$H_2O(l)^{10} = -68.3174$; $Al(OH)_3(\text{amorph})^{10} = -304.2$; $H_3BO_3(\text{cryst})^4 = -261$; $Al_2O_3(\text{cryst, corundum})^{10} = -399.09$; $B_2O_3(\text{cryst})^{11} = -303$

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(12) W. E. Wallace and G. Stegeman, unpublished results, 1945.

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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.

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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.

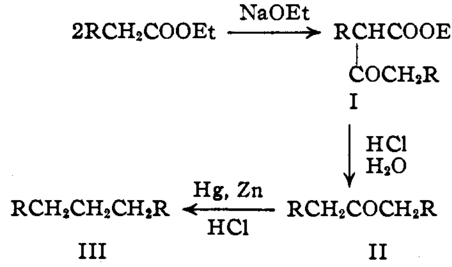
(3) R. E. Lutz, R. L. Wayland, Jr., and H. G. France, THIS JOURNAL, **72**, 5511 (1950).

(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 ($R = CH_3(CH_2)_{10}-$).



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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(2) Department of Chemistry, University of Texas, Austin.

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