# GENERAL METHOD FOR THE SYNTHESIS OF 1,3- AND 1,4-DITHIACYCLOALKANES BY THE HOMOLYTIC ADDITION OF DITHIOLS TO ALKYNES

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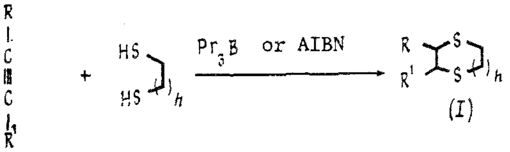
The homolytic addition of compounds containing a thiol function to alkenes and alkynes is an efficient method for the alkylation of the sulfur atom [1].

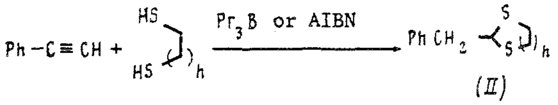
We have found that the reaction of 1,2- and 1,3-dithiols with alkynes under radical initiation conditions by the action of tripropylborane in the presence of $O_2$ [2] or azobis(isobutyronitrile) (AIBN) [1] gives heterocyclization with the formation of 1,3- and 1,4-dithiacycloalkanes. The structure of the heterocycle formed depends on the nature of the substituent in the alkyne.

Mono- or disubstituted alkynes, containing alkyl substituents at the C≡C bond, and 1,2-ethanedithiol or 1,3-propanedithiol react regioselectively in 40-70% yield to give 1,4-dithianes (I, n = 1) or 1,4-dithiepanes (I, n = 2).



R = Pr, Bu, $C(Me)_2OH$, $CH_2Cl$, $R^1$ = H, Pr, $n$ = 1, 2.

In the case of phenylacetylene, 1,1-addition occurs selectively with the formation of 2-benzyl-1,3-dithiolane (II, n = 1) or 2-benzyl-1,3-dithiane (II, n = 2) in ~40% yield instead of 1,2-addition.



The heterocyclization of ethyl propiolate with 1,2-ethanedithiol leads nonregioselectively to 2-(ethoxycarbonylmethyl)-1,3-dithiolane and 2-ethoxycarbonyl-1,4-dithiane in 2.5:1 ratio.

The only reported example of such a homolytic reaction is the formation of 2,3-bis(acetoxymethyl)-1,4-dithiane in 27% yield from 1,2-ethanedithiol and 1,4-diacetoxy-2-butyne initiated with peroxide upon irradiation [3].

A sample of 4 ml 1 M $Pr_3B$ (4 mmoles) in hexane was added to a solution of 0.34 g (4 mmoles) 2-methyl-3-butyn-2-ol, 0.37 ml (4.4 mmoles) 1,2-ethanedithiol, and 0.65 ml (16 mmoles) methanol in 40 ml benzene in an argon atmosphere at ~20°C was stirred for 24 h. The reaction mixture was treated with 25 ml 1 M $NH_4Cl$. The aqueous phase was extracted with three 15-ml portions of ethyl acetate. The extracts were combined with the organic layer, dried over magnesium sulfate, and evaporated. The residue was subjected to chromatography on a silica gel column using 2:1 hexane–ether as the eluent to give 0.40 g (56%) 2-(1-hydroxy-1-methylethyl)-1,4-dithiane as a colorless oil. PMR spectrum at 250 MHz (δ, ppm): 1.27 s and 1.30 s (6H), 1.95 br.s (1H), 2.63-3.15 m (7H).

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# NONTRADITIONAL APPROACH TO THE SYNTHESIS OF 3-SUBSTITUTED TETRAHYDROTHIOPHENES AND TETRAHYDROSELENOPHENES

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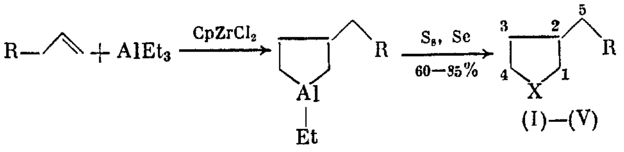
We are the first to report that the reaction of cyclooctasulfane ($S_8$) or selenium with β-alkyl-substituted alumocyclopentanes taken in 3:1 ratio in absolute benzene at 80°C over 6 h gives the corresponding 3-alkyltetrahydrothiophenes (I)-(IV) and 3-alkyltetrahydroselenophene (V) in 60-85% yield with 100% selectivity.

The alumocyclopentanes were obtained by the reactions of 1-hexene, 1-heptene, 1-decene, and 1-undecene in benzene with $AlEt_3$ in the presence of catalytic amounts of $Cp_2ZrCl_2$ (the olefin:Al:Zr ratio was 100:110:2) at 25°C over 8 h. Then, $S_8$ or Se was added to the solution of the alumocyclopentane thereby prepared. At the end of the reaction, the reaction mass was treated with 5% hydrochloric acid. The product was extracted with ether and distilled in vacuum.



X = S, R=$C_3H_7$ (I), $C_4H_9$ (II), $C_7H_{15}$ (III), $C_8H_{17}$ (IV); X = Se, R = $C_8H_{17}$ (V).

Products (I)-(V) were identified by spectral methods and by comparison with authentic samples.

3-Butyltetrahydrothiophene (I), bp 68-70°C (2 mm), $n_D^{22}$ 1.4861 (bp 210°C (760 mm), $n_D^{20}$ 1.4868 [1]). PMR spectrum (δ, ppm): 0.76-0.98 m (3H, $CH_3$), 1.21-1.54 m (6H, $CH_2$), 1.92-2.48 m (3H, CH, $CH_2$), 2.65-3.01 m (4H, $CH_2$—S). $^{13}C$ NMR spectrum (δ, ppm): 36.80 t ($C^1$), 44.77 d ($C^2$), 33.27 t ($C^3$), 30.80 t ($C^4$), 36.80 t ($C^5$), 30-97 t ($C^6$), 22.91 t ($C^7$), 14.07 q ($C^8$). $M^+$ 144.

3-Amyltetrahydrothiophene (II), bp 72-74°C (1 mm), $n_D^{22}$ 1.4835 [1]. $M^+$ 158.

3-Octyltetrahydrothiophene (III), bp 123-125°C (1 mm), $n_D^{22}$ 1.4802 [1]. $M^+$ 200.

3-Nonyltetrahydrothiophene (IV), bp 138-140°C (1 mm), $n_D^{22}$ 1.4798. PMR spectrum (δ, ppm): 0.81-1.02 m (3H, $CH_3$), 1.17-1.59 m (16H, $CH_2$), 1.87-2.51 m (3H, CH, $CH_2$), 2.59-2.96 m (4H, $CH_2$—S). $^{13}C$ NMR spectrum (δ, ppm): 36.76 t ($C^1$), 44.77 d ($C^2$), 33.57 t ($C^3$), 30.75 t ($C^4$), 36.76 t ($C^5$), 28.76 t ($C^6$), 29.86 t ($C^7$), 29.65 t ($C^8$), 29.65 t ($C^9$), 29.39 t ($C^{10}$), 31.94 t ($C^{11}$), 22.71 t ($C^{12}$), 14.13 q ($C^{13}$). $M^+$ 214.

3-Nonyltetrahydroselenophene (V), bp 120-122°C (1 mm). PMR spectrum (δ, ppm): 0.82-0.93 m (3H, $CH_3$), 1.14-1.66 m (16H, $CH_2$), 1.96-2.58 m (3H, CH, $CH_2$), 2.79-3.01 m (4H, $CH_2$—Se). $^{13}C$ NMR spectrum (δ, ppm): 29.93 t ($C^1$), 46.52 d ($C^2$), 33.79 t ($C^3$), 29.41 t ($C^4$), 38.79 t ($C^5$), 28.76 t ($C^6$), 29.67 t ($C^7$, $C^8$, $C^9$), 29.26 t ($C^{10}$), 31.97 t ($C^{11}$), 22.73 t ($C^{12}$), 14.15 q ($C^{13}$). $M^+$ 262.

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