

experiments with cracking catalysts do not necessarily prove heterogeneity of surface. We do not intend to imply by this that silica-alumina has a homogeneously active surface—there is considerable evidence for heterogeneity, and in theory we should expect such heterogeneity depending on the geometry of the aluminum and silicon atoms in the surface. We wish merely to indicate that by using the concept of the mobility of the surface, poisons need not be present in amounts stoichiometrically equivalent to the total active surface to cause essentially complete deactivation. The surface of cracking catalysts then behaves to a certain degree like a two-dimensional mobile acid.

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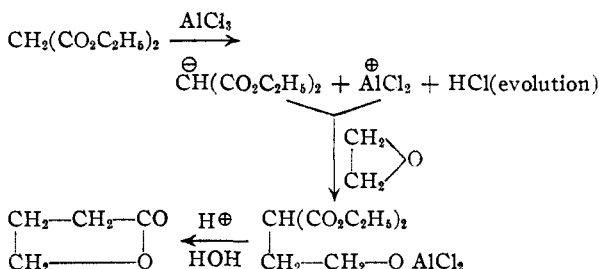
### Alkylation of Malonic Ester by Ethylene Oxide Catalyzed by Anhydrous $\text{AlCl}_3$

BY CHITTARANJAN RAHA

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Available methods<sup>1-3,5-14</sup> of synthesis of  $\gamma$ -butyrolactone are not easily workable and give poor yields. A consideration of the mechanism of reaction of ethylene oxide as discussed by Hammett<sup>15</sup> suggested that the alkylation of malonic ester by ethylene oxide in the presence of anhydrous aluminum chloride might be an effective method for the preparation of  $\gamma$ -hydroxy acids. Breslow and Hauser<sup>4</sup> have previously described the alkylation of acetoacetic ester with benzyl chloride in the presence of boron trifluoride.

The present reaction may be explained as



#### Experimental

Sixty-four grams (0.4 mole) of malonic ester dissolved in 50 ml. of absolute chloroform was added slowly to 34 g. (0.25 mole) of coarsely powdered anhydrous  $\text{AlCl}_3$ <sup>16</sup> in a 3-

- (1) S. W. Chaikin and W. G. Brown, *THIS JOURNAL*, **71**, 122 (1949).
- (2) F. F. Blicke, S. B. Wright, Jr., and M. F. Zienty, *ibid.*, **63**, 2488 (1941).
- (3) W. L. Nelson and L. H. Cretcher, *ibid.*, **52**, 3702 (1930).
- (4) D. S. Breslow and C. R. Hauser, *ibid.*, **62**, 2358 (1940).
- (5) N. Fröschl and C. G. Danoff, *J. prakt. Chem.*, **144**, 217 (1936); *C. A.*, **30**, 3777<sup>4</sup> (1936).
- (6) W. H. Bentley, E. Haworth and W. H. Perkin, Jr., *J. Chem. Soc.*, 161 (1896).
- (7) W. H. Perkin, Jr., and C. H. G. Sprankling, *ibid.*, 17 (1899).
- (8) S. S. Guhasarkar, *ibid.*, 898 (1928).
- (9) F. Fichter and A. Herbrand, *Ber.*, **29**, 1192 (1896).
- (10) Fittig, *Ann.*, **226**, 331 (1884).
- (11) *Ibid.*, **267**, 192, 200 (1892).
- (12) Saytzeff, *ibid.*, **171**, 266, 279, 282.
- (13) Traube and Lehmann, *Ber.*, **32**, 720 (1899); **34**, 1971, 1976 (1901).
- (14) Curtius, *ibid.*, **37**, 1277 (1904).
- (15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 1940, 301.
- (16) The yield depends on the freshness of anhydrous  $\text{AlCl}_3$ .

necked flask fitted with a reflux condenser, a dropping funnel, an all-glass stirrer and a gas inlet tube. Hydrogen chloride was evolved. Ethylene oxide, generated by dropping 21 g. (0.26 mole) of ethylene chlorohydrin slowly on 20 g. (0.5 mole) of powdered sodium hydroxide under absolute toluene, was passed into the reaction mixture at room temperature with mechanical stirring. The rate of introduction of ethylene oxide was regulated so that the ether refluxed. After addition was complete, the mixture was cautiously acidified with 5 *N* hydrochloric acid, and then refluxed for five hours. The solid which separated on acidification dissolved within a few minutes. The light greenish mixture was then cooled, saturated with salt and extracted with benzene. The benzene extract was washed with a small amount of water, dried over anhydrous sodium sulfate and concentrated. The residual thin liquid was fractionated under reduced pressure.

The yield of  $\gamma$ -butyrolactone obtained as a colorless thin liquid, b.p. 85–110° (11 mm.); 105–120° (15 mm.), was quantitative (based on the ethylene chlorohydrin used).

*Anal.* Calcd. for  $\text{C}_4\text{H}_6\text{O}_2$ : C, 55.8; H, 6.9; neut. equiv., 86. Found: C, 55.42; H, 7.3; neut. equiv., 84, 86;  $n_D^{20}$  1.3760.

The liquid  $\gamma$ -lactone which boiled usually over a range could be collected in two distinctly different fractions which had the same contents of carbon and hydrogen and same saponification equivalent. This property is possibly due to a dimorphism as suggested by Sueur.<sup>17</sup>

In one experiment the two fractions were: I, b.p. 85° (11 mm.), 105° (15 mm.), yield 5 g.; II, b.p. 130° (11 mm.), 140° (15 mm.), yield 17 g. In other experiments the relative proportions of the two fractions varied.

In more or less identical yield the two fractions gave a 2,4-dinitrophenylhydrazide, m.p. 93–94°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_8$ : C, 42.26; H, 4.225; N, 19.72. Found: C, 42.48; H, 4.323; N, 19.59.

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(17) Sueur, *Ann. Rept. Chem. Soc. (London)*, **9**, 90 (1912).

BOSE INSTITUTE  
CALCUTTA, INDIA

### Anhydrous $\text{AlCl}_3$ -Catalyzed Alkylation of Ethyl Cyanacetate by Ethyl Chloroacetate

BY CHITTARANJAN RAHA

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Breslow and Hauser<sup>1</sup> have observed that a reactive methylene compound, e.g., acetoacetic ester, can be ar-alkylated by benzyl chloride in the presence of an acid catalyst such as boron trifluoride. A similar reaction, viz., alkylation of cyanoacetic ester by means of ethyl chloroacetate in presence of anhydrous aluminum chloride, has been studied by the present author.

The yield of the alkylated product varied with the amount of catalyst used, but unlike a base-catalyzed reaction even a large amount of the acid catalyst failed to produce in a single step a di-condensation product. The results of comparative runs of experiments carried out in presence of an acidic catalyst and a basic catalyst are tabulated.

#### Experimental

**Alkylation of Cyanoacetic Ester with Ethyl  $\alpha$ -Chloroacetate to Yield the Monocondensation Product. Acid Cata-**

- (1) D. S. Breslow and C. R. Hauser, *THIS JOURNAL*, **62**, 2385, 2389 (1940).