

ACYLATION OF A CARBONYL ANION EQUIVALENT: AN EFFICIENT METHOD OF PREPARING
 ALPHA-HYDROXYCARBONYL SYSTEMS, ALPHA-DICARBONYL SYSTEMS,
 AND KETENE THIOACETAL MONOXIDE DERIVATIVES

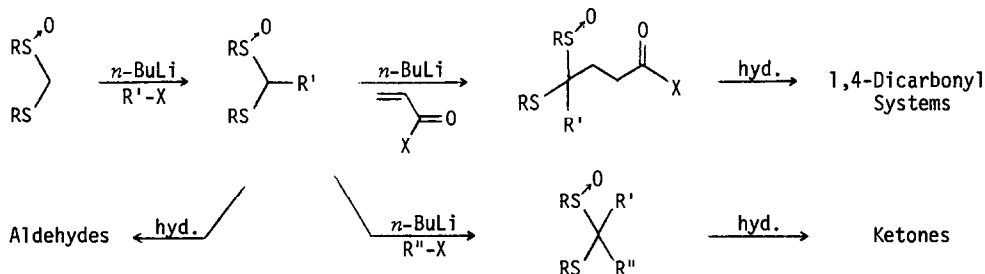
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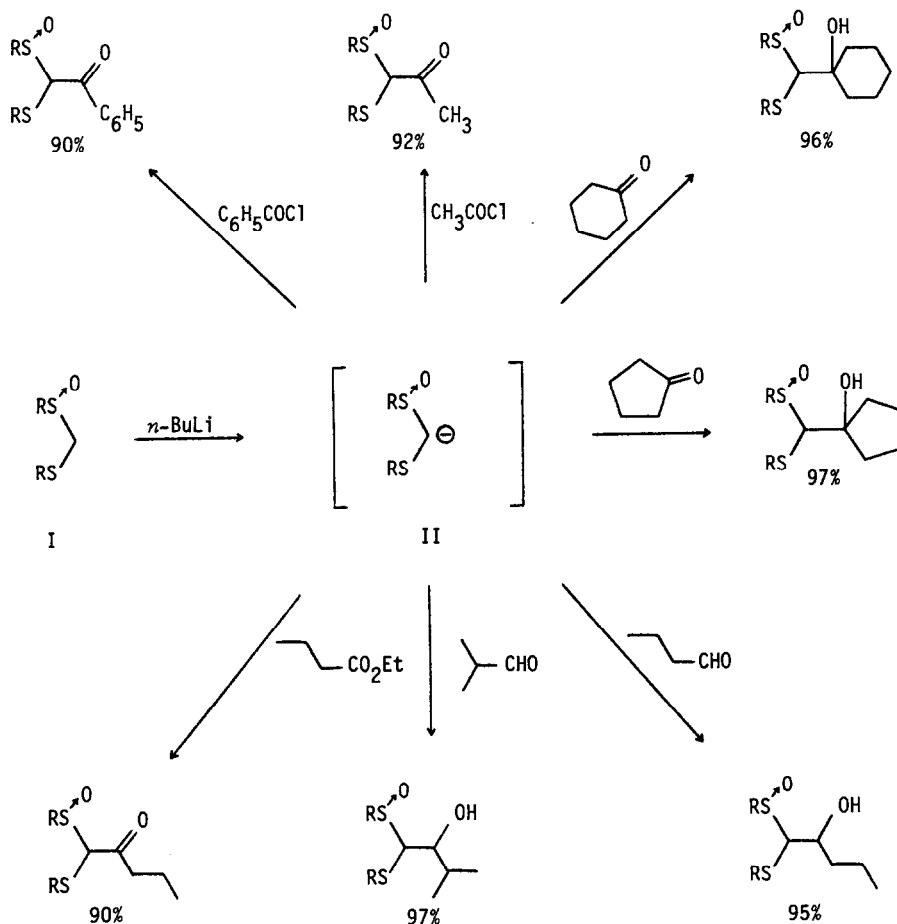
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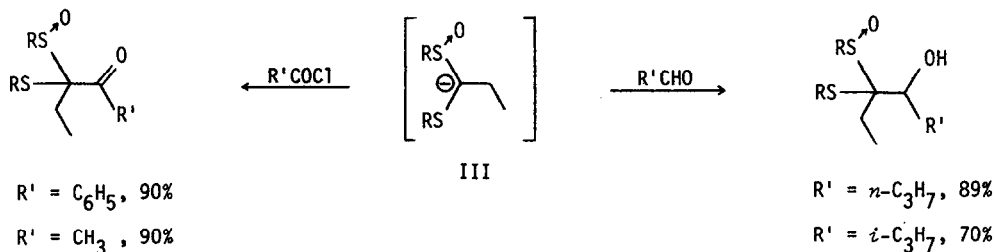
We have recently described the nucleophilic properties of the carbonyl anion equivalent I ($R = C_2H_5$) with respect to alkylation¹ and conjugate addition,² reactions which result in highly efficient preparations of aldehydes, ketones, and 1,4-dicarbonyl systems. In addition, high yield total syntheses of *cis*-jasmone and dihydrojasmone using both the alkylation and conjugate addition reactions of I have been reported.³ Herein, we wish to describe a third mode of nucleophilic behavior for I, namely acylation, and to report that this type of reaction leads to several kinds of α -functionalized carbonyl compounds as well as to electron deficient olefins.



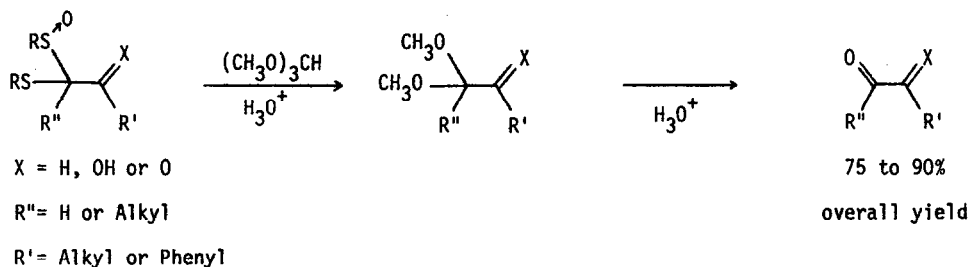
A solution of I (1 equivalent, 1 molar in THF) when treated at 0° with *n*-butyllithium (1 equivalent) quantitatively affords the anion II (20 minutes). This anion undergoes smooth 1,2 addition to aldehydes, ketones, esters, and acid chlorides. Reactions using either aldehydes or ketones are carried out by adding the desired carbonyl component (1 equivalent, neat) to the anion II (1 equivalent, 1 molar in THF) at 0°, and then stirring the resulting mixture at this temperature for 5 hours. Esters and acid chlorides require 2 equivalents of the anion II per equivalent of the acid derivative used. Temperatures of -10° and reactions times of 5 to 8 hours are employed for esters, whereas acid chlorides react at -78° in a period of 5 hours or less.⁴ A summary of some typical addition reactions of II are given below.⁵



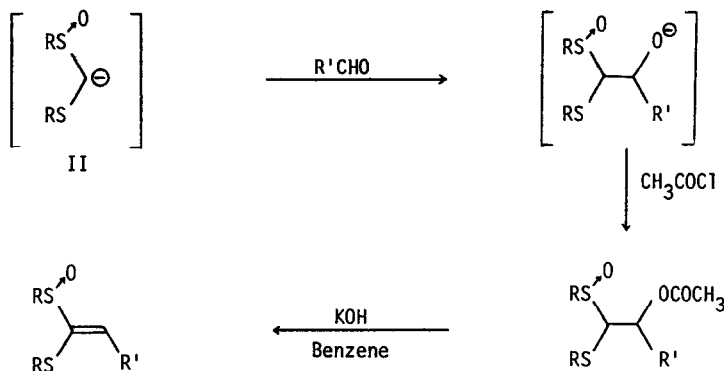
Substituted analogues of II such as the anion III also undergo high yield addition to aldehydes and acid chlorides but react only sluggishly with esters and ketones.⁶



All of the addition products obtained from both II and III undergo smooth hydrolytic conversion into their corresponding carbonyl analogues using the procedures previously reported.⁷



The addition products arising from the reaction of anion II with aldehydes have been converted into ketene thioacetal monoxide derivatives by the sequence outlined below.⁸ These stable electron deficient olefins exhibit extremely interesting properties as Michael receptors and their chemistry with respect to the conjugate addition reaction is outlined in the following communications.



In summary, it is clear that a variety of α -functionalized aldehydes and ketones as well as ketene thioacetal monoxide systems can be readily prepared by acylation of the carbonyl anion equivalents II and III. These reactions should be of considerable use in organic synthesis since they are convenient to carry out on both a small and large scale, and furthermore, they are compatible with nearly ideal stoichiometry.

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REFERENCES

1. J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, *Tetrahedron Letts.*, in press.
2. J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, in press.
3. J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, in press.
4. All reactions described herein were worked-up by quenching with saturated ammonium chloride at 0° or below.
5. The yields given are for isolated products and are based on the amount of carbonyl component used. All compounds exhibited satisfactory spectral and physical properties. These acylation results compare favorably with those reported for 1,3-dithiane systems and in some instances are superior with respect to yield. For examples of comparable 1,3-dithiane reactions, see E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971), and references cited therein.
6. The reactions of III are best carried out in a manner identical to that described for anion II.
7. For a detailed description of this hydrolysis procedure, see reference 1.
8. A similar preparation of this type of olefin, applicable only with aryl aldehydes, has been reported by K. Ogura and G. Tsuchihashi, *Tetrahedron Letts.*, 1383 (1972).