Tetrahedron Letters No. 52, pp 5161 - 5162.
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0040-4039/78/1222-5161$02.00/0

# AN EFFICIENT SYNTHESIS OF 1,3-DITHIOL-2-THIONES FROM PROPARGYL HALIDES AND SODIUM *TERT*-BUTYLTRITHIOCARBONATE

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Recently, 1,3-dithiol-2-thiones have been used extensively as precursors for tetrathiafulvalenes, a class of compounds with interesting electrical properties.[1,2] We describe here a new high-yield synthesis of 1,3-dithiol-2-thiones (6) from acetylenic halides (2) and sodium *tert*-butyltrithiocarbonate (1). This new synthesis, besides being facile and essentially one-step, allows direct introduction into the dithiol ring of functional groups that were difficult if not impossible to introduce by older methods (e.g., vinyl, benzyl).[2]

The synthetic procedure is outlined in the scheme. Treatment of propargyl bromide (2a) with sodium *tert*-butyltrithiocarbonate (1) in acetone at 0°C instantaneously gives trithioester 3a in quantitative yield. After the sodium bromide is filtered and the acetone evaporated, trithioester 3a (bp 78-80°C/0.1 torr) is heated (100°C, 15 min) with one equivalent of trifluoroacetic acid (TFA) in acetic acid, giving 4-methyl-1,3-dithiol-2-thione (6a) (identified by comparison with an authentic sample[3]) in 96% yield. Isobutylene was evolved during the reaction (identified as its dibromide). The intermediates 4a and 5a can be observed by proceeding stepwise through the reaction sequence in the following manner. Treatment of trithioester 3a with excess TFA at ambient temperature gives 2-*tert*-butylthio-4-methylene-1,3-dithiolanium salt 4a, NMR(TFA,$\delta$) 5.65(multiplet, 1H), 5.43(multiplet, 1H), 4.52(triplet, 2H), 1.45 (singlet, 9H). Heating 4a at 100°C for a few minutes causes the exocyclic double bond to migrate internally yielding 2-*tert*-butyl-4-methyl-1,3-dithiolylium salt 5a, NMR(TFA, $\delta$) 7.75 (quartet, 1H, J = 1.2Hz), 2.42(doublet, 3H, J = 1.2 Hz), 1.43(singlet, 9H). Elimination of isobutylene is not observed until acetic acid is added, whereupon dithol 6a is produced in quantitative yield after heating (100°C) for a few minutes. 6a is isolated by dilution with water followed by extraction ($Et_2O$).

When acetylenic bromo alcohols 2c,d, or e are employed in the reaction sequence (see Scheme) a 1,4-dehydration occurs spontaneously resulting in the introduction of a vinyl substituent into 6 (7c-e). Following the reaction by NMR indicates that the dehydration step occurs after the formation of 4(R = $CH_2OH$).

Mechanistically, the acid-catalyzed ring closure of 3 to 4 is reminiscent of the well-known formation of a heterocyclic carbonium ion via neighboring-group participation by various functions.[4] A close analogy would be the regio specific neighboring-group participation by the dithiocarbamate function during protonation of α-substituted S-allyl N,N-dimethyldithiocarbamates as reported by Nakai and co-workers.[5] However, we found no evidence of six-membered ring formation (i.e. 8) as did Nakai for his allyl-dithiocarbamates. We also found the ring closure of 3 to 4 is stereospecific about the resulting double bond in 4. Ring closure of 3a in deuterated TFA gave only 9; NMR(TFA, δ) 5.43(triplet, 1H, J = 1.8 Hz), 4.51(doublet, 2H, J = 1.8 Hz), 1.45(singlet, 9H). The stereochemistry shown for 9 was determined by an NOE experiment on 4a from which the chemical shifts of the exocyclic methylene protons were assigned (see Scheme).

We are currently pursuing the unsymmetrical tetrathiafulvalenes derived from 6 and 7 as well as the chemistry of the ring closure of 3 with reagents other than acids.[7]

References and notes

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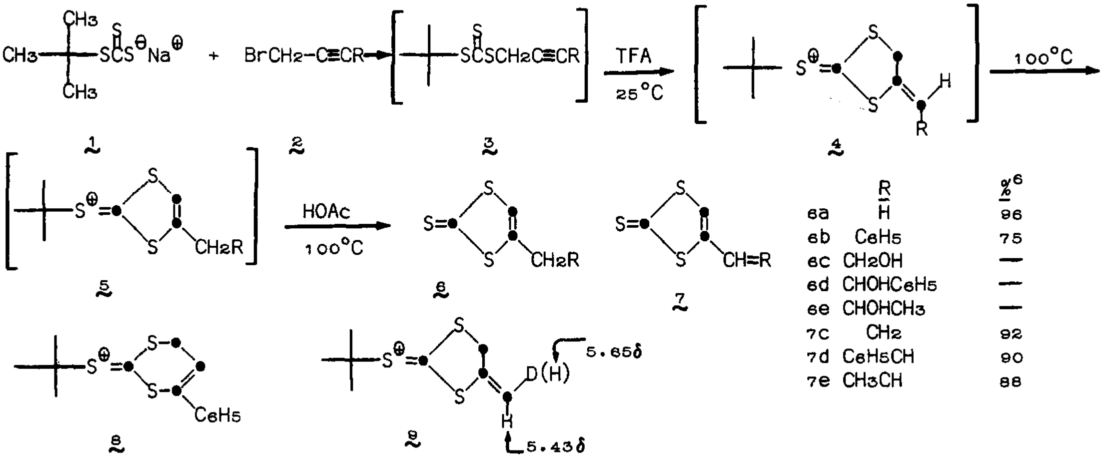
7. The author thanks M. W. Fichtner for technical assistance and M. J. Bogdanowicz and F. Chen for helpful theoretical discussions.



| | R | %[6] |
|---|---|---|
| 6a | H | 96 |
| 6b | C6H5 | 75 |
| 6c | CH2OH | — |
| 6d | CHOHC6H5 | — |
| 6e | CHOHCH3 | — |
| 7c | CH2 | 92 |
| 7d | C6H5CH | 90 |
| 7e | CH3CH | 88 |

Scheme

(Received in USA 23 October 1978)