Bereidingswijzen en reacties van aethylthioaethyn

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SUMMARY

In the first chapter of this thesis a short review of data pertaining to the influence of the ethylthio group on the ground states of organic molecules and on the transition states of reacting molecules is given.

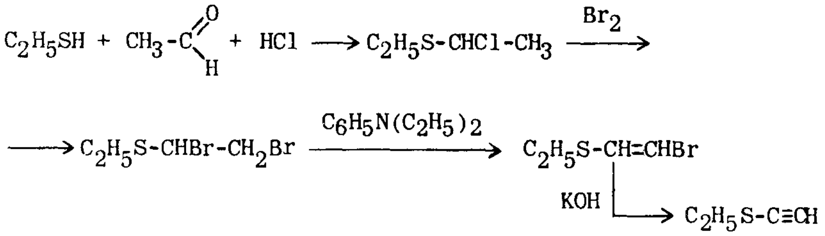
The following conclusions were proposed:

1. The S-alkyl group excerts a weak electron attracting influence on the ground state of non reacting saturated systems (-I effect).
2. The influence on a non reacting conjugated system depends on the nature of the other groups present. If conjugated with electron acceptors, the SR group acts as a donor; if conjugated with donors, it acts as an acceptor, by expanding its octet.
3. The influence on reacting molecules is of the same nature. If the reagent is electrophilic, the SR group donates electrons, if it is nucleophilic, the SR group accepts electrons.

The conclusions have been verified by the experiments described in this thesis.

In the second chapter some preparations of ethylthioethyne ($C_2H_5S\text{-}C{\equiv}CH$) and of the carbinols derived from it ($C_2H_5S\text{-}C{\equiv}C\text{-}C(OH)R_1R_2$) are described.

Ethylthioethyne was prepared according to the following reaction scheme.



$$C_2H_5SH + CH_3\text{-}\overset{O}{\underset{H}{C}} + HCl \longrightarrow C_2H_5S\text{-}CHCl\text{-}CH_3 \xrightarrow{Br_2} C_2H_5S\text{-}CHBr\text{-}CH_2Br \xrightarrow{C_6H_5N(C_2H_5)_2} C_2H_5S\text{-}CH{=}CHBr \xrightarrow{KOH} C_2H_5S\text{-}C{\equiv}CH$$

A second method for preparing ethylthioethyne consisted of a reaction between butyllithium and 1,2-bis-ethylthioethene.

$$C_2H_5S\text{-}CH{=}CH\text{-}SC_2H_5 + 2\ LiC_4H_9 \longrightarrow C_2H_5SLi + C_2H_5S\text{-}C{\equiv}CLi + 2\ C_4H_{10}$$

During this reaction butane was evolved and a white precipitate of lithium ethanethiolate was formed, which was filtered off. After hydrolysis of the filtrate, ethylthioethyne could be obtained in 47% yield.

From 1-ethoxy-2-ethylthioethene in the same way an ethereal solution of lithium ethylthioethyne was obtained.

When carbonyl compounds (aldehydes or ketones) were added to the filtrate, the carbinols ($C_2H_5S\text{-}C\equiv C\text{-}C(OH)R_1R_2$) were formed. The synthesis of these carbinols could also be effected from ethylthioethynyl-magnesium bromide.

Three different reaction types of ethylthioethyne and some carbinols derived from it were investigated:

a. reactions with electrophilic reagents (chapter III);
b. free radical addition reactions (chapter IV);
c. reactions with nucleophilic reagents (chapter V).

a) Reactions with electrophilic reagents.

In contrast to what is found with ethoxyethyne, the acid catalysed hydration of ethylthioethyne was a very slow reaction, which gave acetic acid.

However the reaction of 1-ethylthio-3-methyl-but-1-yne-3-ol $(CH_3)_2C(OH)\text{-}C\equiv C\text{-}SC_2H_5$ under the same conditions was rapid and yielded $(CH_3)_2C{=}CH\text{-}COSC_2H_5$(ethyl-β- methyl thiolcrotonate). This reaction was therefore not considered an electrophilic hydration, followed by a dehydration but a 'Meyer Schuster' rearrangement.

b) Free radical additions.

The additions of thiols, thioacids and ethaneselenol to ethylthioethyne in ethereal solution, took place initially with heat production. Mono adducts ($RS(c.q.Se)CH{=}CH\text{-}SC_2H_5$) were obtained in rather high yields.

The structures of the mono adducts appeared from the fact that acid hydrolysis yielded substituted acetaldehydes with the general formula $RS(Se)CH_2\text{-}CH{=}O$, which were isolated as their 2,4-dinitrophenylhydrazones.

The configuration of one addition product viz. of 1,2-bis ethylthioethene was found to be cis on the basis of the electric dipole moment.

The additions of thiols and thioacids to the carbinol, derived from acetone and ethylthioethyne, were performed in dioxane and catalysed by peroxides. The addition products ($(CH_3)_2C(OH)\text{-}C(SR){=}CHSC_2H_5$ so obtained, were identified by acid hydrolysis, which yielded aldehydes $(CH_3)_2C{=}C(SR)\text{-}CH{=}O$ isolated as their 2,4-dinitrophenylhydrazones.

c) Reactions with nucleophilic reagents.

On comparing the reactions of nucleophilic reagents with ethoxyethyne and ethylthioethyne a great difference was observed.

For example, the addition of ethanol to ethoxyethyne in alkaline solution yielded ethyl orthoacetate, whereas under the same conditions ethylthioethyne yielded 1-aethoxy-2-ethylthioethene. A similar addition to the β-carbon atom of ethylthioethyne was observed with diethylamine, piperidine ethanethiol and hydrocyanic acid.

$$C_2H_5OH \quad + \quad HC{\equiv}C\text{-}OC_2H_5 \xrightarrow{C_2H_5O^{\ominus}} CH_3\text{-}C(OC_2H_5)_3$$

$$C_2H_5OH \quad + \quad HC{\equiv}C\text{-}SC_2H_5 \xrightarrow{C_2H_5O^{\ominus}} C_2H_5O\text{-}CH{=}CH\text{-}SC_2H_5$$

$$C_2H_5S^{\ominus} \quad + \quad HC{\equiv}C\text{-}SC_2H_5 \xrightarrow{C_2H_5OH} C_2H_5S\text{-}CH{=}CH\text{-}SC_2H_5$$

$$(C_2H_5)_2NH + HC{\equiv}C\text{-}SC_2H_5 \xrightarrow{\qquad} (C_2H_5)_2N\text{-}CH{=}CH\text{-}SC_2H_5$$

The structures of the mono adducts appeared from the fact that acid hydrolysis in the presence of 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazones of ethylthioacetaldehyde.

The addition of nucleophilic reagents to 1-ethylthio-3-methylbut-1-yne-3-ol or to the corresponding acetate did not succeed. Instead of giving the expected conversion, the molecule dissociated into acetone and ethylthioethyne, which reacted further with the nucleophilic reagent present.