

viously reported technique. The temp. range used was from 200–500°, with a flow of the alc. of 25 cc./hr. The products of reaction were analyzed for the aldehyde, H, CO, satd. and unsatd. hydrocarbons and O. In the temp. range about 400° the yield of the aldehyde was found to reach 38.9%. No appreciable decompn. of aldehyde was observed until 400° was reached. It was noted that the amt. of CO in the effluent gases is considerably below that of the satd. hydrocarbons, indicating some hydrogenation of CO in presence of Re by H split off from the alc. The low content of unsatd. hydrocarbons is also explicable by hydrogenation. This circumstance has led to errors by many previous investigators of the dehydrogenation of alcs. Thus, Re is a very good catalyst for dehydrogenations, in that good yields of the main product are readily obtained and side reactions are comparatively weak.

G. M. Kosolapoff

**Effects of zinc chloride on octyl alcohol.** M. M. Gerashimov and V. E. Glushnev. *Compt. rend. acad. sci. U. S. S. R.* 29, 462–5 (1940) (in English).—Into a reaction tube contg. 200 cc. of pumice grains impregnated with 52.6% by wt. of ZnCl<sub>2</sub> and surrounded by an elec. furnace, octyl alc. ( $d_4^{20}$  0.8273,  $n_D^{20}$  1.4304, I no. 13.31, b. 186–90°) was passed at a rate of 50 cc. per hr. at 225, 250, 275 and 325°. The ZnCl<sub>2</sub> reacted vigorously with the octyl alc. vapor, the yield of liquid products increasing with temp. The fractions b. 116–20° and 120–52.5° contained mostly octenes from the dehydration of the alc. The dehydration also yielded other unsatd. hydrocarbons, below 88° hexenes and heptenes, 88–116° heptenes, and 152.5–80° olefinic condensation products. The 180–90° fraction contained aldehydes. Blanks run without ZnCl<sub>2</sub> showed only small changes in the starting material. Water sepd. in the ZnCl<sub>2</sub> reactions, the amt. increasing with the temp. Gaseous products in the runs included isobutylene, propylene (predominantly) and ethylene as well as satd. hydrocarbons and H. Phys. data and analyses of the fractions are given.

Sara Anne Cassaday

**Reaction of a halogen and magnesium with alcohols and complex esters.** V. Reaction of iodine and magnesium with alcohols. M. T. Dangyan. *J. Gen. Chem.* (U. S. S. R.) 11, 616–18 (1941); cf. *C. A.* 35, 6565<sup>6</sup>.—D. studied the reaction of I and Mg with a no. of aliphatic alcs. MeOH (3.42 cc.) and 9.16 g. I at 40–50° were treated with 1.03 g. Mg, followed by 6 cc. MeOH, let stand and distd., to yield 54.5% MeI. Abs. EtOH (20 cc.) and 23.23 g. I were treated with 2.23 g. Mg (last portions added after careful warming of the vessel) and the mixt. distd. to yield 61.19% EtI. A mixt. of 12.71 g. I and 8.844 g. BuOH treated with 0.83 g. Mg and distd. gave 80.3% BuI. A mixt. of 9.26 g. I and 10.5 cc. iso-AmOH treated with 0.887 g. Mg at 100–115° and distd. yielded 60% of iso-AmI. The proposed reaction mechanism is the formation of an oxonium compd. which is decompd. by heating.

G. M. Kosolapoff

**Organic compounds of mercury.** V. The reaction of dialkylmercury with mercuric salts of tribasic acids. N. N. Mel'nikov and M. S. Rokitskaya. *J. Gen. Chem.* (U. S. S. R.) 11, 592–5 (1941); cf. *C. A.* 32, 2084<sup>1,2</sup>.—The authors investigated the possibility of prepg. dialkylmercury salts of tribasic acids by a method which is simpler than those available at present and is more adaptable for manufg. purposes. The general method used was the reaction of R<sub>2</sub>Hg with mercuric salts of phosphoric, arsenic and nitric acids. A mixt. of 13 g. Me<sub>2</sub>Hg, 15 g. Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and 0.5 cc. H<sub>2</sub>O was heated under a reflux condenser for 0.5 hr. at 100°, cooled and recrystd. from alc., yielding *tris(methylmercury) phosphate*, decomp. 182°, in 80% yield. A mixt. of 25 g. Et<sub>2</sub>Hg, 25.5 g. Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and 5 cc. H<sub>2</sub>O heated under a reflux at 115° for 15 min., cooled and recrystd. from H<sub>2</sub>O, yielded 98% of *tris(ethylmercury) phosphate*, m. 179–80°; hydrate (formed on recrystn. from H<sub>2</sub>O), m. about 110°. A mixt. of 15.4 g. Et<sub>2</sub>Hg and 17.4 g. Hg<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> heated under a reflux at 120° for 1 hr., cooled and recrystd. from EtOH, yielded 75% of *tris(ethylmercury) arsenate*, m. 184–6°. To 11.5 g. Hg(NO<sub>3</sub>)<sub>2</sub> there was added 8.5 g. Et<sub>2</sub>Hg and the mixt. heated under a reflux for 15 min. on a steam bath, cooled

and recrystd. from H<sub>2</sub>O to yield 80–5% *ethylmercury nitrate*, m. 86–6.5°, which crystd. from H<sub>2</sub>O as a *monohydrate*. A mixt. of 14 g. Pr<sub>2</sub>Hg, 15 g. Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and 0.5 cc. H<sub>2</sub>O was heated at 170° for 35 min., cooled and recrystd. from benzene to yield 98% of *tris(propylmercury) phosphate*, m. 96°. A mixt. of 18 g. Bu<sub>2</sub>Hg, 15 g. Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and 0.5 cc. H<sub>2</sub>O was heated for 1.5 hrs. at 170°, cooled and recrystd. from benzene to yield 88% of *tris(butylmercury) phosphate*, m. 75°. A mixt. of 19 g. iso-Am<sub>2</sub>Hg and 15 g. Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, heated 2 hrs. at 180°, gave 62% *tris(iso-amymercury) phosphate*, m. 105° (from benzene).

G. M. Kosolapoff

**Some acyl derivatives of iodine.** J. W. H. Oldham and A. R. Ubbelohde. *J. Chem. Soc.* 1941, 368–75.—Dry Ag salts of the fatty acids are conveniently prepd. by adding a very slight excess of NH<sub>4</sub>OH to the acid, warming to dissolve it in a convenient vol. of H<sub>2</sub>O or aq. EtOH, and stirring in a slight excess of concd. AgNO<sub>3</sub>; the final product is dried at about 100°. Solns. of I acyls are prepd. by adding I to the dry Ag salt of the fatty acid in a specially dried solvent (C<sub>6</sub>H<sub>6</sub>, petr. ether, CCl<sub>4</sub>) to convert all the Ag into AgI; the reaction is completed by warming to about 40° and the AgI allowed to settle; for longer-chain fatty acids the equation is: 3RCO<sub>2</sub>Ag + 2I<sub>2</sub> = 3AgI + I(OCOR)<sub>3</sub>; for the shorter chains, other acyl derivs. appear to be formed in appreciable proportions. For the isolation of the solid I acyls, the solns., freed of Ag salts by filtration, are cooled to about –20° and the solid filtered off, care being taken to exclude moisture. The solids usually must be recrystd. They resemble long-chain esters in appearance, but solns. of the triacyls have a faint color of vin rose even when freed as carefully as possible from the excess of I. After removal of all solvent by gentle warming in a vacuum, before exposure to the air, they have been kept for weeks in a desiccator, without undergoing serious decompn. When solid acyls are warmed, melting is usually first observed; marked evolution of gas then takes place suddenly around 120° and a complex mixt. of products is formed, which includes the ester (e. g., C<sub>17</sub>H<sub>35</sub>CO<sub>2</sub>C<sub>17</sub>H<sub>35</sub> from I tristearate), CO<sub>2</sub>, I, some alkyl iodide and possibly very small amts. of hydrocarbons. Noteworthy features of the thermal decompn. are the low temp. at which it occurs and the fact that as the chain length of the acid is shortened, decompn. occurs with increasing violence. When the I acyls are warmed in C<sub>6</sub>H<sub>6</sub> or CCl<sub>4</sub>, CO<sub>2</sub> is evolved; the products of thermal decompn. are qualitatively similar to those obtained from the dry solids. Other solvents, such as PhMe or C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, appear to react with the I acyls; in such cases the vol. of free CO<sub>2</sub> from a given wt. of acyl is much smaller and more complex products are formed. When I acyls are warmed in nonreactive solvents in the presence of excess of I, the evolution of CO<sub>2</sub> is increased and up to 80% of alkyl iodides is formed. It is not necessary to filter off the AgI before using solns. of I acyls in this way. A simple method of decarboxylation is to heat the Ag salt, under a solvent such as C<sub>6</sub>H<sub>6</sub> or CCl<sub>4</sub>, with excess of I till there is no further evolution of CO<sub>2</sub> (2–3 hrs.). The I acyls are remarkably sensitive to moisture; when quite free from solvents, substances such as I tristearate can be transferred from 1 vessel to another without much decompn. but if they are wetted even with supposedly hydrophobic org. solvents, they rapidly become pink in the air, owing to the liberation of I. The H<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub> insufficiently dried over Na can frequently be detected by adding it to a soln. of an I acyl in really dry C<sub>6</sub>H<sub>6</sub>. With small quantities of H<sub>2</sub>O (as H<sub>2</sub>O dissolved in ether or C<sub>6</sub>H<sub>6</sub>) HIO<sub>3</sub> seps. Other properties of solns. of I acyls are the rapid interaction with metallic Hg at room temp. and also with unsatd. hydrocarbons, with Et<sub>2</sub>S and with *m*- and *p*-xylene. The thermal decompn. of the I acyls is most simply regarded as primarily giving free acyl radicals, the I reverting to the univalent state. Details are given of the decompn. of Ag laurate with I in C<sub>6</sub>H<sub>6</sub>, petr. ether and CCl<sub>4</sub> and of Ag stearate in C<sub>6</sub>H<sub>6</sub>. C. J. West

**Acetone glyceraldehyde and optically active glycerides.** IX. Configuration of the natural batyl, chimyl and sel-achyl alcohols. Erich Baer and Hermann O. L. Fischer.