New Addition Reactions. V.
Dimerization of Diketene

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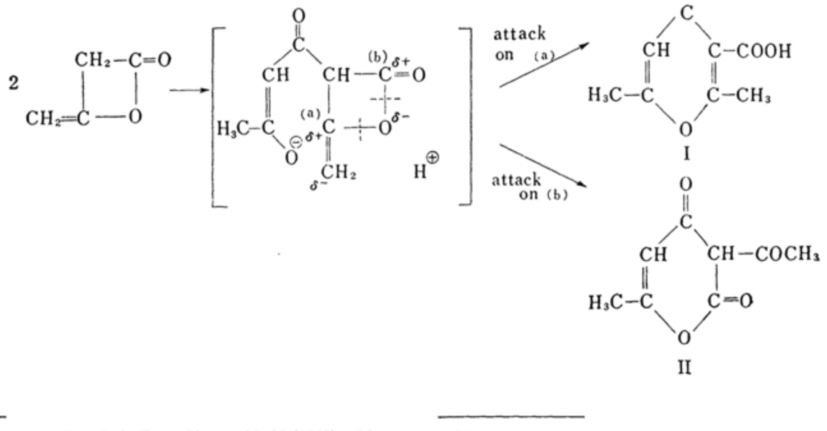
It is well known that diketene easily dimerizes to give dehydroacetic acid in the presence of a basic catalyst such as sodium ethoxide, sodium phenolate, triethylamine, or pyridine[1]. We now wish to report the formation of two isomeric diketene dimers by the use of aluminum tribromide as a catalyst. This result is in contrast to other Lewis acid-catalyzed reactions, where polymerizations of diketene to a polyketone[2] (by boron trifluoride and aluminum trichloride) or a polyester[3] (by mercuric chloride) were achieved.

When diketene was treated with 5∼10 mol. % of aluminum tribromide in ethylene dichloride at 10∼20°C for about thirty hours, a mixture of two dimers, 2,6-dimethyl-γ-pyrone-3-carboxylic acid (I) and dehydroacetic acid (II), was obtained in a fair yield without any formation of a polymeric byproduct. Compound I was separated from II by fractional crystallization using a ligroin-chloroform mixture, and their yields were 20 and 35% respectively. Both structures were confirmed by mixed melting point determinations with respective authentic samples. Here, the authentic material of I was prepared from II by the method of Feist[4]. It is interesting to note that the exclusive formation of II was observed (in ca. 20∼25% yields) when chloroform or carbon disulfide was used as a solvent, but no plausible explanation for this solvent effect can be offered.

Collie and Hilditch[5] reported that II could be converted to I in hot 85% sulfuric acid. However, when II was treated with aluminum tribromide in cold ethylene dichloride, no isomeric I was found, rather a small amount of an unidentified product (m.p. 230°C) resulted. Therefore, both dimers would be directly produced from diketene as shown in the following scheme. The formation of the anion III (or its protonated form) as a common intermediate seems probable in view of the fact that, in the presence of aluminum trichloride, a similar acylation of benzene with diketene has been achieved with ease[1a].



Experimental

Dimerization of Diketene.—To a stirred mixture of 30 g. (0.11 mol.) of aluminum tribromide and 300 ml. of dry ethylene dichloride, 100 g. (1.20 mol.) of diketene was added dropwise at the rate of 30 g./hr. The temperature was maintained below 10°C by means of an ice-bath. On the completion of the addition, the mixture was held at that temperature for 5 hr., and allowed to stand at room temperature for additional ca. 20 hr. (until the odor of diketene almost disappeared). Then 250∼300 ml. of ca. 5 N hydrochloric acid was gradually added to the reaction mixture to destroy the catalyst. The organic layer separated was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The residue which solidified on cooling was washed with cold ethanol, dried, and weighed 62 g. By recrystallization from ca. 500 ml. of ligroin-chloroform (3 : 2), 20 g. (20%) of light-brown crystals separated. Concentration of the

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[1] a) A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 21 (1940); b) A. B. Steele et al., *J. Org. Chem.*, **14**, 460 (1949); c) T. Isozima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kōgyō Kagaku Zassi*), **57**, 773 (1954).

[2] a) R. Oda et al., *Makromol. Chem.*, **43**, 149 (1961); b) J. Furukawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 254 (1962).

[3] J. Furukawa et al., *Makromol. Chem.*, **39**, 243 (1960).

[4] F. Feist, *Ann.*, **257**, 253 (1890).

[5] J. N. Collie and T. P. Hilditch, *J. Chem. Soc.*, **91**, 787 (1907).

filtrate gave 35 g. (35%) of other crystals. The first compound, after two recrystallizations from chloroform or ethanol, showed m. p. 96~98°C. Based on its analytical data, spectral (infrared and ultraviolet) data and chemical reactivities (neutralization with aqueous alkaline, decarboxylation, reaction with amine etc.), formula I was proposed for this compound. The structure was further confirmed by a mixed melting point determination with an authentic material, which was prepared from II, by chlorination with phosphorus pentachloride, and by treatment with concentrated sulfuric acid[4]. The second substance melted at 108~109°C after recrystallization from aqueous ethanol. This compound showed an infrared spectrum identical with that of authentic II, and no mixed melting point depression was observed.

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