# SYNTHESIS OF ENYNE SULFIDES FROM DIACETYLENES AND THIOLS IN AMMONIA SOLUTION

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Nucleophilic addition of thiols to diacetylene (DA) in the presence of alkalis is readily effected in a variety of solvents [1]. In many cases, however, the reaction is complicated by subsequent addition of the thiol to the unsaturated sulfide, which substantially reduces the yield of the latter. The generation of the thiolate ion from S-alkylisothiourea salts or thiolacetates directly in the reaction mixture in the presence of alkali enables the use of free thiols to be avoided, and therefore also competition by the free-radical reaction, resulting in yields of the enyne sulfides of 60-80% [2]. The use of liquid ammonia (LA) or aqueous ammonia as solvent for the nucleophilic thiylation of diynes opens up new possibilities for the preparation of unsaturated sulfides [3], and the use of DA, which is available as a 6-10% solution in ammonia from a number of domestic chemical plants, is also practicable.

The present communication describes in detail a study of the reaction of DA with thiols both in LA and in aqueous ammonia of 25-70% concentration over the range —33 to +20°. In developing this method of thiylation of diynes, due regard was had to the high solvent capacity of ammonia for many types of organic compounds, owing to its moderate dielectric constant ($\varepsilon = 22$ at —33°) and polarity ($\mu = 1.49$ D at 20.5°), its relatively high basicity ($pK_b$ 4.75), and its capacity to form hydrogen bonds [4, 5]. The basic properties of ammonia enhance not only the solubility of compounds which are proton donors, but also the formation of ammonium salts, for example with thiols ($pK_a$ 11-12), which apparently exist in ammonia solution both as contact ion-pairs and as the free ions. The thiolate ion thereby acquires increased reactivity, since it is weakly solvated by ammonia molecules.

In practice, the addition of thiols to DA in LA proceeds under extremely mild conditions (—33°, 2-3 h, allowing for complete evaporation of the ammonia), and is complete immediately following the addition of the addend. The molar ratio of DA to thiol is not critical, since under all conditions (1:0.5; 1:1; 1:1.2; 1:2) the enyne sulfides (I)-(IX) only were isolated, in yields of 84-98%, i.e., the secondary reaction resulting in the formation of 1,4-dialkylthio-1,3-butadienes is completely avoided (cf. Tables 1 and 2).

TABLE 1. Conditions of Synthesis of Sulfides (I) and (II)

| Compound | Amount in moles | | Solvent, ml | T., °C | Time, h | Conversion of diacetylene | Yield |
|---|---|---|---|---|---|---|---|
| | diacetylene | thiol | | | | % | |
| (I) | 0,146 | 0,272 | LA (100) | −33 | 2,5 | 100 | 89 |
| (II) | 0,104 | 0,124 | LA (75) | −33 | 3,0 | 100 | 87 |
| (II) | 0,060 | 0,042 | LA (55) | −33 | 2,0 | — | 82* |
| (I) | 0,100 | 0,120 | 70% $NH_3$ (75) | −15 | 1,5 | 100 | 83 |
| (II) | 0,058 | 0,070 | 50% $NH_3$ (90) | 5 | 1,0 | 86 | 71 |
| (II) | 0,048 | 0,058 | 25% $NH_3$ (50) | 20 | 2,4 | 80 | 72 |
| (I) | 0,072 | 0,085 | Pyridine (30) | 20 | 1,5 | 98 | Trace |
| (I) | 0,040 | 0,048 | » (15) | 50 | 3,0 | 100 | 4 |
| (II) | 0,043 | 0,050 | Triethylamine (15) | 30 | 1,0 | 86 | 56 |
| (I) | 0,080 | 0,096 | » (15) | 60 | 2,0 | 100 | 68 |
| (I) | 0,084 | 0,098 | DMSO (15) | 60 | 3,0 | 100 | Trace |
| (I) | 0,080 | 0,096 | DMF (15) | 60 | 3,0 | 100 | » |
| (I) | 0,067 | 0,132 | 20% NaOH (85) | 20 | 2,5 | 19 | 10 |
| (II) | 0,031 | 0,040 | The same | 60 | 1,0 | 84 | 52 |

*Calculated on thiol taken.

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TABLE 2. Properties of the Sulfides Prepared

| Compound | Yield, % | bp, °C (p, mm Hg) | $n^{20}_D$ | Found/Calculated, % |  |  | Molecular formula | Ratio of cis : trans isomers |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H | S |  |  |
| 1-Ethylthio-1-buten-3-yne (I) | 89 | 67–68 (17) | 1,5420 | 64,05/64,27 | 6,91/7,19 | 28,78/28,54 | $C_6H_8S$ | 5 : 1 |
| 1-Butylthio-1-buten-3-yne (II) | 87 | 73–75 (6) | 1,5250 | 68,30/68,54 | 8,61/8,63 | 23,07/22,83 | $C_8H_{12}S$ | 10 : 1 |
| 1-Hexylthio-1-buten-3-yne (III) | 85 | 92–93 (2,5) | 1,5135 | 71,42/71,39 | 9,50/9,59 | 19,04/19,02 | $C_{10}H_{16}S$ | 5 : 1 |
| 1-(2-Hydroxyethylthio)-1-buten-3-yne (IV) | 95 | 84 (1) | 1,5795 | 56,20/56,22 | 6,21/6,29 | 24,85/25,01 | $C_6H_8OS$ | 4 : 1 |
| 1-(2,3-Dihydroxypropylthio)-1-buten-3-yne (V) | 98 | – | 1,5818 | 53,03/53,02 | 6,42/6,32 | 20,25/20,20 | $C_7H_{10}O_2S$ | 2 : 1 |
| 1-Trimethoxysilylmethylthio-1-buten-3-yne (VI) | 94 | 77–80 (1) | 1,5053 | 43,69/44,00 | 6,32/6,42 | 14,79/14,68 | $C_8H_{14}O_3SSi$ | 2 : 1 |
| 1-Trimethoxysilylethylthio-1-buten-3-yne (VII) | 92 | 110–112 (3) | 1,5040 | 46,29/46,54 | 6,89/6,94 | 13,76/13,78 | $C_9H_{16}O_3SSi$ | 5 : 1 |
| 1-Trimethylsilylmethylthio-1-buten-3-yne (VIII) | 96 | 63–64 (3) | 1,5208 | 56,45/56,25 | 8,29/8,31 | 18,80/18,73 | $C_8H_{14}SSi$ | 2 : 1 |
| 1-Triethylsilylmethylthio-1-buten-3-yne (IX) | 91 | 112 (5) | 1,5143 | 62,12/62,19 | 9,46/9,49 | 15,12/15,09 | $C_{11}H_{20}SSi$ | 2 : 1 |

$$HC{\equiv}CC{\equiv}CH \xrightarrow[NH_3]{HSR} HC{\equiv}CCH{=}CHSR \overset{HSR}{\underset{NH_3}{-\!\!\times\!\!\rightarrow}} RSCH{=}CHCH{=}CHSR$$

$$\text{(I)—(IX)}$$

$R = C_2H_5$ (I), $C_4H_9$ (II), $C_6H_{13}$ (III), $CH_2CH_2OH$ (IV), $CH_2CH(OH)CH_2OH$ (V), $CH_2Si(OCH_3)_3$ (VI), $CH_2CH_2Si(OCH_3)_3$ (VII), $CH_2Si(CH_3)_3$ (VIII), $CH_2Si(C_2H_5)_3$ (IX).

Ammonia apparently activates not only the thiolate ion, but also DA, by the formation of hydrogen bonds, which is no less important in the activation of the triple bond than polarization by various substituents.

It is also known [6, 7] that solvents which are capable of forming complexes involving the hydrogen of DA lead to infringement of the trans-nucleophilic addition rule. In protonic solvents such as methanol, the anion formed is synchronously stabilized, resulting in the sole formation of the cis-adducts. Hence, the lack of stereospecificity in the addition of thiols to DA in LA which we have observed is not unexpected. Adducts (I)-(IX) are mixtures of the cis and trans isomers, as shown by their PMR spectra, which contain signals for the protons of the cis- and trans-ethylenic groups having typical SSCC values of 10 and 15 Hz, respectively [8]. As Table 2 shows, the proportion of the trans isomer increases with the bulk of the radical R, reaching a maximum (∿30%) when the branching in the immediate vicinity of the sulfur atom is greatest [compounds (V), (VI), (VIII), and (IX)]. This shows the substantial contribution of steric interactions to the stereochemical outcome of the reaction, since the percentage amount of the trans isomer remains constant both before and after thermal treatment of these compounds. The reaction apparently proceeds via the intermediate carbanion, followed by external protonation which enables both the cis and trans isomers to be formed.

The sensitivity of DA to the presence of thiols in LA is such that the reaction may be used for the qualitative detection of DA, or for its quantitative isolation as the 1-alkylthio-1-buten-3-yne. This method for the thiylation of DA may be used successfully for the preparation of silicon-containing thioethers (cf. Table 2) in particular 1-(trialkoxysilylalkylthio)-1-buten-3-ynes, which cannot be obtained by the method described in [9], since the starting trialkoxysilylalkyl thiols are unstable in the presence of alkali. The mild conditions of our reaction enable thiols to be used which contain other functional groups. For example, with 2-mercaptoethanol and 1,2-dihydroxy-3-mercaptopropane the reaction proceeds exclusively with the participation of the thiol group, the corresponding sulfides being obtained in yields of ∿100% (cf. Table 2).

Thiylation of DA may be effected to a substantial extent in aqueous ammonia solution, and the yield of the adducts remains fairly high, although the conversion of DA drops to 80% (cf. Table 1). When 20% aqueous NaOH is used, the other conditions remaining the same, the yield of the thioethers is only 10%, whereas at 60° it is 52%. Reaction of DA with thiols in solution in other nitrogenous bases such as pyridine ($pK_b$ 9.38) proceeds very slowly, since pyridine is incapable of forming an active thiolate ion. In the more strongly basic triethylamine ($pK_b$ 3.12), reaction occurs at elevated temperatures, but the yield of the thioethers does not exceed 68% (Table 1).

Thus, the most successful method for the synthesis of 1-alkylthio-1-buten-3-ynes is the thiylation of DA in LA.

## EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) for 20% solutions in $CCl_4$, relative to HMDS.

Method for the Thiylation of Diacetylene (DA). To a solution of 0.11 mole of the thiol in 40-80 ml of LA was added a solution of 0.1 mole of DA in 40 ml of LA. The mixture was stirred until all the $NH_3$ had evaporated (∿1-2 h), the ammonia being collected in a cold trap. Sulfides (I)-(IX) were obtained from the residues (cf. Table 2).

In the experiments carried out at 5-60° (cf. Table 1), DA was passed through the thiol in a stream of nitrogen. The product was isolated by distillation.

Sulfides (I) and (II) were extracted from aqueous solutions of ammonia and NaOH by extraction with ether, drying over $MgSO_4$, and distillation.

## CONCLUSIONS

A new general method has been developed for the thiylation of diacetylene in liquid ammonia for the preparation of enyne sulfides containing various substituents and functional groups.

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# ROLE OF COMPONENTS OF THE REACTION MEDIUM IN REACTIONS OF ELECTROCHEMICALLY GENERATED RADICAL ANIONS.

## 2. ELECTROCHEMICAL HYDRODIMERIZATION OF α-THIOPHENE ALDEHYDE IN ORGANIC SOLVENTS*

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The most advantageous of the existing methods for preparing aromatic pinacols comprises electrochemical hydrodimerization of the corresponding aldehydes or ketones [2, 3]. The yield of pinacols obtained by electrolysis of aromatic carbonyl compounds in aqueous organic solvents depends considerably on the nature of the inert electrolyte, e.g., varying from 40 to 70% in the case of the reduction of acetophenone [3]. At the same time, the yield of pinacols can be increased sharply, e.g., to 95% in the case of 2,3-diphenyl-2,3-butanediol [4], by electrochemically reducing such compounds in nonaqueous media. The best results for the electrochemical synthesis of aromatic pinacols are obtained by using nonaqueous polar solvents (DMF or MeCN) and ammonium salts as supporting electrolytes [5]. This conclusion, however, is not in accord with the results obtained by electrolyzing acetophenone in dry acetonitrile [6].

It is known [7, 8] that the synthesis of pinacols by electrochemical reduction of thiophene carbonyl derivatives is hampered by the formation of considerable amounts of resinous products. Only comparatively recently has a yield of 56% been achieved for pinacol synthesis from α-acetylthiophene in 70% aqueous DMF containg AcOK as supporting electrolyte [9]. The reductive dimerization of α-benzoylthiophene in MeCN containing 0.1 mole of tetraethylammonium perchlorate and added organic acids gives a pinacol yield of 68% [10].

In the present work we have investigated the influence of the composition of the reaction medium on the previously unstudied electrochemical hydrodimerization of α-thiophene aldehyde (I) to 1,2-di(α-thienyl)-1,2-ethanediol (II). The latter has previously been prepared by enzymatic reduction of α,α'-thienoin [11].

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*See [1] for communication 1 of this series.

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