

# Communications TO THE EDITOR

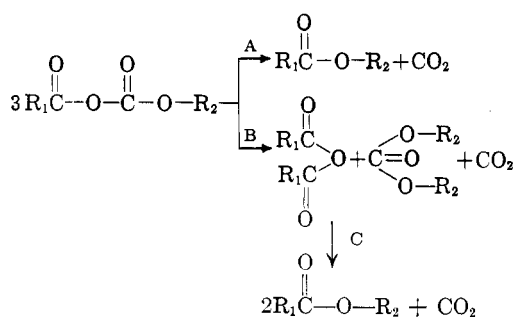
## Decomposition of Mixed Carboxylic-Carbonic Anhydrides

Sir:

In connection with our research we have investigated the stability and decomposition products of mixed carboxylic-carbonic anhydrides.<sup>1</sup> Two recent publications<sup>2</sup> 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 CO<sub>2</sub> 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 anhydrides<sup>3</sup>:



The course of the reaction was followed by measurement of the CO<sub>2</sub> evolution, isolation of some intermediates and correlation by infrared analysis. The structure of R<sub>1</sub> 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

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(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.

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## 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 reported<sup>1</sup> 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 reported<sup>2</sup> 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 metal<sup>3</sup> to give the corresponding organo-

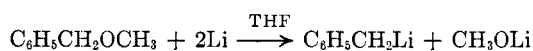
(1) (a) K. Ziegler and F. Dersch, *Ber.*, **64**, 448 (1931); (b) T. V. Talalaeva and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, **77**, 621 (1951) [*Chem. Abstr.* **45**, 10191 (1951)]; *Izvest Akad. Nauk S.S.S.R., Otdel, Khim. Nauk*, **1953**, 290 [*Chem. Abstr.*, **48**, 6389 (1954)]; *Bull. 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).

metallic compound in good yield. However, this cleavage had not been accomplished previously by the use of lithium metal. Alkali metal derivatives of  $\alpha$ -substituted benzyl ethers also are prepared by cleavage reactions. Benzhydrysodium is made by cleaving benzhydryl methyl ether<sup>4</sup> and ethyl diphenylacetate.<sup>5</sup> Benzhydrylpotassium is formed by the cleavage of both benzhydryl benzyl and benzhydryl ethyl ethers.<sup>6</sup> Several instances are reported in which phenylisopropylpotassium is prepared by cleaving phenylisopropyl methyl ether.<sup>7</sup> It also is possible to prepare 1,1-diphenylethyl- and 1,1-diphenylpropylpotassium from 1,1-diphenylethyl and 1,1-diphenylpropyl methyl ethers, respectively.<sup>7a</sup>

In this laboratory benzyl lithium has been prepared in satisfactory yields by the cleavage of ethers of the type  $\text{PhCH}_2\text{OR}$  in tetrahydrofuran (THF), where R is methyl, ethyl, phenyl, and benzyl. The yield of benzyl lithium, as determined by double-titration,<sup>8</sup>



was consistently in the range 75 to 83% within 1 hr. Derivation with the theoretical amount of chlorotriphenylsilane gave yields of 57 to 61% of benzyltriphenylsilane, m.p. 98–100°. Benzyl phenyl ether is an exception, giving a titer for only 61% of RLi and affording 37% of the silane derivative. These experiments were carried out by adding dropwise with vigorous stirring 55 ml. of a THF solution of 0.023 mole of the ether to be cleaved to a mixture of 0.36 g. atom of finely cut lithium wire and 60 ml. of THF at  $-5^\circ$  to  $-15^\circ$ . Experiments using 0.069 mole of benzyl methyl ether

required a considerably longer period for the reaction to begin. The reaction appears to start no more readily, but goes further to completion if a creased reaction flask is used. This and other procedures are being examined for the preparation of related RLi compounds like allyllithium.

In a similar reaction using diethyl ether as the solvent, dibenzyl ether (0.023 mole) has been cleaved to give a titer of 40% as a maximum. Derivatization gave 16% of benzyltriphenylsilane.

The preparation of  $\alpha$ -methylbenzyl lithium from bis( $\alpha$ -methylbenzyl) ether has been accomplished under the same conditions used to make benzyl lithium. The titer for  $\alpha$ -methylbenzyl lithium varied from 62 to 68%. Derivatization gave from 32 to 38% of  $\alpha$ -methylbenzyltriphenylsilane, m.p. 124.5–126.5°) *Anal.* Calcd. for  $\text{C}_{28}\text{H}_{24}\text{Si}$ : C, 85.66; H, 6.64; Si, 7.70. Found: C, 85.58, 85.69; H, 6.30, 6.26; Si, 7.65, 7.58.

In addition to the foregoing, benzyl sulfide and benzyltriphenylsilane have been cleaved by lithium in THF. In the reaction with benzyl sulfide Color Test I<sup>9</sup> was not positive at any time. Carbonation of the products from the cleavage of benzyltriphenylsilane gave 9.6% phenylacetic acid, 4.2% hexaphenyldisilane, 11% triphenylsilanol, and a 13.2% recovery of unreacted starting material. Another experiment gave 18.5% of phenylacetic acid, 0.5% tetraphenylsilane, 0.6% hexaphenyldisilane, and 0.08 g. of an unknown compound, m.p. 134–137°. A similar, though more clean cut cleavage has been reported<sup>10</sup> using sodium-potassium alloy to cleave  $\alpha,\alpha$ -dimethylbenzyltriphenylsilane.

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