off. The product which had collected in the receiving flask and the trap was poured back into the decomposition flask from which it was steam distilled. The distillate was extracted with ether, washed with sodium carbonate and dried over Drierite. After removing the ether, the remaining liquid was distilled under reduced pressure; b.p. 91–92° at 60 mm., 168–169° at 750 mm., m.p. 4°, yield 23.5 g. (80%).

Anal. Calcd. for $C_6H_3Cl_2F$: C, 43.68; H, 1.83; Cl, 42.98. Found: C. 43.7; H, 1.9; Cl, 42.8.

3. Measurement of Spectra.—The absorption spectra were determined on solutions in 95% ethanol by means of a Cary Recording Spectrophotometer (Model 12), using 2-cm. matched fused quartz absorption cells against the solvent as reference.

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Low Pressure Hydrogenation and Several Properties of Methyl and *n*-Butylketene Dimers[1]

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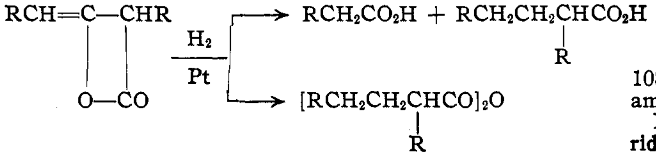
It has been demonstrated in this Laboratory that hydrogenation of mono-substituted alkylketene dimers at high pressures and temperatures and in the presence of Raney nickel catalyst produces dialkyl glycols.[2] It was thought profitable to report the response of ketene dimers of this type to hydrogen at low pressures and in the presence of Adams platinum catalyst. It was desired also to study the influence which a reactive solvent might have on the nature of the reduction products.

Treatment of methylketene dimer with hydrogen at 4.8 atm. and in platinum catalyst and petroleum ether gave 2-methylvaleric and propionic acids. Similar results were observed when *n*-butylketene dimer dissolved in petroleum ether was treated with hydrogen at 3.5 atm.

From an experiment in which *n*-butylketene dimer was treated with hydrogen at 3.4 atm. and in acetic acid anhydride, 2-*n*-butyloctanoic acid anhydride and acetic acid were isolated. It is probable that 2-*n*-butyloctanoic acid was formed as an intermediate product but was dehydrated by the acetic anhydride to form 2-*n*-butyloctanoic acid anhydride and acetic acid.



Where R = CH_3 and *n*-C_4H_2.

Experimental[3]

Preparation of Ketene Dimers.—The dimers were prepared by dehydrohalogenation of propionyl and *n*-caproyl chlorides with triethylamine.[4]

Characterization of Ketene Dimers.—Methylketene dimer reacted with concentrated ammonia to yield α-propionylpropionamide, m.p. 83–84° (reported[5] m.p. 82°); with aniline to give α-propionylpropionanilide, m.p. 115–116°; and with water to form diethyl ketone, from which the semicarbazone was prepared. Melting point of the semicarbazone was 135–136°; m.p. of the semicarbazone prepared from an authentic sample of diethyl ketone was 135–136°; mixed m.p. 135–136°. *n*-Butylketene dimer reacted with 15% sodium hydroxide solution to yield di-*n*-amyl ketone, b.p. 225° (755 mm.) and m.p. 14–15°; reported[6] m.p., 14–15°.

Catalytic Hydrogenation of Methylketene Dimer.—A mixture of 5.14 g. (0.04 mole) of methylketene dimer (b.p. 50–52° (9 mm.)) dissolved in 50 ml of petroleum ether and 0.3 g. of platinum oxide was treated with hydrogen at 4.8 atm. for four hours. The catalyst was separated and the solvent removed by distillation. Distillation of the residue from a Claisen flask gave two fractions: propionic acid (9.5%), b.p. 140° (755 mm.), n^{20}_{D} 1.3950, neutral equivalent calcd. for $C_3H_6O_2$: 74, found: 75; and 2-methylvaleric acid (75%), b.p. 88–90° (8 mm.) and 192° (750 mm.), d^{20}_{4} 0.9309, n^{20}_{D} 1.4170, MR_{D} (calcd.) 31.45, (found), 31.41, neutral equivalent calcd. for $C_6H_{12}O_2$: 116, found, 115. Reported[7] b.p., d^{20}_{4} and n^{20}_{D} of 2-methylvaleric acid are 192–193.6° (748 mm.), 0.9230 and 1.4136, respectively.

Bromination of Methylketene Dimer.—A solution of 6.5 g. of dry bromine in 10 ml. of carbon tetrachloride was added dropwise to a solution of 5 g. of methylketene dimer in 40 ml. of carbon tetrachloride at 0°. Three grams of the reaction product was added slowly to a chilled suspension of 10 ml. of absolute ethanol and 5 g. of pulverized sodium acetate. Removal of the ethanol and distillation of the residue gave 2 g. of product, b.p. 86–88° (4 mm.), d^{20} 1.3200. Saponification equivalent of the product calculated on basis of one ester group and one reactive bromine is 119; found, 119.

Anal. Calcd. for $C_8H_{13}O_3Br$: Br, 33.75. Found: Br, 34.00.

Catalytic Hydrogenation of *n*-Butylketene Dimer.—A mixture of 10.8 g. (0.06 mole) of *n*-butylketene dimer (b.p. 115–116° (4 mm.)) dissolved in 50 ml. of petroleum ether and 0.2 g. of platinum oxide was treated with hydrogen at 3.5 atm. for 45 minutes. Two reduction products were isolated: *n*-caproic acid (22%), b.p. 74–76° (5 mm.), n^{20}_{D} 1.4170 (n^{20}_{D} observed for an authentic sample of *n*-caproic acid, 1.4169), d^{20}_{4} 0.8580; m.p. of amide 100–101° (reported[8] m.p. for *n*-caproamide 101°), neutral equivalent calcd. for $C_6H_{12}O_2$: 116, found, 111; and 2-*n*-butyloctanoic acid (72%), b.p. 156–158° (7 mm.), d^{20}_{4} 0.8923, n^{20}_{D} 1.4390, MR_{D} (calcd.) 59.17, (found) 59.09; neutral equivalent calcd. for $C_{12}H_{24}O_2$: 200, found 197; amide m.p. 108–109°; m.p. of the amide prepared from an authentic sample of 2-*n*-butyloctanoic acid, 108–109°; mixed m.p. 107–108°.

Catalytic hydrogenation of this dimer was repeated using 8.5 g. (0.04 mole) of the dimer, 0.15 g. of platinum oxide, 30 ml. of pure acetic acid anhydride and 3.4 atm. of hydrogen pressure. The theoretical amount of hydrogen was absorbed within 15 minutes. Products isolated were: 2-*n*-butyloctanoic acid anhydride (73%), b.p. 175–177° (3 mm.), d^{20}_{4} 0.8913, n^{20}_{D} 1.4440, equivalent weight calcd. for $C_{24}H_{46}O_3$: 191, found 197; and 2 g. of acetic acid. The 2-*n*-butyloctanoic anhydride was further identified by treatment with concentrated ammonia. This gave 2-*n*-butyloctanoamide, m.p. 108–109°, mixed m.p. 107–108°; and 2-*n*-butyloctanoic acid, b.p. 134–135° (4 mm.); amide m.p. 107.5–108.5°.

Reaction of *n*-Butylketene Dimer with Hydrogen Chloride.—Dry hydrogen chloride gas was bubbled through 3 g. of *n*-butylketene dimer at 0° for 2 hours. Distillation of the product gave 1 g. of α-caproylacaproyl chloride boiling at 198–200° (4 mm.).

Anal. Calcd. for $C_{12}H_{21}O_2Cl$: Cl, 15.23. Found: Cl, 15.32.

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[1] The experimental portion of this paper is based largely on the doctoral thesis, "Studies of Ketenes and Their Derivatives," of C. M. Hill, Cornell University, 1941.

[2] C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, THIS JOURNAL, **74**, 166 (1952); C. M. Hill, L. Haynes and M. E. Hill, *ibid.*, 3423 (1952).

[3] All melting points are corrected.

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[5] H. Pingel, *Ann.*, **245**, 87 (1888).

[6] R. R. Briese and S. M. McElvain, THIS JOURNAL, **55**, 1698 (1933).

[7] M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

[8] I. Simon, *ibid.*, **38**, 47 (1929).