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A METHOD OF PREPARATION OF ALKALINE ACETYLIDES AND THEIR UTILIZATION IN ALKYNYLATION REACTIONS

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The discovery of the sodium salt of dimethylsulfoxide (1), so called "dimsylsodium", and analytical checking of its quantitative metallation reaction with compounds containing active hydrogen (2) showed to the authors of the present communication the possibility to obtain, in preparative amounts, alkaline acetylides in situ in dimethylsulfoxide which had been ascertained as a suitable medium for some alkynylation reactions (3) and shown to possess a number of advantages over the present methods (4).

Alkaline acetylides were prepared by introducing 1-alkyne into the solution of an equimolecular amount of "dimsylsodium" or the still unknown "dimsyllithium" in dimethylsulfoxide or its mixture with tetrahydrofuran. Respective acetylides were thus obtained practically in quantitative yields; at usual initial concentrations of alkaline salt of dimethylsulfoxide they were soluble in the reaction system only in part. By introducing excess of 1-alkyne into the system the resulting acetylides may be converted to blue-black stained, completely soluble complexes which react with alkynylated compounds in the same way as free acetylides. At present the nature of these complexes is being stu in detail.

For the preparation of alkynyl derivatives, free acetylides in a partl heterogenous form as well as their soluble complexes were used. In most cases sodium acetylides showed to be preferable, only in the case of readily enolizable ketones lithium acetylides gave better results.

The solution of "dimsylsodium" was prepared from sodium hydride and dimethylsulfoxide as described by (4), the solution of "dimsyllithium" was prepared analogously by heating lithium hydride with excess of dimethylsulfoxide under inert atmosphere (argon) to 70 - 75° C up to the end of hydrogen development, in both cases usually at concentration of the alkaline component amounting to 2.0 - 2.5 mole/l. To the solution cooled to normal temperature, a small amount of triphenylmethane was added and respective 1-alkyne introduced until the red colouration of triphenylmethyl anions disappeared. If a soluble complex was used, corresponding excess of alkyne was introduced. To the alkynylation mixture thus obtained, the respective alkynylated compound was added under inert atmosphere during one or more hours, usually at room temperature. The reaction products were isolated by distillation under normal or reduced pressure. In the case of alkynylation of carbonyl compounds the resulting alcoholate was decomposed by means of ammonium chloride and liberated alcohol was removed by distillation or extraction with petroleum ether after diluting the reaction mixture with water. In the Table I a few examples of synthesis according to this technique are given.

The same technique was used for alkynylation of number of alkylhalogenides, aldehydes and ketones. With an adequate intensity of stirring of the system no essential differences were found in the yield of product between the use of free acetylides and their complexes.

It is of interest that in the preparation of butyne-2 good yields were obtained with the use of methyl iodide which forms with dimethylsulfoxide readily a quarternary compound (5). Since analogous results were obtained with the use of pre-made solution of methyl iodide in dimethylsulfoxide, it may be assumed that this quarternary compound is capable of methylation reactions.

The results permit to conclude that the described method offers certain advantages over present techniques, particulary in that it is not labour-consuming and gives in most cases comparatively high yields of products, especially in synthesis of relatively volatile products where the classical use of liquid ammonia leads to losses and difficulties during isolation .

TABLE 1

Synthesis of Alkynyl Derivatives

Initial Compound	Acetylide	Product	Yield, %
$(CH_3)_2SO_4$	HC≡CNa	$CH_3C{\equiv}CH$	90.5 [a]
CH_3I	$CH_3C{\equiv}CNa$	$CH_3C{\equiv}CCH_3$	82.4 [a]
CH_3CHO	HC≡CNa	$CH_3CH(OH)C{\equiv}CH$	78.1 [a]
$C_6H_5COCH_3$	HC≡CLi	$C_6H_5C(OH)(CH_3)C{\equiv}CH$	83.1 [b]

[a] yield based on acetylide

[b] excess of acetylide, yield based on acetophenone

REFERENCES

1. E.J. Corey and M. Chaykovsky, J. Am. Chem. Soc. 84, 866 (1962).
2. G.G. Price and M.C. Whiting, Chem. Ind. (London) 1963, 775.
3. J.H. Blumenthal, U.S. Pat. 3 028 423 (1962); Chem. Abstr. 57, 8442 (1962).
4. W. Ziegenbein, Einführung der Äthinyl- und Alkinyl-Gruppe in organische Verbindungen, Verlag Chemie, Weinheim (1963).
5. R. Kuhn, Angew. Chem. 69, 570 (1957).