$H_2O(l)$[10] = −68.3174; $Al(OH)_3$(amorph)[10] = −304.2; H_3BO_3(cryst)[4] = −261; Al_2O_3(cryst, corundum)[10] = −399.09; B_2O_3(cryst)[11] = −303

The heat of vaporization of aluminum borohydride is 7.2 kcal./mole.[5]

It was believed that ±4 kcal./mole was a reasonable estimate of the experimental errors of determination of the heats of reaction. In the case of reactions (a) and (b), 0.5% of inert impurity in the sample would produce a difference of about 1 kcal. in $\Delta H_f(Al(BH_4)_3)$. One per cent. error in measuring the energy change of the reaction would result in an additional 2 kcal. error in $\Delta H_f(Al(BH_4)_3)$. In reaction (c), however, 0.5% impurity would cause about 5 kcal. error in $\Delta H_f(Al(BH_4)_3)$, and 1% error in $\Delta H°$ would result in 10 kcal. error in $\Delta H_f(Al(BH_4)_3)$. No assignment of error due to uncertainties in the heats of formation of the other participants in the reactions has been made, but it may be noted that a 2% error in $\Delta H_f(B_2O_3)$ (which is quite possible) would alter $\Delta H_f(H_3BO_3)$ by 3 kcal. and this would be reflected as 9 kcal. error in $\Delta H_f(Al(BH_4)_3)$ calculated from $\Delta H°$ for (a) and (b). Two per cent. error in $\Delta H_f(B_2O_3)$ would produce 10 kcal. error in $\Delta H_f(Al(BH_4)_3)$ from (c).

The value for $\Delta H°$ of −989.1 from (c) is in good agreement with a value of −984 kcal. obtained earlier in this Laboratory for the heat of combustion of aluminum borohydride in the liquid state.[12]

[10] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," 1949.

[11] E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project Na-onr-8-49, 1948. C. C. Nathan, Thesis, University of Pittsburgh, 1948.

[12] W. E. Wallace and G. Stegeman, unpublished results, 1945.

PITTSBURGH, PENNSYLVANIA RECEIVED APRIL 18, 1951

The Reduction of 1,3-Dichloroacetone with Lithium Aluminum Hydride[1,2]

BY HERMANN SCHLENK AND BEVERLY LAMP

The selective reduction of carbonyl groups of α-monohaloketones by $LiAlH_4$ was reported for several compounds in the recent literature.[3] In developing synthetic methods for preparation of glycerol containing radioactive carbon we were interested in the reduction of 1,3-dichloroacetone to 1,3-dichlorohydrin. Using aluminum isopropylate for this reaction the yields were between 20 and 25%, being unacceptably low. We found it possible, however, to obtain 1,3-dichlorohydrin in yields of 70–80% by $LiAlH_4$. These results are in accordance with, and an extension of the observations of the previous authors to include an α,α'-dihaloketone.

Experimental

Dichloroacetone was prepared following the procedure of Arndt and Eistert[4] in a yield of 71.8% based upon chloroacetyl chloride. The product, 7.41 g. or 0.0583 mole (boiling point 168–172°), was dissolved in 100 ml. of absolute ether and was added to 0.022 mole of $LiAlH_4$ in 25 ml. of absolute ether during one hour. The reaction was carried out at −2° under nitrogen, using a mechanical stirrer and a reflux condenser. After continuing the stirring for ten more minutes the Fehling test for dichloroacetone was negative. The solution was poured into 100 ml. of ice-cold 2 *N* HCl and the aqueous phase was twice extracted with ether. The combined ether solutions were dried over Drierite and the solvent then was evaporated. In distilling the product, the main fraction was 1,3-dichlorohydrin boiling at 69–70° at 16 mm. pressure, having a refractive index n^{34} 1.4729 comparing well with that of authentic dichlorohydrin n^{34} 1.4743. The yield was 5.79 g. or 77% based upon dichloroacetone. Hydrolysis of this product gave the same yield of glycerol (n^{25} 1.4738) as authentic samples of dichlorohydrin.

DEPARTMENT OF BIOCHEMISTRY AND NUTRITION
TEXAS AGRICULTURAL EXPERIMENT STATION
TEXAS AGRICULTURAL AND MECHANICAL SYSTEM
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[1] This investigation was supported in part by a grant from the United States Atomic Energy Commission.

[2] Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

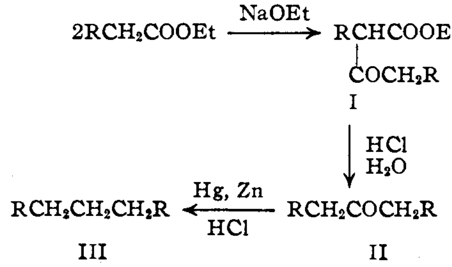
[3] R. E. Lutz, R. L. Wayland, Jr., and H. G. France, THIS JOURNAL, **72**, 5511 (1950).

[4] F. Arndt and B. Eistert, *Ber.*, **61**, 1124 (1938).

Clemmensen Reduction of a Long Chain β-Ketoester[1]

BY DAVID A. SHIRLEY AND GUSTAV A. SCHMIDT[2]

In connection with a study of the synthesis of certain long chain fatty acids containing twenty-six carbon atoms, we evaluated a route to these types which involved a Claisen condensation of a long chain carboxylic ester followed by a Clemmensen reduction of the resulting β-ketoester. The reduction of ethyl 2-tridecanoyltridecanoate (I), from Claisen condensation of ethyl tridecanoate, with amalgamated zinc, absolute ethanol and dry hydrogen chloride gave an 87% yield of pentacosane (III) rather than the expected ethyl 2-tridecyltridecanoate. The formation of the hydrocarbon was apparently due to the hydrolysis and decarboxylation of the β-ketoester under conditions of the Clemmensen reduction to give 13-pentacosanone followed by normal reduction of this ketone to the corresponding hydrocarbon. These transformations are shown in the accompanying diagram ($R = CH_3(CH_2)_{10}-$).



$$2RCH_2COOEt \xrightarrow{NaOEt} \underset{\substack{|\\ COCH_2R\\ I}}{RCHCOOEt} \xrightarrow{HCl,\ H_2O} \underset{II}{RCH_2COCH_2R} \xrightarrow[HCl]{Hg,\ Zn} \underset{III}{RCH_2CH_2CH_2R}$$

Connor and Adkins[3] have shown that in the action of absolute alcohol and dry hydrogen chloride on β-ketoesters there is no alcoholysis or removal of carbethoxy group. The apparent removal of the carbethoxy group during the Clemmensen reduction under our conditions must have occurred as a result of the action of water formed by the reaction of ethanol and hydrogen chloride. The presence of the zinc chloride in the reaction mixture would have aided this latter process.

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[1] This work was carried out as a part of a project supported by a F. G. Cottrell grant from the Research Corporation.

[2] Department of Chemistry, University of Texas, Austin.

[3] R. Connor and H. Adkins, THIS JOURNAL, **54**, 3420 (1932).

Experimental

Ethyl 2-Tridecanoyltridecanoate.—A suspension of finely divided sodium (5.75 g. or 0.25 g. atom) in 60 ml. of xylene was treated with 11.5 g. (0.25 mole) of absolute ethanol and the mixture heated under reflux until all the sodium had disappeared. The solvent was removed under reduced pressure and 130 g. (0.54 mole) of ethyl tridecanoate[4] added to the dry powdered sodium ethoxide.

The reaction mixture was heated to 130° at 14 mm. pressure for four hours, during which time all ethanol was removed. Excess dilute acetic acid was added to the cooled residue which caused an oily layer to appear on the surface of the mixture, and a gelatinous material adhered to the bottom of the flask. The oily layer was separated and recrystallized from methanol to give 80 g. (67% yield) of ketoester melting at 32–33°.

Anal. Calcd. for $C_{28}H_{54}O_3$: C, 76.8; H, 12.3. Found: C, 76.9; H, 12.3.

The gelatinous material from the above reaction mixture was separated and washed thoroughly with dilute acetic acid. The product was recrystallized from methanol to yield 4.5 g. of solid which melted at 73–74°. The melting point of 13-pentacosanone is reported[5] as 73–74° and Briese and McElvain[6] have reported the tendency of long chain β-ketoesters to undergo loss of carbethoxy group on distillation. It was considered likely that part of the β-ketoester had been converted to 13-pentacosanone during the four-hour heating period of the Claisen condensation.

A semicarbazone of the 13-pentacosanone was prepared in the usual manner and melted at 61–62°.

Anal. Calcd. for $C_{26}H_{53}N_3O$: N, 9.90. Found: N, 9.93.

Clemmensen Reduction of Ethyl 2-Tridecanoyltridecanoate.—A mixture of 43 g. (0.1 mole) of ethyl 2-tridecanoyltridecanoate, 1 l. of commercial absolute ethanol and 262 g. of zinc amalgam was saturated with dry hydrogen chloride and heated under reflux for 20 hours. The cooled mixture was saturated again with hydrogen chloride and refluxed for a second 20-hour period. The liquid phase was separated and cooled and the precipitated solid separated. The solid was recrystallized from methanol to yield 39 g. of product melting at 52–54°. Eighteen grams of this product was recrystallized several times from petroleum ether and two times from ethyl ether to give 14 g., corresponding to an 87% yield, of product melting at 53.5–55°. The melting point of pentacosane has been reported[7] as 53.5–54°.

A small amount of the 13-pentacosanone, obtained as described above, was subjected to Clemmensen reduction to give pentacosane melting at 54–55°. A mixed melting point between this material and the 53.5–55° melting product obtained above showed no depression.

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[4] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 292–293.

[5] R. N. Meals, *J. Org. Chem.*, **9**, 211 (1944).

[6] R. Briese and S. M. McElvain, THIS JOURNAL, **55**, 1697 (1933).

[7] W. Gluud, *Ber.*, **52**, 1039 (1919).

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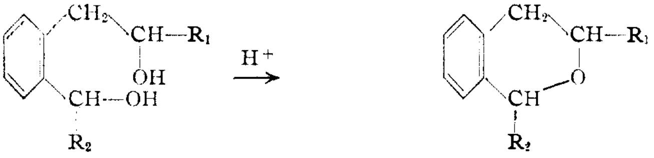
The Preparation of Isochromans

BY SAMUEL SIEGEL AND SEYMOUR COBURN

The purpose of this note is to report a method for the synthesis of isochroman[1] (V) and 3-phenylisochroman (VI) and to display the application of these and related procedures to the synthesis of substituted isochromans.

Isochromans form readily *via* the acid-catalyzed dehydration of the appropriate glycol.[2,3] Homophthalic acid, which is now easily obtained,[4] provides a convenient starting point for the preparation of these glycols. Thus, the reduction with lithium aluminum hydride of homophthalic anhydride or methyl homophthalate[1] yields homophthalyl alcohol (I) which can in turn be converted to isochroman (V). Or the anhydride may be condensed with benzene[5,6] to form *o*-phenacylbenzoic acid whose lactone, 3-phenylisocoumarin,[5] may be reduced to the glycol II, which can yield 3-phenylisochroman (VI).



I, $R_1 = R_2 = H$ V, $R_1 = R_2 = H$
II, $R_1 = C_6H_5$, $R_2 = H$ VI, $R_1 = C_6H_5$, $R_2 = H$
III, $R_1 = R_2 = C_6H_5$ VII, $R_1 = R_2 = C_6H_5$
IV, $R_1 = R_2 =$ alkyl or aryl VIII, $R_1 = R_2 =$ alkyl or aryl

A further extension of this synthesis follows from the addition of phenylmagnesium bromide to 3-phenylisocoumarin which yields 2-phenacylbenzophenone. The preparation of 1,3-diphenylisochroman (VII) by this procedure was described earlier.[3]

Perhaps the simplest way to obtain 1,3-dialkyl- or 1,3-diarylisochromans (VIII) is through the dehydration of the "abnormal" product, a glycol (IV), obtained in the reaction of benzylmagnesium chloride with aldehydes.[2,3,7]

Isochroman is readily oxidized when exposed to the air and a crystalline substance, apparently a peroxide, is easily isolated. 3-Phenylisochroman is also sensitive to oxidation, although 1,3-diphenylisochroman is less reactive.

Experimental[8]

Homophthalyl Alcohol.—Homophthalyl alcohol was prepared by the reduction of homophthalic anhydride according to the method of Nystrom and Brown[9] which is used for compounds with a low solubility in ether. The product was isolated in a manner described previously[3] and was distilled *in vacuo*. From 20 g. of the anhydride was obtained 8 g. of the alcohol, b.p. 164–165° (2 mm.); $n^{20}D$ 1.5556.

Isochroman.—A mixture of homophthalyl alcohol (2.6 g.) and potassium acid sulfate (1 g.) was heated to 45° for 20 minutes. The oily residue was distilled; 1.2 g., b.p. 67–69° (2 mm.); $n^{20}D$ 1.5422.

2-(2-Hydroxy-2-phenylethyl)-phenylcarbinol (II).—3-Phenylisocoumarin (2 g.) was reduced with $LiAlH_4$ in the usual way.[9] The product was distilled at 1×1^{-4} mm. (105° bath temperature) in a short path still; 1.22 g., $n^{20}D$ 1.5986.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 78.9; H, 7.08. Found: C, 79.16; H, 6.75.

3-Phenylisochroman.—To a solution of the glycol (II) in glacial acetic acid was added a few drops of sulfuric acid. Water was added to decrease the solubility of the product and the crystalline 3-phenylisochroman formed. The product was recrystallized from acetone; m.p. 114–115°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.67; H, 6.71. Found: C, 86.27; H, 6.17.

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[1] Our work, carried out independently, confirms the method of preparation of isochroman recently published by F. L. Anderson and F. G. Holliman, *J. Chem. Soc.*, **1037** (1950).

[2] W. G. Young and S. Siegel, THIS JOURNAL, **66**, 354 (1944).

[3] S. Siegel, S. Coburn and D. R. Levering, *ibid.*, **73**, 3163 (1951).

[4] (a) C. C. Price, *Org. Syntheses*, **22**, 61 (1942); (b) Buck, O. Grummitt and Egan, *ibid.*, **29**, 49 (1949).

[5] C. Graebe and F. Trumpy, *Ber.*, **31**, 377 (1898).

[6] See also A. Horeau and J. Jacques, *Bull. Soc. Chim.*, **15**, 53 (1948).

[7] S. Siegel, W. M. Boyer and R. R. Jay, THIS JOURNAL, **73**, 3237 (1951).

[8] Elementary analysis by Micro-Tech Laboratories, Skokie, Illinois.

[9] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).