anthracene and its mono- and dialkyl derivatives is described.

Desoxybenzoin was condensed with dimethyl succinate to yield α-(1,2-diphenylvinyl)-succinic acid, I, which was reduced to two stereoisomeric saturated acids, α-(1,2-diphenylethyl)-succinic acids, II and IIa. The mixture of acids was cyclized with liquid, anhydrous hydrogen fluoride to form two stereoisomeric diketones, III and IIIa, and a keto acid, IV.

The diketone was reduced to a diol, V, which was dehydrated and dehydrogenated to 1,2-benzanthracene, VI. The diketone was also converted to 3,10-dimethyl-1,2-benzanthracene, X, by reaction with methylmagnesium bromide followed by dehydration and dehydrogenation.

The keto acid was identified as (1,2,3,4-tetrahydro-1-oxo-3-phenyl-2-naphthyl)-acetic acid, by its conversion to the known 3-methyl-1,2-benzanthracene, IX, in the following synthetic steps: Clemmensen reduction to (1,2,3,4-tetrahydro-3-phenyl-2-naphthyl)-acetic acid, VII, cyclization with hydrogen fluoride to 3-keto-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene, VIII; and reaction with methylmagnesium bromide followed by dehydration and dehydrogenation to 3-methyl-1,2-benzanthracene, IX.

COLUMBUS, OHIO RECEIVED OCTOBER 14, 1946

[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

Isomeric Chlorinated Long-Chain Esters

BY HERBERT H. GUEST

In a recent paper from this Laboratory[1] it was shown that certain long-chain methyl esters react with chlorine to form mixtures and that attempts to find a method of determining the position of the substituent chlorine, using alkaline reagents, were unsuccessful.

The results now reported were obtained by the use of sodium acetate in acetic acid solution. This reagent, acting on the monochloro ester fraction, gave products which could be quantitatively differentiated. The more difficult problem of the structure of the dichloro esters is not considered in this paper.

Preliminary work involved the preparation of monochloro esters in which the position of the chlorine was definitely known and the study of their reaction with sodium acetate. Thus it was found that α-chloro esters formed exclusively acetoxy esters, β-chloro esters formed only α,β-unsaturated esters and γ- or Δ-chloro esters formed acetoxy esters which were readily hydrolyzed to the corresponding lactones.[2]

Trial of the methods described in the literature for preparing α-chloro acids led to the conclusion that the most suitable was that used by Staudinger and co-workers[3] to prepare α-chlorobutyric acid.

The beta isomer was prepared by the Perkin-Knoevenagel reaction, as modified by Zaar[4] followed by the addition of hydrogen chloride.

This addition took place only when the double bond was in the alpha-beta position. It was found that oleic and undecylenic acids, for example, were not acted on by hydrogen chloride under similar conditions. On the other hand, the usual iodine absorption methods gave erratic results with α,β-unsaturated esters.[5] In order to estimate the latter, it was found necessary to use bromine.

The method of Noyes and Cox[6] gives excellent yields of γ-chloro esters from the corresponding γ-lactones. A representative of the Δ-chlorinated series was obtained by hydrolysis and esterification of 4-chlorovaleronitrile.[7]

For an extended study of the products of direct chlorination, hexoyl chloride was chosen as the starting material. After chlorination, the reaction mixture was esterified with methanol. The monochloro ester fraction, obtained by careful distillation *in vacuo*, was caused to react with fused sodium acetate in glacial acetic acid solution. This procedure was also followed in the study of the products obtained by chlorinating methyl hexoate, octoate and stearate. The products obtained by chlorinating either the acid chloride or the methyl ester were almost identical.

Experimental

Preparation of α-Chloro Acids.—Alkyl malonic acids were obtained by following the directions given in "Organic Syntheses."[8] Butyl, hexyl, heptyl, dodecyl and hexadecylmalonic acids thus prepared, were chlorinated in boiling ethereal solution by the gradual addition of one mole of sulfuryl chloride. The reaction mixture was refluxed for three hours and was then washed with cold water. The latter operation requires care since the chloro acids are water-soluble.

Upon heating at 130–140° for thirty minutes, the chloro-

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[1] H. H. Guest and C. M. Goddard, Jr., THIS JOURNAL, **66**, 2074 (1944).

[2] L. Henry, *Z. physik. Chem.*, **10**, 111 (1892); H. S. Taylor and H. W. Close, THIS JOURNAL, **39**, 422 (1917).

[3] H. Staudinger, E. Anthers and H. Schneider, *Ber.*, **46**, 3539 (1913); *cf.* A. M. Clover, *Ann.*, **319**, 357 (1902).

[4] B. Zaar, *Ber., Schimmel & Co.*, 299 (1929); "Organic Reactions," Vol. I, John Wiley & Sons, New York, N. Y., 1942, p. 252; *cf.* A. M. Clover, ref. 3.

[5] *Cf.* G. Ponzio and C. Gastaldi, *Gazz. chim. ital.*, **42**, 92 (1912).

[6] W. A. Noyes and I. J. Cox, THIS JOURNAL, **25**, 1094 (1903).

[7] German Patent 120,138 (*Chem. Centr.*, **72**, I, 1126 (1901); I. K. Phelps and E. W. Tillotson, Jr., *Am. J. Sci.*, [4] **26**, 264 (1908).

[8] "Organic Syntheses," Coll. Vol. I, p. 245; A. W. Dox, THIS JOURNAL, **46**, 1707 (1924).

malonic acids lose carbon dioxide to form α-chloro fatty acids, listed in Table I.

TABLE I

	RCHCl-COOH where R is:	B. p., °C. at 4 mm.	% Cl Found	% Cl Calcd.	Sapn. equiv. Found	Sapn. equiv. Calcd.
a	C_4H_9	102–107	23.0	23.7	75.6	75.4
b	C_6H_{13}	140–145	19.5	19.8	89.8	88.0
c	C_7H_{15}	163–167	18.5	18.4	95.6	96.4
d	$C_{12}H_{25}$	190–198	13.1	13.5	127	129
e	$C_{16}H_{33}$	M. p. 66°	11.7	11.2	156	157

[a] New: gave α-hydroxycaproic acid, m. p. 60°; anilide, oil. Methyl α-acetoxycaproate, b. p. 89–93°. [b] New: gave α-hydroxycaprylic acid, b. p. 160–165° (10 min.), m. p. 70° agreeing with data given in Beilstein. [c] New: anilide, oil: methyl ester, b. p. (10 mm.) 117–121°. [d] New: gave α-acetoxymyristic acid, m. p. 78°. [e] J. J. Frewing, *Proc. Roy. Soc.* (London), **A182**, 270 (1944). This acid gave α-acetoxystearic acid, described by Levene and West, *J. Biol. Chem.*, **16,** 477 (1913).

Preparation of β-Chloro Acids.—Hexenoic acid was prepared from malonic acid and butyraldehyde in the presence of pyridine and purified by distillation *in vacuo*. It was dissolved in a four-fold weight of ether and saturated with hydrogen chloride at ice-water temperature. The reaction mixture was allowed to stand in the refrigerator for four days. After removal of the ether the product was distilled; b. p. (4 mm.) 95–98°, yield 80% of theoretical. The acid was esterified with methanol; b. p. (5 mm.) 65°; anilide m. p. 70°.

Anal. Calcd. for $C_7H_{13}O_2Cl$: Cl 21.6, sapn. equiv., 81.0. Found: Cl 20.1, sapn. equiv., 86.3.

Nonenoic acid was prepared from malonic acid and heptaldehyde, b. p. (8 min.) 146°.

It was converted into β-chlorononanoic acid, b. p. (4 mm.) 150–156°, which was esterified with methanol, all in a similar manner as in the preceding example; methyl ester, b. p. (3 mm.) 110–114°; anilide, m. p. 78°.

Anal. Calcd. for $C_{10}H_{19}O_2Cl$: Cl, 17.1, sapn. value, 542 (sap. equiv. 104). Found: Cl, 17.4; sapn. value, 534 (sap. equiv., 105).

Preparation of Ethyl γ-Chlorovalerate.—Valerolactone dissolved in an equal weight of ethanol was saturated with dry hydrogen chloride and allowed to stand in the cold for three days. The product was purified by distillation; b. p. (20 mm.) 90–95°.

Preparation of Methyl δ-Chlorovalerate.—δ-Chlorovaleronitrile was dissolved in 3 volumes of methanol and an equal volume of 80% sulfuric acid. The mixture was heated to refluxing for fifty hours at which time a sample portion gave no test for nitrogen. Most of the methanol was removed by distillation. Water was added to the reaction mixture and the oil which separated was taken up in ether. After drying over calcium chloride and removing the ether, the oil was distilled; b. p. (18 mm.) 89–92°.

Anal. Calcd. for $C_6H_{11}O_2Cl$: Cl, 23.6; sapn. value, 744. Found: Cl, 23.9; sapn. value, 789.

Chlorination of Hexoyl Chloride.—Hexoic acid was converted into hexoyl chloride, b. p. 58° (30 mm.). Chlorine was passed slowly into the latter at 45° until the increase in weight corresponded to the introduction of one chlorine atom. The product was added slowly to excess methanol. The methyl esters were carefully distilled through an efficient fractionating column. A comparison (Table II) of the monochlorinated ester fraction with methyl α- and β-chlorohexoates shows the impossibility of separation of isomers by fractional distillation.

TABLE II

	B. p., °C. (5 mm.)	$n^{20}D$
$C_3H_7CH_2CHClCOOCH_3$	68–73	1.4320
$C_3H_7CHClCH_2COOCH_3$	65–67	1.4390
Me chlorohexoates from hexoyl chloride	72–77	1.4393

Action of Sodium Acetate on Chloro Esters.—Methyl α-chlorohexoate (30 g.) was digested with anhydrous sodium acetate (25 g.) in glacial acetic acid for twenty-four hours. Part of the acetic acid was removed by distillation and to the residue water was added. The oil was separated and the aqueous layer extracted repeatedly with ether. After removal of the solvent the oil was distilled at 6 mm., b. p. 90–95°. The yield was quantitative. The product is identical with the methyl α-acetoxyhexoate obtained from methyl α-bromohexoate on similar treatment. It gave no bromine absorption value.

Anal. Calcd. for $C_9H_{16}O_4$: sapn. equiv., 94. Found: sapn. equiv., 92.

After saponification the resulting α-hydroxy acid crystallized in rhombic plates; m. p. 59–60°, neut. value, 430; calcd. for $C_6H_{12}O_3$: neut. value, 424.

This reaction was carried out with all the α-chloro acids described in Table I. In no case was there a significant amount of unsaturated acid or of lactone formed. For example, chlorocaprylic acid gave α-hydroxycaprylic acid (yield 80%) b. p. (10 mm.) 160–165°; m. p. 70°. Chlorostearic acid gave α-hydroxystearic acid, m. p. 90°; yield 100%. The physical constants are identical with those given in the literature.

The neutralization values found agree with the calculated values.

When methyl β-chlorohexoate was subjected to this reaction, the time required for elimination of chlorine was only four hours. The reaction product distilled at 7 mm. pressure, b. p. 53–56°; yield 95%.

Anal. Calcd. for $C_7H_{12}O_2$: sapn. equiv., 128; bromine value, 125. Found: sapn. equiv., 129; bromine values 105 and 119.

The iodine value as determined by means of Wijs solution, was only 10% of the calculated amount. The bromine value was obtained by allowing 0.2 *N* bromine in glacial acetic acid solution to stand for eighteen hours. A blank determination using methyl hexoate showed that there was no substitution under these conditions.

Methyl β-chlorononylate (22 g.) was digested with 15 g. of sodium acetate in acetic acid solution for eight hours. After washing with water there was obtained 18 g. of oil; a quantitative yield.

Anal. Calcd. for $C_{10}H_{18}O_2$: sapn. equiv., 170; iodine value, 149. Found: sapn. equiv., 166; iodine value, 136.

Ethyl γ-chlorovalerate was digested with sodium acetate in acetic acid solution for twelve hours. The γ-acetoxyvalerate was distilled at 25 mm., b. p. 118–121°. There was no unsaturated ester present.

Anal. Calcd. for $C_9H_{16}O_4$: sapn. equiv., 94. Found: sapn. equiv., 93.

After saponification of the acetoxy ester with alkali and treatment with dilute mineral acid, the resulting oil was identified as γ-valerolactone, b. p. (7 mm.) 86°. There was only a 50% recovery, due to the solubility of the oil in water: Koettstorfer value (sap. value), 542; neut. value, 37.

Methyl δ-chlorovalerate (25 g.) was digested with sodium acetate as in the previous experiments. The acetoxy ester, b. p. (12 mm.) 114°, was recovered in 91% yield. After saponification, acidifying with dilute sulfuric acid and repeated extraction with ether, the δ-lactone[9] was obtained, in theoretical yield, b. p. (7 mm.) 130–135°, m. p. 53°. These values are higher than those given by Fichter.

Anal. Calcd. for $C_5H_7O_2$: sapn. value, 565, sapn. equiv., 99. Found: sapn. value, 552; sapn. equiv., 102; neut. value, 60.

Taylor and Close[2] have shown that the transformation

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[9] F. Fichter and A. Beisswenger, *Ber.*, **36**, 1200 (1903).

of δ-hydroxyvaleric acid to the lactone is not complete but that 8% acid is present in the final equilibrium mixture.

Action of Sodium Acetate on Products of Direct Chlorination.—Fifty-five grams of the monochlorinated methyl ester fraction from the chlorination of hexoyl chloride was digested in 70 g. of acetic acid with 45 g. of sodium acetate for thirty hours. Upon treatment as previously described, 55 g. of oil was obtained. Care was taken to extract all the products of the reaction from the aqueous wash-waters.

The material thus obtained was thoroughly saponified with an excess of 50% aqueous alcoholic potassium hydroxide solution. Sulfuric acid was added and the reaction products were extracted with ether. At least twenty extractions were necessary but the recovery was almost quantitative; b. p. (5 mm.) 98–105°.

The mixture of acids and lactones thus obtained had the following characteristics

Iodine value (bromine absorption)		51
Saponification equiv.		110
Sapn. value (Koettstorfer)		508
Neutralization equiv.		231
Neut. value		242
Calcd. for $C_6H_{10}O_2$	iod. value	222
	sapn. equiv.	114
Calcd. for $C_6H_{12}O_3$	neut. equiv.	132
	neut. value	424

The above iodine values indicate that there is 23% of unsaturated acid present. This is an approximate estimate of the amount of β-chloro ester originally present. The difference between the saponification and neutralization values is a measure of the lactones. This corresponds to 52% γ- and Δ-chloro esters, approximately.

In order to verify these deductions the reaction mixture was caused to react in methanol solution with hydrogen chloride. It was found that the product contained 15.8% chlorine which agrees with the calculated value of 16.2%. The higher proportion of beta, gamma and delta isomers shown to be present makes it reasonable to assume that the remaining 25% is largely α-chloro ester. Proof of this assumption, however, could not be obtained by any of the several methods tried.

The chlorinated esters of hexoic acid, octoic and octadecoic acids were subjected to this reaction with comparable results in each case.

Summary

Several new chlorinated acids were prepared and their reaction with sodium acetate in acetic acid studied. It was thus found that characteristic reaction products, depending on the position of the chlorine, were formed.

These data were used to estimate the proportion of monochlorinated isomers formed in the direct chlorination of representative long-chain methyl esters. It is thus shown that approximately half of the chlorine is in the gamma or delta position and 25% is in the beta position.

GLASTONBURY, CONN. RECEIVED[10] SEPTEMBER 26, 1946

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[10] Original manuscript received February 7, 1946.

[CONTRIBUTION FROM RIDBO LABORATORIES, INC.]

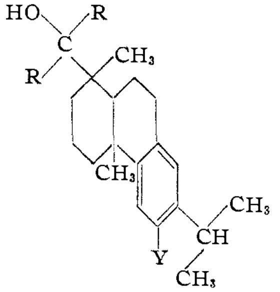
Studies on Resin Acids. I. Carbinols

BY HAROLD H. ZEISS

The work of Fieser, Campbell and Morgana[1,2] on reactions of the resin acids has stimulated interest in this group of natural products. The major portion of their work has been concerned chiefly with substitution on the aromatic ring of dehydroabietic acid. The preparation of 6-hydroxydehydroabietinol was of particular significance in this work because of its reported estrogenic activity. These studies have been extended in a new direction with the purpose of obtaining other derivatives having perhaps enhanced physiological properties.

The primary carbinols of the resin acids have usually been prepared by reduction methods. This present paper describes the synthesis of tertiary carbinols *via* the Grignard reaction and further confirms the conclusions of Campbell and Todd[3] regarding the configuration of the C_1 carboxyl groups of dehydroabietic and podocarpic acids. According to the excellent paper of those authors the carboxyl group of dehydroabietic acid occupies a *trans* position in space relative to the angular C_{12} methyl group. On this basis Stewart models admit the possibility of a diphenylcarbinol although a very close fit is involved.

Use of the Grignard reaction as employed by Wieland, *et al.*,[4] on the bile acid esters was found to be effective in the preparation of diphenyl-*t*-dehydroabietinol (I) from methyl dehydroabietate. Further application of the method to the methyl ester of 6-methoxydehydroabietic acid gave after demethylation the corresponding diphenylcarbinol (II). Methyl O-methylpodocarpate in which the carbomethoxy group is *cis* to the C_{12} angular methyl group failed to react detectably under the same conditions with phenylmag-



I. R = C_6H_5, Y = H
II. R = C_6H_5, Y = OH

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[1] (a) Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938); (b) **60**, 2631 (1938); (c) **61**, 2528 (1939).

[2] Campbell and Morgana, *ibid.*, **63**, 1838 (1941).

[3] Campbell and Todd, *ibid.*, **64**, 928 (1942).

[4] Wieland, Schlichting and Jacobi, *Z. physiol. Chem.*, **161**, 80 (1926).