

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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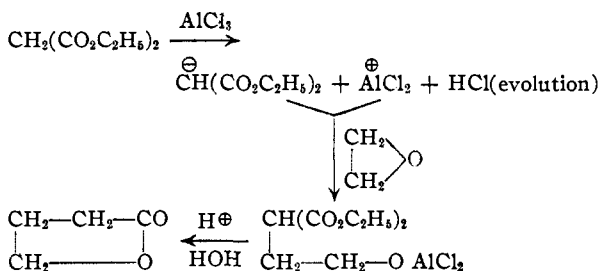
Alkylation of Malonic Ester by Ethylene Oxide Catalyzed by Anhydrous AlCl_3

BY CHITTARANJAN RAHA

RECEIVED DECEMBER 31, 1952

Available methods^{1-3,5-14} of synthesis of γ -butyrolactone are not easily workable and give poor yields. A consideration of the mechanism of reaction of ethylene oxide as discussed by Hammett¹⁵ 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 γ -hydroxy acids. Breslow and Hauser⁴ 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 AlCl_3 ¹⁶ 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**, 3777⁴ (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 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 γ -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 γ -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.¹⁷

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.

Acknowledgment.—Thanks are due to Dr. D. M. Bose, Director of the Bose Institute, for his encouragement and interest in this work. The author is indebted to Dr. S. K. Mukherjee, Department of Applied Chemistry, for his valuable help.

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

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Anhydrous AlCl_3 -Catalyzed Alkylation of Ethyl Cyanacetate by Ethyl Chloroacetate

BY CHITTARANJAN RAHA

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Breslow and Hauser¹ 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 α -Chloroacetate to Yield the Monocondensation Product. Acid Cata-

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

TABLE I

Reactive methylene compound	Alkylating agent	Catalyst	% Yield of product*
Cyanoacetic ester	Ethyl chloroacetate	1. 1 mole of AlCl ₃	50%
		2. 2 moles of AlCl ₃	Quantitative
		3. 1 mole of NaOC ₂ H ₅	50% mono-condensation product + 10% dicondensation product
		4. 2 moles of NaOC ₂ H ₅	35% dicondensation product + 10% mono-condensation product
α-Cyanosuccinic ester	Ethyl chloroacetate	5. 1-7 moles of AlCl ₃	Nil
		6. 1 mole of NaOC ₂ H ₅	30% dicondensation product

* The yield depends on the freshness of the AlCl₃.

lyst (1 M).—To 13 g. (0.1 mole) of coarsely powdered anhydrous aluminum chloride was added dropwise a solution of 11.3 g. (0.1 mole) of cyanoacetic ester and 12 g. (0.1 mole) of ethyl α-chloroacetate in 25 ml. of dry chloroform with constant shaking of the externally cooled reaction mixture. The addition of the solution was attended with evolution of hydrogen chloride followed by dissolution of the catalyst. The brown reaction mixture was left at room temperature till gas evolution had ceased. After careful decomposition of excess aluminum chloride with ice the reaction mixture was worked up in the usual manner. The residual liquid after removal of the solution was fractionated under vacuum.

The yield of colorless liquid product, b.p. 105° (10 mm.), was 11.5 g. (50%). *Anal.* Calcd. for C₂H₃NO₂: C, 54.27; H, 6.5; N, 7.03. Found: C, 53.97; H, 6.63; N, 7.32.

A portion (2 g.) of the distillate on hydrolysis with 20% hydrochloric acid and subsequent crystallization proved to be succinic acid (0.8 g.), m.p. 185°, singly and on admixture.

The catalyst even if increased to 2 moles or more always gave the above monocondensation product alone in quantitative yield but never any dicondensation product.

Sodium Ethoxide Catalyst.—To sodium ethoxide (prepared from 1 g. (less than 0.05 mole) of sodium metal and 12 ml. of absolute alcohol) was added 5.65 g. (0.05 mole) of cyanoacetic ester with constant shaking and external cooling. The sodio salt formed was left at room temperature for an hour or so after which 6 g. (0.05 mole) of ethyl chloroacetate in 5 ml. of absolute alcohol was dropped in with external cooling and constant shaking of the reaction mixture. Eight to ten hours reflux on a water-bath and subsequent working up in the usual manner gave 4.9 g. (50%) of the monocondensation product and 1.4 g. (10%) of a glycerol-like dicondensation liquid product, b.p. 145° (10 mm.). *Calcd.* for C₃H₅NO₂: C, 54.73; H, 6.66; N, 4.91. Found: C, 54.52; H, 6.77; N, 4.83.

Acid hydrolysis of the dicondensation product (3 g.) gave tricarballic acid (1.5 g.), m.p. 165°; on admixture with an authentic sample the m.p. was 164–165°.

As already pointed out the acid catalyst yielded no dicondensation product under any of the above experimental conditions. It could be prepared only when a base catalyst was employed as described below.

In One Step.—2.3 g. (0.1 mole) of sodium metal was dissolved in 30 ml. of absolute alcohol. To the cold sodium ethoxide was added 5.7 g. (0.05 mole) of cyanoacetic ester. The resulting mixture was intermittently warmed on a water-bath for about an hour. A solution of 12 g. (0.1 mole) of ethyl α-chloroacetate in 10 ml. of absolute alcohol was added dropwise to the cold sodio salt. After leaving overnight the mixture was refluxed on a steam-bath for 10 hours. The reaction mixture was cooled and worked up in the usual way to get 1 g. (10%) of monocondensation product, b.p. 105° (10 mm.), and 4.9 g. (35%) of dicondensation product, b.p. 145° (10 mm.).

Monocondensation to Dicondensation Product.—Three grams (0.025 mole) of ethyl α-chloroacetate was added to the sodio salt of ethyl α-cyanosuccinate prepared from 4.98 g. (0.025 mole) of the ester and 0.681 g. (0.025 mole) of sodium metal. The reaction mixture was colored violet. The usual processing gave (30%) of the ethyl α-cyanotricarballylate, b.p. 145° (10 mm.).

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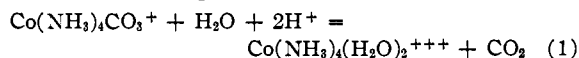
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Mechanism of Aquotization of Carbonato Complex Ions

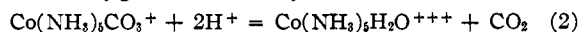
BY FRANZ A. POSEY AND HENRY TAUBE

RECEIVED FEBRUARY 20, 1953

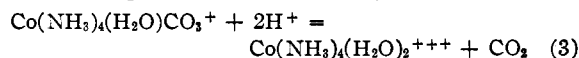
Stranks and Harris¹ have reported that there is no carbon isotope discrimination in the reaction



In an oxygen tracer study on a related reaction



Hunt, Rutenberg and Taube² showed that in release of carbonate, the Co–O bond is not severed, but rather the C–O bond. Since reaction (2) is analogous to what can reasonably be supposed to be a stage in the net reaction (1)



there is an apparent inconsistency in the two observations which, while it can be resolved by one of several assumptions, forces none as a conclusion. We have therefore undertaken an oxygen tracer study of reaction (1), for comparison with the results obtained in reaction (2), similar to that conducted for this reaction, but have increased the power of the tracer results by examining also the isotopic composition of the carbon dioxide liberated both in reactions (1) and (2). The method for isotopic assay of the water bound in Co(NH₃)₄(H₂O)₂⁺⁺⁺ was developed during the course of other research on the ion, and will be described more fully when these results are published.

Experimental

The salt (Co(NH₃)₄CO₃)NO₂·1/2H₂O was prepared according to the method of Grubitsch.³ The purity was checked by electrolytic determination of the cobalt content (calculated, 22.84%; observed, 22.86%). The salt (Co(NH₃)₅CO₃)NO₂·H₂O was part of a preparation used previously.²

The tracer experiments with (Co(NH₃)₄CO₃)NO₂·1/2H₂O were performed by preparing a solution of this compound in water enriched in H₂O.¹⁸ Perchloric acid in water of isotopic composition very near to that in the solution was

(1) D. R. Stranks and G. W. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

(2) J. P. Hunt, A. C. Rutenberg and H. Taube, *THIS JOURNAL*, **74**, 268 (1952).

(3) H. Grubitsch, "Anorganisch-präparative Chemie," Springer Verlag, Vienna, 1950, p. 441.