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 CO_2 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 R_1 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

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 Benzyllithium by Cleavage Reactions

Sir:

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

A number of indirect methods for the preparation of benzyllithium has been reported¹ wherein the benzyllithium 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 benzyllithium 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-

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