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A NEW SYNTHETIC ROUTE TO 1,1-BIS(METHYLTHIO)-1,3-BUTADIENES VIA THE [2,3]SIGMATROPIC REARRANGEMENT OF DITHIOCARBENES[1]

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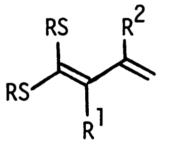
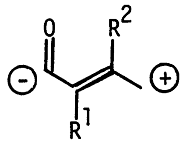
Thermolysis of the sodium salts of S-allyl-S'-methyldithiocarbonate tosylhydrazones (4) followed by methylation provided good yields of the corresponding 1,1-bis(methylthio)-1,3-butadiene (1) via the [2,3]sigmatropic rearrangement of the dithiocarbenes (5).

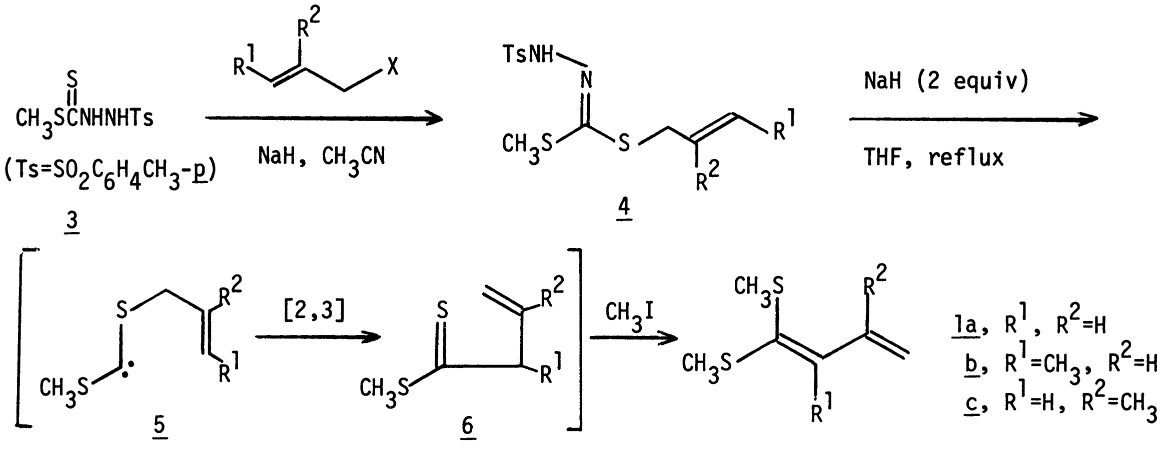
1,1-Bis(alkylthio)-1,3-butadienes (1) have been well secured as versatile reagents for the synthesis of α,β-unsaturated carbonyl compounds, since 1 can serve not only as the useful synthetic equivalent (2)[2] with "reactivity umpolung"[3] of the two carbon atoms but also as diene components in Diels-Alder reactions.[4]


(1)


(2)

Thioacetals 1 have previously been prepared via the Peterson olefination using lithiated trimethylsilylformaldehyde thioacetal and α,β-unsaturated carbonyl compounds.[5] A recent publication dealing with the preparation of 1 via the [2,3]sigmatropic process of acetylenic sulfonium ylides[6] prompts us to report a new, convenient preparation of 1 ($R=CH_3$) via the [2,3]sigmatropic rearrangement of dithiocarbenes in this communication. Scheme 1 illustrates the overall reaction course in which the [2,3]sigmatropic process[7] of dithiocarbenes 5 generated from tosylhydrazones 4 to the β,γ-unsaturated dithioesters (6) is involved as the key step. Notable advantages of the present procedure compared with previous ones are the easy accessibility of the starting materials

Scheme 1



or the reagents, the simplicity of the procedure, and the great flexibility owing to the availability of various allylic halides.

The starting tosylhydrazones (4)[8] were quantitatively obtained by reactions of the sodium salts of dithiocarbazate (3) with allylic halides according to the literature procedure.[9] The typical procedure for the preparation of 1 is as follows. To a suspension of S-allyl tosylhydrazone (4a, R^1, R^2=H) in tetrahydrofuran were added 2 equivalents of 50% oily sodium hydride. The brown reaction mixture was then heated at reflux for 6 hr, during which time the reaction was followed by the evolution of nitrogen. Upon cooling to room temperature, methyl iodide (1.5 equiv) was added to the resulting mixture and the mixture was allowed to stand overnight with stirring. Usual extractive work-up followed by distillation yielded 66% of 1,1-bis(methylthio)-1,3-butadiene (1a); bp 41-46°C/0.071 mmHg; NMR (CCl_4, TMS), δ 6.90 (ddd, J=18, 10, and 10 Hz, 1H), 6.33 (d, J=10 Hz, 1H), 5.17 (dd, J=18 and 2 Hz, 1H), 5.07 (dd, J=10 and 2 Hz, 1H), 2.27 (s, 6H); MS, m/e 146 (M^+).

Similar decompositions of 4b and 4c followed by methylation afforded the corresponding thioacetal (1); 1b: yield, 52%; bp 49-52°C/0.015mmHg; NMR (CCl_4, TMS), δ 7.33 (dd, J=18 and 11 Hz, 1H), 5.24 (dd, J=18 and 2 Hz, 1H), 5.11 (dd, J=11 and 2 Hz, 1H), 2.31 (s, 3H), 2.24 (s, 3H), 2.10 (s, 3H); MS, m/e 160 (M^+); 1c: yield, 44%; bp 51.5-55°C/0.016mmHg; NMR (CCl_4, TMS), δ 6.30 (s, 1H), 4.98 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H), 1.97 (s, 3H). These spectral data are consistent with those reported for the corresponding 2-alkenylidene-1,3-dithianes.[5a]

Thioacetals 1b and 1c are of particular interest, since they are potential isoprenoid synthons which allow a number of synthetic transformations to be carried out. Applications of these thioacetals in terpenoid synthesis are now under investigation.

References and Notes

1) Part I on "Applications of [2,3]Sigmatropic Rearrangement in Organic Synthesis." This work was supported in part by the Grant-in-Aid from the Ministry of Education which is acknowledged.

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8) 4a (R^1,R^2=H), mp 107-108°C (EtOH); 4b (R^1=CH_3, R^2=H), mp 69-71°C (MeOH-H_2O); 4c (R^1=H, R^2=CH_3), mp 86-87°C (MeOH). These tosylhydrazones possess the E geometry (by NMR assay).

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