

PREPARATION OF SYMMETRIC 1,4-DISUBSTITUTED BUT-2-IN-1,4-DIOLS

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The ethynylation procedure of ZANYINA, SERGINA and KOTLJAREVSKIJ was successfully applied in the cases of diethyl ketone, benzophenone, cyclopentanone and cyclohexanone to yield the corresponding 1,4-disubstituted but-2-in-1,4-diols. It is supposed that the method may be generalized to and easily carried out with compounds of relative structure.

The simplest method for the preparation of symmetric 1,4-disubstituted but-2-in-1,4-diols involves the ethynylation of the corresponding oxo compound. There are several versions concerning the accomplishment of the reaction, but the process essentially consists of the addition of acetylene upon the oxo compound.

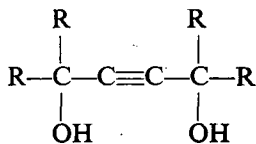
The ethynylation may be carried out easily with calcium carbide in the presence of potassium hydroxide [1—5].

JOSZICS [6] applied acetylene-bis-magnesium bromide, which has been successfully used in the preparation of several products [7—12], however, preparation and high sensitivity of the 'Jozsics complex' render the procedure troublesome.

VIEHE and FRANCHIMONT [13—14] reacted 1,2-dichloroethylene with methyl or butyl lithium to give lithium chloroacetylide, a powerful ethynylating agent, and they used it with success for the preparation of a number of ethynyl compounds.

In most cases, however, the desired product is made in various anhydrous solvents in the presence of basic catalysts [15—20]; with direct application of acetylene gas either under elevated [21—23] or at atmospheric [24—28] pressure, respectively.

ZANYINA, SERGINA and KOTLJAREVSKIJ [26] synthesized 1,1,4,4-tetramethylbut-2-in-1,4-diol (Ia) with atmospheric acetylene in anhydrous dichloromethane in the presence of powdered potassium hydroxide. The procedure appears to be very simple and we found it reasonable to study the process. We were also successful in the preparation of a number of such derivatives (cf. Table I).



I

Table I

Ia: R = CH₃

Ib: R = C₂H₅

Ic: R = C₆H₅

Id: $\begin{array}{l} \text{R} \\ \diagdown \\ \text{C} = \text{C} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \\ \diagdown \text{CH}_2-\text{CH}_2 \end{array} \end{array}$

Ie: $\begin{array}{l} \text{R} \\ \diagdown \\ \text{C} = \text{C} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \\ \diagdown \text{CH}_2-\text{CH}_2 \end{array} \end{array} \text{CH}_2$

The melting points and yields of the compounds prepared are given in Table II.

Table II

Mark	Starting ketone	Yield %	Product	M. p., °C
Ia	Acetone	59,0	1,1,4,4-tetramethylbut-2-in-1,4-diol	96
Ib	Diethyl ketone	52,7	1,1,4,4-tetraethylbut-2-in-1,4-diol	76—77
Ic	Benzophenone	50,0	1,1,4,4-tetraphenylbut-2-in-1,4-diol	194
Id	Cyclopentanone	41,0	1,2-bis-(1-hydroxycyclopentyl)-acetylene	108
Ie	Cyclohexanone	43,0	1,2-bis-(1-hydroxycyclohexyl)-acetylene	109

From these results the conclusion may be drawn that the method of ZANYINA, SERGINA and KOTLJRAEVSKIJ [26] is applicable not only in the case of 1,1,4,4-tetramethylbut-2-in-1,4-diol (Ia), but also in that of the compounds enlisted in Table I and furthermore the authors suppose that it may even be generalized for a number of relative derivatives.

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Experimental

All the compounds enlisted in Table I were prepared in the same way, and therefore a general description of the procedure is sufficient.

250 ml. dichloromethane and 100 g. powdered, dry potassium hydroxide were placed in a flask, provided with a mechanical stirrer, a reflux condenser, a dropping funnel, a gas inlet tube and a thermometer; the apparatus was protected from moisture by a CaCl₂ tube at the top of the reflux condenser, filled with anhydrous CaCl₂. The mixture was slowly saturated with acetylene gas with stirring at room temperature and then 0.5 mole ketone was added dropwise within 1 minute. (The solid benzophenone was added as a solution in an equal volume of dichloromethane). Subsequently 0.25 mole acetylene gas was introduced at 40° over a period of 1 hour. The mixture was kept at room temperature overnight and 200 ml. water was added with cooling and stirring. The organic phase was separated, dried and concentrated in vacuo, and the residue crystallized, to give the corresponding symmetric 1,4-disubstituted but-2-in-1,4-diol.

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ПРОИЗВОДСТВО СИММЕТРИЧНЫХ 1,4-ЗАМЕЩЕННЫХ-БУТ-2-ИН-1,4-ДИОЛОВ

П. Агоч и К. Коцка

Успешно применился метод этилирования А. С. Занины, С. И. Шергины и И. Л. Котляревского (26) в случае диэтилкетона, бензофенона, цикло-пентанона, цикло-гексанона и получены 1,4-замещенные-бут-2-ин-1,4-диола (I). Предполагается, что метод применим и легко осуществляется и в случае соединений родственного строения.