

in the usual manner.<sup>8</sup> To 290 ml. of the Grignard solution (0.33 mole) in a flask fitted with a moisture-protected reflux condenser was added 54 g. (0.20 mole) of bromochloro-undecene. After the initial vigorous reaction had subsided, the mixture was boiled overnight. Hydrolysis was carried out with dilute sulfuric acid. The ether layer was washed with dilute aqueous sodium bicarbonate and with water, and was dried over magnesium sulfate. Removal of solvent left the crude coupling product which was purified by fractionation under reduced pressure. Material boiling at 100–108° (0.7 mm.) with bath temperature 165–200° was collected (22 g. or 51%) as 16-chlorohexadecene-7,  $n_D^{20}$  1.4570.

*Anal.* Calcd. for  $C_{16}H_{31}Cl$ : C, 74.3; H, 12.0. Found: C, 74.1; H, 12.0.

Judging from the absence of characteristic vinyl group absorption at 10.05  $\mu$ , this material was free of branched chain products.

**Alkylation of Malonic Ester with 16-Chlorohexadecene-7.**—Sodium ethoxide was prepared by dissolving 2.3 g. (0.10 atom) of sodium in 250 ml. of ethanol. Malonic ester (20 g. or 0.12 mole), potassium iodide (2 g.) and 16-chlorohexadecene-7 (III) (22 g. or 0.085 mole) were added and the mixture boiled under a moisture-protected condenser for 24 hours. Precipitated solids were removed by filtration and the filtrate, after concentration, was diluted with 100 ml. of ether. The ethereal solution was washed with water until the washings were neutral to litmus and finally dried over magnesium sulfate.

Ether and excess malonic ester were removed by distillation first at atmospheric pressure and then at 15 mm. Further fractionation yielded 24 g. (74%) of hexadecenyl-malonic ester, b.p. 170–172° (0.3 mm.);  $n_D^{20}$  1.4493.

*Anal.* Calcd. for  $C_{23}H_{42}O_4$ : C, 72.2; H, 11.0. Found: C, 71.8; H, 10.7.

**Vaccenic Acid.**—The malonic ester was saponified by stirring a mixture of 25 g. of sodium hydroxide, 250 ml. of water, 100 ml. of alcohol and 24 g. (0.063 mole) of the ester for 3 hours at steam-bath temperature. The mixture first became homogeneous and then deposited a precipitate. The alkaline mixture was allowed to stand overnight.

After one extraction with ether, the cold (0°) aqueous solution was brought to pH 1 by addition of dilute sulfuric acid, and the acid mixture shaken several times with ether. All traces of sulfuric acid were removed from the ether by thorough washing with water, and the ether solution dried with anhydrous magnesium sulfate. Evaporation of all solvent left 19 g. (93%) of the solid malonic acid.

Decarboxylation was carried out by holding test-tubes containing 1 to 9 g. portions of the malonic acid in a metal-bath at 180° for 12 minutes. In every case the decrease in weight due to loss of carbon dioxide corresponded to that calculated. The combined decarboxylation products were dissolved in approximately 80 ml. of acetone, and the solution cooled to –20°. The resulting precipitate was collected by rapid filtration through a precooled sintered glass funnel. A second crop was obtained in the same way from the concentrated mother liquor. The combined solids (8.3 g.) after two crystallizations from acetone at –20° weighed 7.4 g. (42%). The melting point, 44.5–45°, agreed with published values for synthetic vaccenic acid (43–44°<sup>9</sup>; 45–45.5° sintering at 44.5°; 42.5–43.5°<sup>4</sup>; 43.5–44.5°<sup>6</sup>) and was not depressed when the material was mixed with a sample of vaccenic acid prepared before.<sup>2</sup>

**Hydroxylation and Cleavage of Vaccenic Acid.**—Application of the hydroxylation method of Swern and co-workers,<sup>9</sup> to a mixture of 0.20 g. (0.002 mole) of vaccenic acid, 1 ml. of 25% hydrogen peroxide and 17 ml. of 87% formic acid afforded 0.230 g. of 11,12-dihydroxystearic acid, m.p. 125–126°. Two crystallizations from ethanol brought the melting point of the acid, either before or after admixture with the same material (m.p. 127.5–128.3°) prepared by Ahmad, Bumpus and Strong,<sup>8,10</sup> to 126.5–128°.

The expected products were obtained from the 11,12-dihydroxystearic acid on cleavage with periodic acid.<sup>3–5</sup> Heptanal 2,4-dinitrophenylhydrazone melted at 104.8–105.5° and, when mixed with authentic material (m.p.

106–107°), at 105–107°. The 2,4-dinitrophenylhydrazone of 10-formyldecanoic acid, after crystallization from aqueous alcohol, melted at 93–95° with some sintering noted at 86°.

*Anal.* Calcd. for  $C_{17}H_{22}N_4O_6$ : C, 53.7; H, 6.3. Found: C, 53.8; H, 6.4.

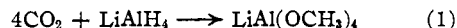
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## The Reduction of Carbon Dioxide to Formic Acid with Lithium Aluminum Hydride

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An extensive study has been made of the reaction of carbon dioxide with lithium aluminum hydride to form methanol.<sup>1–4</sup> Side reactions have been reported to give formic acid, formaldehyde and methyl formate. It has been suggested<sup>3</sup> that the reduction of carbon dioxide may proceed first to a formate, then to the methylene glycol salt and finally to the alcoholate. Thus at least three reactions seem possible, each of which represents a definite degree of reduction



Hydrolysis or alcoholysis of the salts would give formic acid, formaldehyde or methanol. The plausibility of the suggested mechanism has been strengthened in this work by the preparation of formic acid in good yield according to equation (1). A similar reduction of carbon dioxide to a formate in yields of 69–88% has been accomplished with lithium borohydride<sup>5</sup> although the reaction takes a different course with the formation of diborane as a by-product.

A high ratio of carbon dioxide to hydride is essential for a good yield of formate. This was maintained by the experimental techniques described below. Dilute hydride solutions and highly purified lithium aluminum hydride were other surprisingly critical conditions for good yields.

The importance of concentration may be seen in Table I. A diethyl ether solution containing 0.44% lithium aluminum hydride gave an 81% yield of formic acid, whereas a 3.53% solution gave only a 43% yield. The results were similar with diethylene glycol diethyl ether as a solvent. Under the experimental conditions employed in this study, the dilute solutions probably contributed to maintaining a high ratio of carbon dioxide to hydride at any reaction site.

The yields of formic acid were erratic, varying from 59 to 84%, unless the lithium aluminum hydride was carefully purified. Hydride originally over 95% pure gradually deteriorated after several months of exposure to light and occasional opening

(1) R. F. Nystrom, W. H. Yanko and W. G. Brown, *THIS JOURNAL*, **70**, 441 (1948).

(2) R. F. Nystrom, W. J. Shraba and R. G. Mansfield, ORNL-395, USAEC (1949).

(3) J. D. Cox, H. S. Turner and R. J. Warne, *J. Chem. Soc.*, **70**, 3167 (1950).

(4) H. I. Schlesinger and A. E. Finholt, unpublished work.

(5) J. G. Burr, Jr., W. G. Brown and H. E. Heller, *THIS JOURNAL*, **72**, 2560 (1950).

(8) H. Gilman, *et al.*, *THIS JOURNAL*, **45**, 150 (1923).

(9) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, *ibid.*, **67**, 1786 (1945).

(10) We are indebted to Dr. Strong for his kindness in supplying a sample of this dihydroxystearic acid.

TABLE I  
 REDUCTION OF CARBON DIOXIDE

Run	LiAlH <sub>4</sub> concn. % by wt.	LiAlH <sub>4</sub> mmoles.	CO <sub>2</sub> mmoles.	Ratio CO <sub>2</sub> to LiAlH <sub>4</sub>	HCO <sub>2</sub> H yield, %	HCHO yield, %
1 <sup>a</sup>	0.44	3.84	15.6	4.1	81	6.3
2 <sup>a</sup>	0.38	3.36	13.69	4.1	87	"
3 <sup>a</sup>	3.53	10.10	36.90	3.6	43	9.7
4 <sup>b</sup>	0.41	3.04	12.32	4.1	79	5.2
5 <sup>b</sup>	0.53	4.20	16.80	4.0	88	"
6 <sup>b</sup>	2.79	10.70	33.40	3.1	41	17.7

<sup>a</sup> Solvent was diethyl ether. <sup>b</sup> Solvent was diethylene glycol diethyl ether. <sup>c</sup> Product was oxidized with BaO<sub>2</sub> prior to isolation of acid.

to air. Dissolving the deteriorated hydride in ether at room temperature followed by filtration eliminated insoluble oxides or hydroxides but the resulting solution often still gave low yields of formic acid. Evaporation of such a hydride solution to dryness *in vacuo* at 70–80° gave a dark colored solid. Pure lithium aluminum hydride at 80° remains white. The low decomposition temperature suggests that the more unstable aluminum hydride may in some way have been formed by the action of light or air on lithium hydride. Aluminum hydride does react with carbon dioxide, but the highest yield of formic acid which could be obtained was 52%. Thus any binary hydride present as an impurity in the lithium aluminum hydride could cause the above-mentioned irregularities in yield. Lithium aluminum hydride was purified by refluxing an ether solution, a technique which would precipitate aluminum hydride as an insoluble etherate.<sup>6</sup>

Formaldehyde was identified as a by-product in all of the reductions. The yield was determined by weighing the dimedon derivative. In experiments using the more highly concentrated solutions, methanol was also isolated and identified by its vapor pressure at 0° and the characteristic refractive index. In several runs reported in Table I, the overall yield of formic acid was raised to 87–88% by oxidation of the formaldehyde with barium peroxide prior to the final isolation of the acid by distillation.

Several attempts were made to direct the reduction of carbon dioxide according to equation (2) by control of the ratio of reagents. The highest yield of formaldehyde was 23% based on the carbon dioxide which reacted.

The ratio of carbon dioxide to lithium aluminum hydride in many runs was over four. This may possibly be explained by incomplete recovery of carbon dioxide although care was taken to avoid loss of unreacted reagent.

#### Experimental

**Apparatus.**—Standard high vacuum techniques were used.

**Materials.**—A diethyl ether solution of commercial lithium aluminum hydride (Metal Hydrides, Inc.) was refluxed for three hours, filtered under nitrogen through a sintered glass filter and the filtrate evaporated to dryness *in vacuo* at 80°. The solid product was over 98% pure by hydrogen analysis.<sup>6</sup> Solutions of the hydride were made by dissolving the solid in the solvent and filtering *in vacuo* into a reaction vessel just before use. The concentration of hydride was determined by hydrogen analysis of an aliquot which was

(6) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

removed from the reaction vessel with a glass syringe under dry nitrogen.

**Reduction in Diethyl Ether.**—A solution of 0.145 g. (3.84 mmoles) of lithium aluminum hydride in 33.24 g. of diethyl ether was placed in a 100-ml. reaction vessel which was attached to the vacuum system through a ground joint. The solution was cooled with liquid nitrogen and the flask was evacuated. Carbon dioxide, 838 cc. (37.3 mmoles), was condensed into the reaction vessel. The mixture was warmed slowly to room temperature with constant agitation by a magnetic stirrer. As the hydride solution warmed, a reaction took place with the formation of a white precipitate. The volume of the vacuum system was such that the carbon dioxide pressure during the reaction never dropped below 300 mm. After stirring the mixture for one hour at room temperature, the excess carbon dioxide was removed and was separated from ether by fractionation in the vacuum line. The carbon dioxide recovered was 488 cc. indicating that 350 cc. (15.6 mmoles) had reacted.

Ether was removed from the reaction product by adding water and then bubbling nitrogen through the mixture.<sup>6</sup> After addition of 5 ml. of 85% phosphoric acid, a high vacuum distillation brought over water and formic acid. Two more 20-ml. portions of water were added and distilled to ensure complete removal of the formic acid. Titration of the distillate with sodium hydroxide showed 12.6 mmoles (81%) of formic acid had been formed. The acid was identified by the S-benzylthiuronium salt, m.p. 150–151°. Correction for traces of phosphoric acid were made with blank runs. Confirmation of the yield with HgCl<sub>2</sub> gave a slightly higher value than 81%.

The dimedon test of the distillate indicated that 6.3% of the carbon dioxide formed formaldehyde. Only a trace of the aldehyde was found in the residue.

Runs with diethylene glycol diethyl ether were made in the same way as with diethyl ether except that the solvent was not removed before the high vacuum distillation of formic acid.

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### The Decomposition by Heat of *d*-Camphoryl Diesters<sup>1</sup>

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The instability of *d*-camphoric diesters to heat has been reported in the literature but, excepting *d*-camphoric anhydride, no decomposition products have been described.<sup>2</sup>

The decomposition by heat of di-*n*-hexyl *d*-camphorate and diisobornyl *d*-camphorate was investigated. *d*-Camphoric anhydride was the main product. The reaction as to the alcohol part proceeds substantially in the same manner as described for the ester decomposition in the aliphatic monocarboxylic series, since 1-unsaturated hydrocarbons were isolated.<sup>3</sup>

The camphorates are not homogeneous stereochemically but are mixtures of the respective *d*-camphoric and isocamphoric acid esters.<sup>2a,b,c</sup> This was confirmed in case of the di-*n*-hexylcamphorate

(1) Paper presented at the XIIth International Congress of Pure and Applied Chemistry, September 13, 1951, New York, N. Y.

(2) (a) O. Aachan, *Ber.*, **27**, 2005 (1894); (b) *Ann.*, **316**, 221 (1901); (c) *Acta Soc. Sc. Fenn.*, **21**, No. 5, 102, 145 (1898); (d) J. W. Brühl, *Ber.*, **24**, 3408 (1891); (e) T. Hasselstrom, C. E. Balmer, N. E. Kennedy and H. W. Coles, *TAPPI*, **33**, 538 (1950).

(3) F. Kraft, *Ber.*, **16**, 3019 (1883).