of the dimer fraction in 25 ml. of glacial acetic acid was treated with a stream of ozonized oxygen for thirty minutes; the solution became warm and was cooled with water. The acetic acid solution then was diluted with 15 ml. of water and 15 ml. of 30% hydrogen peroxide and the resulting solution refluxed for thirty minutes. The solution was cooled, diluted with 100 ml. of water and extracted with ether. The ether extract was extracted with 10% aqueous sodium hydroxide and this alkaline extract separated and acidified with dilute hydrochloric acid. This acid solution was extracted with ether and the aqueous layer separated. From the ether extract, after evaporation of the solvent, 1.8 g. of a yellow oil remained as a residue. This oil was dissolved in 10 ml. of alcohol containing 1.5 g. of pyridine and 1.5 g. of semicarbazide hydrochloride and the alcoholic solution refluxed for thirty minutes. The alcohol and pyridine then were removed in a current of air and the solid residue recrystallized from alcohol. The semicarbazone of δ-hexahydrobenzoylvaleric acid[3,14] so obtained melted at 169–171°. This semicarbazone was hydrolyzed by heating with 3 ml. of concentrated hydrochloric acid for thirty minutes on a steam-bath. The resulting solution was diluted with 5 ml. of water and cooled in an ice-bath. The silky needles of δ-hexahydrobenzoylvaleric acid[3,14] (II) that separated, after filtration and drying, melted at 52–53°.

The Trimer Fraction.—Titration of a weighed sample of this fraction with a standardized solution of bromine in carbon tetrachloride showed a bromine absorption corresponding to a content of 90% of olefinic trimers.

A 5-g. sample of this fraction was dehydrogenated in benzene solution over reduced nickel chromite as described above. Evaporation of the solvent from the dehydrogenation product left an oil containing a small amount of solid material. The solid, which remained insoluble in the petroleum ether (60–68°) that dissolved the oil, was *p*-terphenyl. It weighed 0.15 g. (3%) and after sublimation melted at 210–211°.[15] After removal of the solvent from the petroleum ether solution the remaining oil was distilled and 1.6 g. boiling at 110–135° (0.1 mm.) and 1.7 g. boiling at 135–140° (0.1 mm.) were collected as separate fractions. The second fraction was seeded with some crystals that collected in the condenser toward the end of the distillation. A crystalline precipitate formed slowly on standing. It was separated and pressed on a porous plate to remove most of the oil and then recrystallized from alcohol. This product proved to be *m*-terphenyl,[14] m. p. 86–87°, and weighed 0.13 g. (3%). Most of the colorless oil that remained after the removal of the *m*- and *p*-terphenyl distilled at 325–330° (740 mm.) but could not be induced to crystallize. Pure *o*-terphenyl is reported[15a] to boil at 332° and to melt at 56–57°.

The Tetramer Fraction: The Solid Tetramer Melting at 269–271°.—This fraction of Table I, as well as the intermediate fractions below and above it in boiling points, became cloudy and slowly deposited crystals on standing. When the fractions were dissolved in ether this crystalline material remained insoluble. It amounted to 2–3% of the weight of the tetramer fraction. After vacuum sublimation it melted at 269–271°. It was slightly soluble in benzene but practically insoluble in ether. In benzene solution it showed a molecular weight of 339 (calcd. for $C_{24}H_{40}$, 328).

Anal. Calcd. for $C_{24}H_{40}$: C, 87.73; H, 12.27. For $C_{24}H_{38}$: C, 88.27; H, 11.73. Found: C, 88.50; H, 11.53.

After a sulfur dehydrogenation converted this material to a coke-like mass that had no melting point and several catalytic dehydrogenations yielded considerable unchanged starting product, the following dehydrogenation procedure was employed. A solution of 0.2 g. of the crystalline tetramer in 20 g. of benzene was shaken with a platinum-carbon catalyst[10] at 300° for forty-eight hours. After cooling the catalyst was filtered off and the benzene solution evaporated. A brownish-yellow residue, weighing about 0.2 g., with the characteristic odor of biphenyl remained. The residue was digested with 20 ml. of alcohol for thirty minutes. Most of the material remained undissolved (tetraphenylene (IX) is reported[12] to be soluble in alcohol) and was filtered off. The residue was again extracted for four hours with 75 ml. of refluxing alcohol. This alcoholic extract contained 0.02 g. of a solid material which melted at 230–250°. The insoluble residue from the second alcohol extraction weighed 0.13 g. and did not melt below 300°. This material was digested with 25 ml. of boiling benzene for thirty minutes. The insoluble residue was sublimed at 270° and 0.1 mm. to a pale yellow powder which softened at 380° and melted to a black liquid at 390–410°. The material that dissolved in the benzene was recovered and sublimed at 270° (0.1 mm.). It, too, was a pale yellow powder which melted at 360–390° to a black liquid.

Anal. (benzene soluble material). Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.30. For $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 94.40; H, 5.25.

The alcoholic solution from the first extraction of the dehydrogenation product was concentrated to 2 ml. and cooled, whereupon a pale yellow crystalline material separated. After filtering and drying, this material weighed 0.04 g. and melted at 230–250°, as did the product from the second alcohol extraction. This product had a lower carbon and slightly higher hydrogen content than the alcohol-insoluble material described above.

Neither of these dehydrogenation products had sufficient solubilities in benzene, camphor, dioxane, etc., to give satisfactory molecular weights.

The alcoholic filtrate from which the material melting at 230–250° was separated, was evaporated to dryness and the residue sublimed at 60° and 8 mm. A small amount of biphenyl, m. p. 67–69°, was obtained as a sublimate. The presence of this compound among the dehydrogenation products indicates that the conditions necessary for the dehydrogenation of the solid tetramer of cyclohexane are sufficiently drastic either to partially cleave the tetramer to biphenyl or to form it by dehydrogenation of molecules of the benzene solvent.

The tetramer fraction of Table I was dehydrogenated in the same manner as were the dimer and trimer fractions but the only crystalline product that could be isolated from the dehydrogenated material was the solid tetramer of cyclohexene, m. p. 269–271°.

Summary

Cyclohexene adds hydrogen fluoride at or below room temperature to yield cyclohexyl fluoride. In the absence of free hydrogen fluoride the cyclohexyl fluoride may be isolated. At 100° cyclohexene and an equivalent of hydrogen fluoride or cyclohexyl fluoride with catalytic amounts of hydrogen fluoride are converted into polymers of cyclohexene. Fluorohydrocarbons appear to be intermediates in this polymerization.

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[14] Hückel and Neunhoeffer, *Ann.*, **477**, 106 (1930).

[15] *Cf.* (a) Bachmann and Clarke, THIS JOURNAL, **49**, 2093 (1927); (b) von Braun, *et al.*, *Ber.*, **66**, 1477 (1933).

The dimer of cyclohexane, which consists of about 80% bicyclohexyl and 20% of cyclohexyl-Δ^1-cyclohexene, is readily dehydrogenated to biphenyl. Among the trimers of cyclohexene are products that yield *m*- and *p*-terphenyl on dehydrogenation.

From the tetramer fraction a small quantity of a solid tetramer, $C_{24}H_{38}$, that melts at 269–271°, was isolated. This tetramer was dehydrogenated with difficulty to a mixture of at least two compounds that approximate the formula $C_{24}H_{16}$ but their properties do not correspond with any known compounds of this formula in the literature.

Fractions that contain pentamers, hexamers, and heptamers have been separated from the polymerization mixture.

MADISON, WISCONSIN
RECEIVED JUNE 12, 1944

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

Branched-Chain Fatty Acids. III. New Method of Introducing the Branching Methyl Group. Synthesis of 15-Methyloctadecanoic Acid and 14-Methyltetracosanoic Acid

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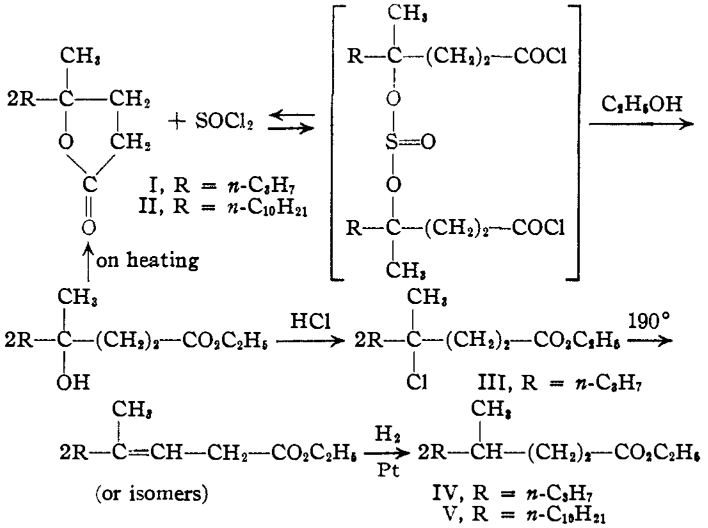
As a continuation of the program[2] of synthesizing branched-chain acids, 15-methyloctadecanoic acid and 14-methyltetracosanoic acid[3] have been prepared by Clemmensen reduction of the esters of the corresponding 10-keto acids. The keto esters were prepared by the previously-used method[2] involving the reaction between a dialkylcadmium compound and ω-carbethoxynonoyl chloride. The dialkylcadmium compounds were obtained from the appropriate alkyl halides by way of the Grignard reagents.

The branched-chain halide necessary for preparation of 15-methyloctadecanoic acid by this method is 1-bromo-5-methyloctane. The corresponding alcohol was initially prepared by us from 2-bromopentane by extending the chain twice by means of the reaction between a Grignard reagent and ethylene oxide. Since the 15-methyloctadecanoic acid obtained from this sample of bromide had the m. p. of 41.0–43.5° it was thought possible that this rather broad m. p. might be due to the presence of an isomeric bromide in the 2-bromopentane used as starting material. The preparation of such a bromide in a strictly pure condition is difficult if at all possible.[4]

In order to test this point, 1-bromo-5-methyloctane was prepared by a method, described in the next paragraph, which involves no branched-chain starting materials and no secondary halides. 15-Methyloctadecanoic acid prepared from this sample of halide also melted at 41.0–43.5°. Since the crystal form of this acid appears to change during melting and since the m. p. varies somewhat, depending on how long the crystals have stood since crystallization, it is felt that the broad m. p. is due to the occurrence of polymorphic forms rather than the presence of an impurity.



The starting material for the above-mentioned preparation of a pure branched-chain alkyl halide is a γ,γ-dialkylbutyrolactone. Such lactones have been prepared by several workers[5] from a Grignard reagent and ethyl levulinate or levulinic acid. Yields have been reported as 35% or less. By carrying out the reaction at 0° and adding sufficient benzene to dissolve the ether-insoluble reaction product, it has been found that γ-

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[1] Taken in part from the M.S. Theses of Clark E. Adams, Leonard L. Bennett, Jr., and Ulma D. Register.

[2] Preceding paper in this series, Cason and Prout, THIS JOURNAL, **66**, 46 (1944).

[3] Prepared for biological testing at the request of Dr. Bruno Gerstl of the Yale University School of Medicine.

[4] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3027 (1929); Sherrill, Baldwin and Hass, *ibid.*, **51**, 3036 (1929); Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 73.

[5] Grignard and Moissan, *Compt. rend.*, **135**, 629 (1902); Jones and Tattersall, *J. Chem. Soc.*, **85**, 1691 (1904); Schritza, *J. Russ. Phys.-Chem. Soc.*, **44**, 1853; *Chem. Abs.*, **7**, 1174 (1913); Noyes and Marvel, THIS JOURNAL, **39**, 1269 (1917); Porter, *ibid.*, **45**, 1086 (1923); Frank, Arvan, Richter and Vanneman, *ibid.*, **66**, 4 (1944).