379. 2 : 3-*Dichlorodioxan.*

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The chlorination of dioxan leads to the production of "2 : 3-dichlorodioxan" (Böeseken, Tellegen, and Henriquez, *Rec. trav. chim.*, 1931, **50**, 909), three of the five theoretically possible 2 : 3 : 5 : 6-tetrachlorodioxans (Butler and Cretcher, *J. Amer. Chem. Soc.*, 1932, **54**, 2987; Summerbell and Christ, *ibid.*, p. 3778; Baker, J., 1932, 2666), and more highly chlorinated products (Böeseken, Tellegen, and Henriquez, *J. Amer. Chem. Soc.*, 1933, **55**, 1284).

"2 : 3-Dichlorodioxan," hitherto known as a liquid, reacts with ethylene glycol to give the two possible stereoisomeric forms (m. p. 111° and 137°) of 2 : 3-ethylenedioxydioxan (naphtho-1 : 4 : 5 : 8-dioxan; Böeseken, Tellegen, and Henriquez, *locc. cit.*; see also Donciu, *Monatsh.*, 1895, **16**, 8; Baker and Field, J., 1932, 86), the simultaneous formation of which might be due to the non-homogeneity of the 2 : 3-dichlorodioxan, *cis*- and *trans*-forms being possible. A single, homogeneous 2 : 3-dichlorodioxan, m. p. 30°, has now been prepared, but yet this reacts with ethylene glycol to give the two 2 : 3-ethylenedioxydioxans, so that inversion about one of the asymmetrical carbon atoms must occur during the reaction. The isolation of the lower-melting ethylenedioxydioxan in the pure state was difficult owing to the separation of the eutectic of the two stereoisomerides. An investigation of the thermal system of the two ethylenedioxydioxans showed that the curve was of the normal **V** shape, and that the eutectic mixture had m. p. 86° and contained 77% of the lower-melting isomeride. Melting points of mixtures containing the following percentages of the lower-melting isomeride were determined: 34, m. p. 120°; 51, m. p. 112°; 61, m. p. 107°; 74, m. p. 94°; 83, m. p. 98°; 91, m. p. 105°. The eutectic softening of all mixtures was easily discernible.

2 : 3-Dicyanodioxan could not be prepared by the interaction of 2 : 3-dichlorodioxan with (1) potassium cyanide alone or in a variety of solvents at the boiling point or under pressure, (2) with hydrogen cyanide in ether and pyridine, or (3) mercuric, silver, cuprous or lead cyanide under various conditions.

Chlorination of 1 : 3-dioxa*cyclo*pentane (also referred to in the literature as glycol formal and ethylene glycol methylene ether) gave an inseparable mixture of 2-chloro-1 : 3-dioxa*cyclo*pentane and a smaller quantity of 4-chloro-1 : 3-dioxa*cyclo*pentane.

Experimental.

2 : 3-Dichlorodioxan, prepared by the method of Böeseken, Tellegen, and Henriquez, isolated as described by Baker (*loc. cit.*), and redistilled under diminished pressure, solidified completely after a few weeks; b. p. 97—98°/20 mm., m. p. 30° (Found: C, 30·5; H, 3·8. Calc. for $C_4H_6O_2Cl_2$: C, 30·6; H, 3·8%). The mixture of the ethylenedioxydioxans prepared from this product was separated by fractional crystallisation from alcohol.

Chlorination of 1 : 3-*Dioxa*cyclo*pentane.*—Chlorine was passed into boiling 1 : 3-dioxa*cyclo*pentane (Baker, J., 1931, 1769) (34 g., distilled over sodium) in sunlight until no further increase in weight occurred (weight, 56 g.). The product was fractionated under diminished pressure; the main fraction boiled at 53—56°/30 mm. (Found: Cl, 32·3. $C_3H_5O_2Cl$ requires Cl, 32·7%). No homogeneous compound could be obtained either by fractional distillation or by freezing. Hydrolysis with water at 100° and addition of *p*-nitrophenylhydrazine hydrochloride (see Baker, J., 1932, 2666) yielded glyoxal *p*-nitrophenylosazone (0·08 mol.), which was doubtless derived from glycollaldehyde produced by the hydrolysis of 4-chloro-1 : 3-dioxa*cyclo*pentane. 2-Chloro-1 : 3-dioxa*cyclo*pentane could not furnish any compound from which the osazone could be obtained.

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