Enige reacties van aethoxyaethynylverbindingen
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1956

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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This thesis contains a study of some aspects of the reactivity of dimethyl-ethoxyethynylcarbinol, \((\text{CH}_3)_2\text{C-C=O-OC}_2\text{H}_5\), and of the preparation and reactivity of carbinols with the general formula \(\text{R-C-C=O-OC}_2\text{H}_5\), derived from aldehydes. These investigations are part of a program on the study of acetylenic ether chemistry, carried out in the laboratory of organic chemistry in Groningen.

The first chapter deals with reactions of dimethyl-ethoxyethynylcarbinol with amines. Three different reaction-types have been observed. One reaction (A, see page 9) yields ethyl-\(\beta,\beta\)-dimethylacrylate. A second reaction (B, see page 9) consists of the dissociation of the carbinol into acetone and ethoxyacetylene (which compound reacts further with the amine used), whereas a third reaction (C, see page 10) leads to the formation of amides of \(\beta\)-methyl-\(\beta\)-hydroxy-butyric acid with evolution of ethylene.

It was found, that the course of the reaction could be influenced by the amine used. With a very weak base as meta or para nitroaniline, reaction A was strongly favoured. A stronger base as diethylamine on the other hand promoted the dissociation of the carbinol (reaction B). With aromatic amines as aniline, p-toluidine, p-anisidine, the \(\beta\)-hydroxy-amide formation with evolution of ethylene was the main reaction (reaction C).

In the second chapter of this thesis we first describe the reaction of ethoxyethynylmagnesiumbromide with aldehydes. Instead of the expected carbinol \(\text{H}\) \(\text{R-C-C=O-OC}_2\text{H}_5\), we obtained from benzaldehyde ethyl-

\(\alpha\)-benzyldiene-\(\beta\)-hydroxy-\(\beta\)-phenyl-propionate (I) (pages 23 – 28). From other aromatic and aliphatic aldehydes analogous substances were formed (pages 28 – 33) (IX, XII, XV). The structures of these substances were proved and a scheme for their formation proposed (see pages 26, 27).
Several transformations of the substances were performed (see reaction schemes on pages 26, 31, 32 - 33). The synthesis of the normal carbinols $\mathbf{R-C-C\equiv C-OC_2H_5}$

viz. 1-ethoxy-3-phenyl-1-propyne-3-ol and 1-ethoxy-1-butyne-3-ol could be effected from the corresponding aldehydes and ethoxyethynyllithium.

The reactions of these carbinols were analogous to those described for 1-ethoxy-3-methyl-1-butyne-3-ol (see reaction schemes on page 36).

The proposed scheme (see pages 26, 27) for the formation of the above mentioned abnormal products (I, IX, XII, XV) was proved by the synthesis of ethyl-$\alpha$-benzylidene-$\beta$-phenyl-$\beta$-hydroxy-propionate from 1-ethoxy-3-phenyl-1-propyne-3-ol and benzaldehyde.