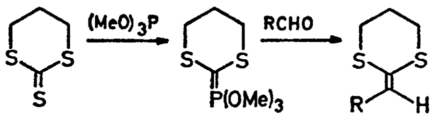
Wittig-type Reactions of 2-Lithio-2-trimethylsilyl-1,3-dithian: an Improved and Extended Synthesis of Alkylidenedithians for 1-Carbon Homologation

By Peter F. Jones and M. F. Lappert*
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

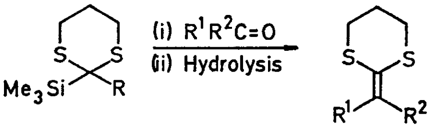
Summary 2-Lithio-2-trimethylsilyl-1,3-dithian reacts with carbonyl compounds R^1R^2CO to give alkylidenedithians, potentially valuable synthetic intermediates for formation of $R^1R^2CHCO_2H$, R^1R^2CHCHO, and $R^1R^2R^3CCHO$.

Corey has investigated the Wittig reactions of the dithian ylide (I).[1] However, the reaction is restricted to aldehydes, ketones being inert, even under more forcing conditions. In addition, trimethyl phosphite, used in excess for the preparation of (I), can in certain cases undergo a competing reaction with the added aldehyde; therefore purification of the air-sensitive and thermally-unstable (I) may be necessary.



(I)

We report that 2-lithio-2-trimethylsilyl-1,3-dithian (IIb), quantitatively prepared by the metallation of (IIa),[2] reacts with *both* aldehydes and ketones at room temperature to give, following aqueous hydrolysis, exclusively the Wittig product (III) in good yield (Table).[3]



(II) a; R=H
b; R=Li

(III)

In all cases there was no spectroscopic evidence for the possible alternative formation of a β-silylmethanol and n.m.r. spectra of the crude reaction mixture showed (III) as virtually the sole product.

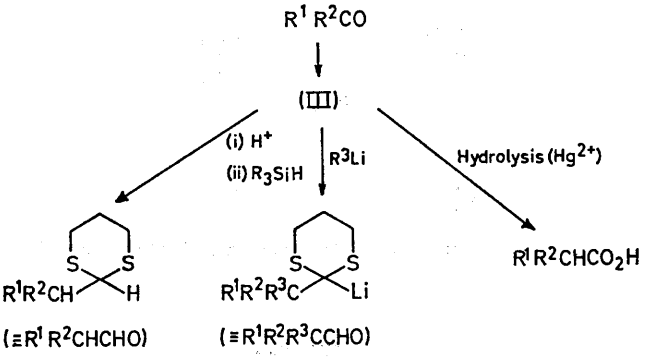
These compounds can also be prepared from 1,3-dithian itself by consecutive reactions in a single reaction mixture. Thus, treatment of 1,3-dithian with successively n-butyllithium, trimethylchlorosilane, n-butyl-lithium, and benzophenone gave, after a reaction time of 85 h, a 75% yield of (III; $R^1 = R^2 = Ph$). Similarly, cyclohexanone gave after 22 h, (III; $R^1 + R^2 = -CH_2[CH_2]_3CH_2-$) in 69% yield.

The present work therefore represents both an improvement in and an extension of the Wittig synthesis of the alkylidenedithians, (III). Their potential as synthetic intermediates is considerable. In addition to their possible conversion into acids,[1] they are reported to react with both electrophiles (*e.g.*, H^+)[4] and, in the case of (III; $R^1 = R^2 = H$), with nucleophiles (*e.g.*, RLi).[5]

Table

Carbonyl precursor	Yield (%) of (III) (reaction time, h)[a]
Pr^{n}CHO	67 (18)
Pr^{i}CHO	69 (20)
PhCH=CH-CHO	66 (18)[b]
PhCHO	68 (18)[b]
MeCOMe	45 (18)
PhCOMe	66 (32)
PhCOPh	75 (70)

[a] Yield of purified product, the spectra (i.r., n.m.r.) of which were in accord with the assigned structure; each compound gave satisfactory analytical (C, H) data and/or showed a molecular ion in the mass spectrum. [b] Physical properties are identical with those reported previously.[1]



Since all the useful reactions of the original dithian synthesis[6] are available to the compounds generated by these latter reactions, it is apparent that the present Wittig synthesis may prove extremely valuable for the systematic structural modification of carbonyl compounds.

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[2] A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 431; E. J. Corey, D. Seebach, and R. Freedman, *ibid.*, p. 434.

[3] For previous examples of Wittig reactions of α-silylcarbanions, see D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780; T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Letters*, 1970, 1137.

[4] F. A. Carey and J. R. Neergaard, *J. Org. Chem.*, 1971, **36**, 2731.

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[6] E. J. Corey and D. Seebach, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1075, 1077.