

Communications TO THE EDITOR

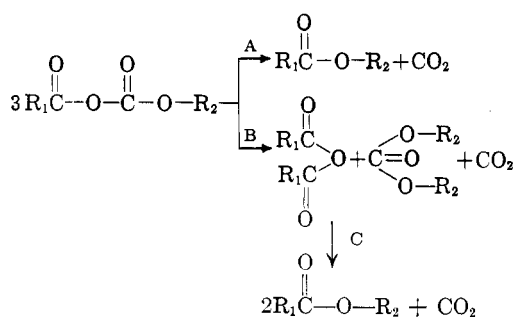
Decomposition of Mixed Carboxylic-Carbonic Anhydrides

Sir:

In connection with our research we have investigated the stability and decomposition products of mixed carboxylic-carbonic anhydrides.¹ Two recent publications² now prompt us to report some of our results.

Our experiments confirm the surprising stability of some mixed carboxylic-carbonic anhydrides. We find that the acetic-ethyl carbonic and the benzoic-ethyl carbonic anhydrides are stable oils, as reported. However, we have found that the *pK* of the carboxylic acid used in the preparation of the mixed anhydrides has a marked effect on the stability of these compounds, the anhydrides from the stronger acids (lower *pK*'s) being considerably less stable. For the following series: acetic (4.76), phenyl acetic (4.31), *p*-nitrophenyl acetic (3.85) and cyanoacetic (2.43)-ethyl carbonic anhydrides, the stabilities as measured by CO₂ evolution decrease in the order given. The *pK* values are included for reference.

We have experimentally demonstrated the following possible paths of decomposition of the mixed carboxylic-carbonic anhydrides³:



The course of the reaction was followed by measurement of the CO₂ evolution, isolation of some intermediates and correlation by infrared analysis. The structure of R₁ greatly influences the direction of the reaction, electron attracting substituents favoring path A. Good yields of esters are obtained from stable mixed anhydrides by heating over 200°. In these cases, reaction path A and reaction path B

(1) T. Wieland H. Bernhard, *Ann.*, **572**, 190 (1951); J. R. Vaughan, Jr., *J. Am. Chem. Soc.*, **73**, 3547 (1951); R. A. Boissonas, *Helv. Chim. Acta*, **34**, 874 (1951).

(2) D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 and 1152 (1958).

(3) Paths A and B have been previously suggested: A. Einhorn, *Ber.*, **42**, 2772 (1909); T. Wieland and H. Bernhard, *Ann.*, **572**, 190 (1951). see also (2).

followed by C both occur simultaneously. The existence of the secondary reaction C was demonstrated by the independent preparation of ethylene glycol dibenzoate from benzoic anhydride and ethylene carbonate by heating over 200°.

Details of this and related work will be reported later.

THOMAS B. WINDHOLZ

RESEARCH LABORATORIES
CELANESE CORPORATION OF AMERICA
SUMMIT, N. J.

Received September 29, 1958

Direct Preparation of Benzyl lithium by Cleavage Reactions

Sir:

We are reporting the first direct preparation of benzyl lithium in good yields and in a manner easily applicable to synthetic use. Hitherto, benzyl lithium had been the least accessible RLi compound of general importance.

A number of indirect methods for the preparation of benzyl lithium has been reported¹ wherein the benzyl lithium has at least a transitory existence. These methods suffer, however, from the necessity of at least one, and sometimes several, intermediate steps, thus decreasing their value for synthetic use. A direct preparation of benzyl lithium has been reported² in which benzyl chloride reacts with lithium metal in diethyl ether to give on carbonation a 1.06% yield of phenylacetic acid and 67.5% of bibenzyl. Ethers containing the benzyl group have been successfully cleaved by sodium metal³ to give the corresponding organo-

(1) (a) K. Ziegler and F. Dersch, *Ber.*, **64**, 448 (1931); (b) T. V. Talalaeva and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, **77**, 621 (1951) [*Chem. Abstr.* **45**, 10191 (1951)]; *Izvest Akad. Nauk S.S.S.R., Otdel, Khim. Nauk*, **1953**, 290 [*Chem. Abstr.*, **48**, 6389 (1954)]; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, **1953**, 263 [*Chem. Abstr.*, **48**, 12672 (1954)]; (c) H. Gilman, G. A. Pacevitz, and O. Baine, *J. Am. Chem. Soc.*, **62**, 1514 (1940); (d) A. H. Haubein, *Iowa State Coll. J. Sci.*, **18**, 48 (1943); (e) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941); (f) A. Lüttringhaus, G. Wagner v. Sääf, E. Sucker and G. Borth, *Ann.*, **557**, 46 (1945); (g) Fr. Hein, F. Petzchner, K. Wagler, and Fr. A. Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1924); (h) W. Schlenk, Jr., Doctoral Dissertation, Techn. Hochschule, Berlin, 1929; (i) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **67**, 1420 (1945); (j) H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951); (k) R. C. Fuson and B. Freedman, *J. Org. Chem.*, **23**, 1161 (1958).

(2) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 3134 (1955).

(3) P. Shorigin, *Ber.*, **57B**, 1627, 1634 (1927).