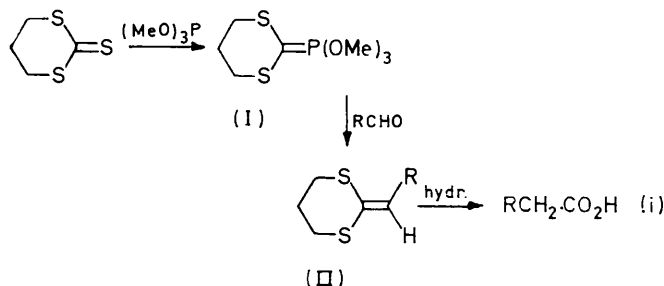


Wittig-type Reactions of 2-Lithio-2-trimethylsilyl-1,3-dithian and Related Reactions

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2-Lithio-2-trimethylsilyl-1,3-dithian reacts with carbonyl compounds, R^1R^2CO , to give alkylidenedithians, $\overline{S} \cdot [CH_2]_3 \cdot S \cdot C=CR^1R^2$ (after acidic hydrolysis), potentially valuable synthetic intermediates for C_1 homology (e.g. $\rightarrow R^1R^2CH \cdot CHO$ or $R^1R^2CH \cdot CO_2H$). In similar reactions, acetyl chloride appears to yield $\overline{S} \cdot [CH_2]_3 \cdot S \cdot C(SiMe_3) \cdot C(:CH_2) \cdot OAc$, styrene oxide gives $\overline{S} \cdot [CH_2]_3 \cdot S \cdot C(SiMe_3) \cdot CH_2 \cdot CH(OH)Ph$, and *cis*- $[PtCl_2(PPh_3)_2]$ gives *cis*- $[PtCl\{C(SiMe_3) \cdot S \cdot [CH_2]_3 \cdot S\}(PPh_3)_2]$. A homologous lithium reagent $\overline{S} \cdot [CH_2]_3 \cdot S \cdot CLi \cdot CH_2 \cdot SiMe_3$ with benzaldehyde furnishes $\overline{S} \cdot [CH_2]_3 \cdot S \cdot C(CH_2 \cdot SiMe_3) \cdot CH(OH)Ph$.

IN 1967, Corey extended his dithian studies to the Wittig reagent (I) [equation (i)].¹ Hydrolysis of the Wittig product (II) completes the selective conversion of an



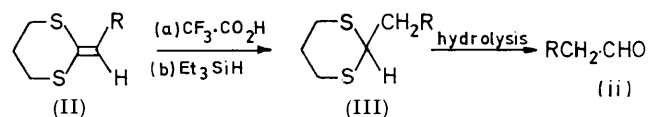
aldehyde, $RCHO$, into the homologous acid, $RCH_2 \cdot CO_2H$. Subsequent investigations have revealed that the

¹ E. J. Corey and G. Märkl, *Tetrahedron Letters*, 1967, 3201.

² F. A. Carey and J. R. Neergaard, *J. Org. Chem.*, 1971, **36**, 2731.

alkylidenedithians (keten thioacetals) (II) can be extremely versatile synthetic intermediates.

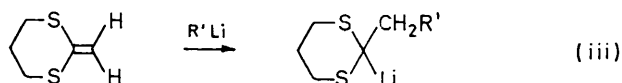
Carey found [equation (ii)] that the double bond of (II) is easily reduced by a protonation-hydride transfer sequence.² Hydrolysis of the product (III) completes the conversion of $RCHO$ into $RCH_2 \cdot CHO$.



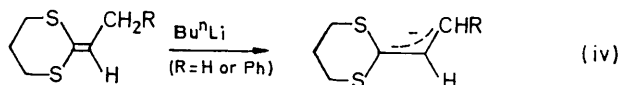
Carlson reported [equation (iii)] that nucleophilic addition to the double bond of the parent compound (II; $R = H$) is a useful homology process for organolithium reagents.³ In contrast, an alkyl group attached to the double bond undergoes metallation

³ R. M. Carlson and P. M. Helquist, *Tetrahedron Letters*, 1969, 173.

[equation (iv)], and the resulting allylic anion can act as an ambident nucleophile.^{4,5}

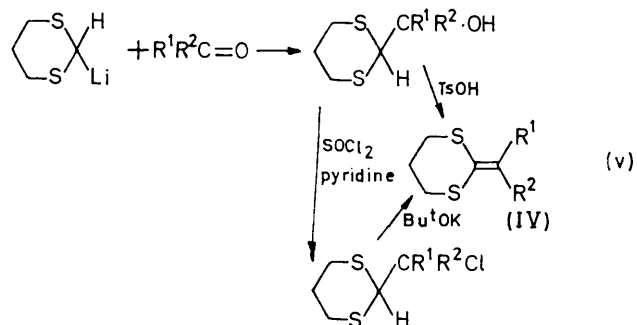


Since the foregoing dithian products are also subject to all the useful reactions of the original Corey dithian synthesis,⁶ the Wittig reaction obviously has great scope for the systematic modification of carbonyl compounds.

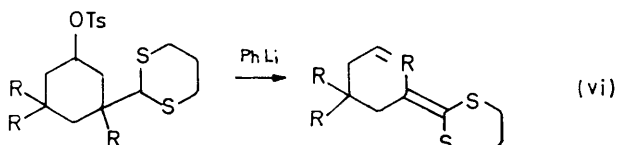


Unfortunately the Wittig synthesis has some drawbacks.¹ Trimethyl phosphite, used in excess for the preparation of (I) [equation (i)], can in certain cases undergo a coupling reaction with the added aldehyde; therefore purification of the air-sensitive and thermally unstable (I) may be necessary. In addition, the Wittig reaction is restricted to aldehydes, ketones being inert even under forcing conditions.

The ketone products (IV) are available from 1,3-dithian, but their preparation requires a multi-step sequence involving the isolation and acid-catalysed dehydration of intermediate carbinols, or conversion into chlorides followed by dehydrohalogenation [equation (v)].⁶ An alternative, but less general, preparation is



the novel fragmentation reaction [equation (vi)] reported by Marshall.⁷



A simplified Wittig synthesis of alkylidenedithians, applicable to both aldehydes and ketones, would be of

⁴ D. Seebach, *Synthesis*, 1969, 17.

⁵ D. L. Coffen, T. E. McEntee, and D. R. Williams, *Chem. Comm.*, 1970, 913.

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

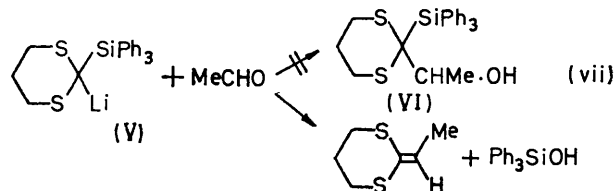
⁷ J. A. Marshall and J. L. Belletire, *Tetrahedron Letters*, 1971, 871.

⁸ P. F. Jones and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 526.

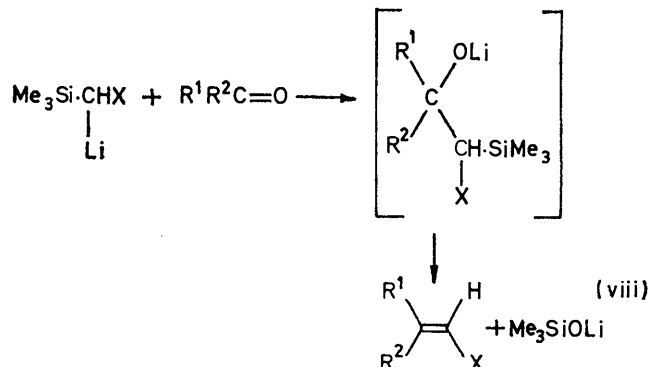
⁹ D. Seebach, B.-Th. Gröbel, A. K. Beck, M. Braun, and K.-H. Geiss, *Angew. Chem. Internat. Edn.*, 1972, **11**, 443.

considerable synthetic value. We have found that the use of the readily available silyldithians satisfies these criteria. Following our preliminary communication,⁸ two other groups^{9,10} have reported similar results independently. We now report details of our experimental procedures and some extensions.

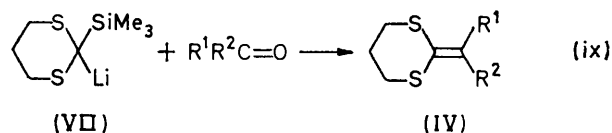
The present work originated in 1968 in an unsuccessful attempt¹¹ to prepare organofunctional acylsilanes by the dithian route. From the reaction of 2-lithio-2-triphenylsilyl-1,3-dithian¹² (V) with acetaldehyde, none of the expected carbinol (VI) was obtained [equation (vii)]. From the nature of the products it was apparent



that this was another example of the Wittig reaction between α -silyl carbanions and carbonyl compounds, at that time newly discovered by Peterson,¹³ and since shown to be a general reaction^{14,15} [equation (viii)], X = Ph, H, SMe, SPh, PPh₂, P(S)Ph₂, or P(O)(OEt)₂.



Since the experimental difficulty in separating the Wittig product from the involatile triphenylsilanol would reduce the synthetic utility of (V), we turned to the trimethylsilyl analogue (VII)^{12,16} as a more viable reagent. Here the silanol (or disiloxane) co-product is volatile and is easily removed by evaporation. We have found that (VII) reacts with both aldehydes and ketones to give (IV) in good yield [equation (ix)].



¹⁰ F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, **37**, 1926.

¹¹ A. G. Brook and P. F. Jones, University of Toronto, 1968, unpublished studies.

¹² A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 431.

¹³ D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.

¹⁴ F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, **37**, 939.

¹⁵ T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Letters*, 1970, 1137.

¹⁶ E. J. Corey, D. Seebach, and R. Freedman, *J. Amer. Chem. Soc.*, 1967, **89**, 434.

Representative compounds from a variety of structural types were examined: branched and unbranched aliphatic aldehydes, aromatic and $\alpha\beta$ -unsaturated aldehydes, aliphatic and aromatic acyclic ketones, and cyclic ketones. Results are shown in Tables 1 and 2. In the

TABLE 1

Conversion of 2-trimethylsilyl-1,3-dithian (VIII) into the 2-alkylidene-1,3-dithian (IV) [equation (ix)]

Product	R ¹ R ² CO		Yield (%)	Reaction time (h)
	R ¹	R ²		
(IVa)	Ph	Ph	75	70
(IVb)	Ph	Me	67	32
(IVc)	Me	Me	45	18
(IVd)	PhCH=CH	H	66	18
(IVe)	Pr ⁿ	H	67	18
(IVf)	Pr ⁱ	H	69	20
(IVg)	Me	H	45	20 ^a
(IVh)	Me ₂ N	H	45	20 ^b

^a Product decomposes upon attempted purification.

^b Characterised only by n.m.r. (see Experimental section).

majority of cases, the Wittig product (IV) was obtained as the sole, spectroscopically pure product. In no case was there any spectroscopic evidence for the formation of a β -silylalcohol. With cinnamaldehyde, 1,2-addition took place exclusively.

Furthermore, we have found that compounds (IV) can be prepared efficiently from 1,3-dithian itself, now commercially available, by multi-step reactions in a single flask without isolation of intermediates. Thus reaction of 1,3-dithian with (successively) butyl-lithium, chlorotrimethylsilane, butyl-lithium again, and the carbonyl compound gave the Wittig product in yields comparable to those obtained starting directly with the trimethylsilyldithian. Results are summarised in Table 2.

TABLE 2

Conversion of 1,3-dithian into the 2-alkylidene-1,3-dithian (IV)

Product	R ¹ R ² CO		Yield (%)	Reaction time (h)
	R ¹	R ²		
(IVa)	Ph	Ph	75	85
(IVi)	-CH ₂ -[CH ₂] ₅ -CH ₂ -		70	22
(IVj)	Ph	H	68	18

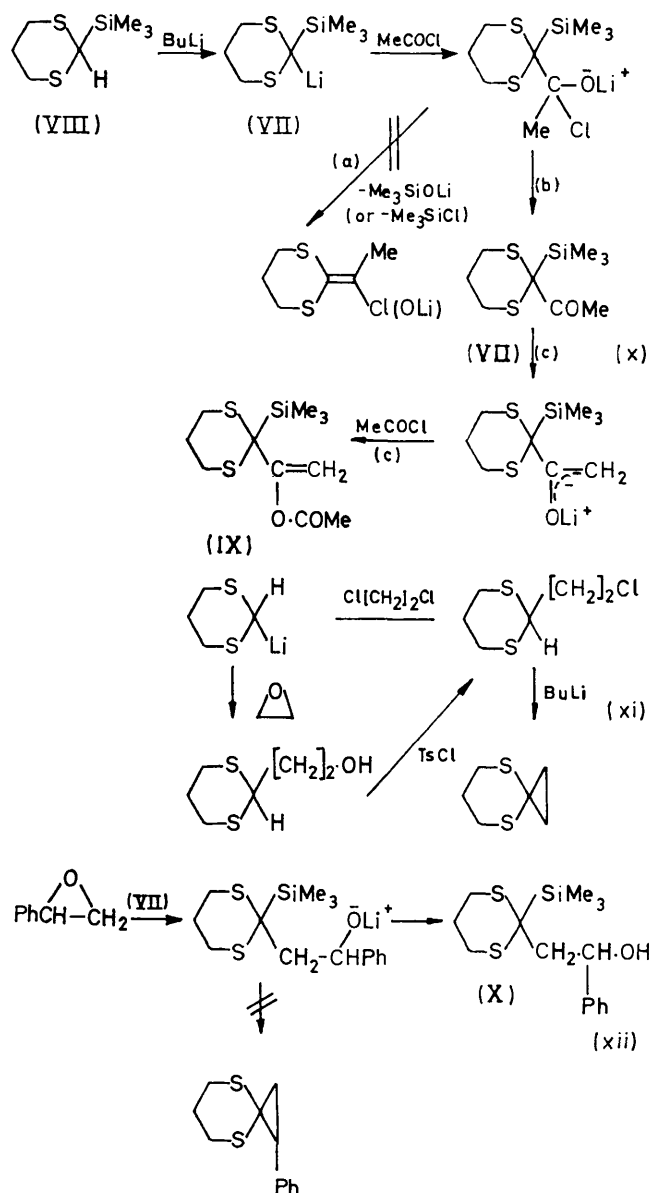
We have briefly investigated the possibility of the synthesis of alkenes bearing heteroatom substituents by studying the Wittig reaction of (VII) with appropriate carbonyl compounds. While dimethylformamide gave the Wittig product (IVh) (Table 1), a different reaction was observed with acetyl chloride. The only product positively identified was the enol ester (IX); the mechanism may involve addition to give a ketone [equation (x), route (b)] rather than the Wittig product [route (a)]. Compound (IX) may then arise from the formation and subsequent reaction of the enolate ion of this ketone [route (c)].

Cyclopropanes have been obtained by the dithian route from multi-step reactions of 2-lithio-1,3-dithian

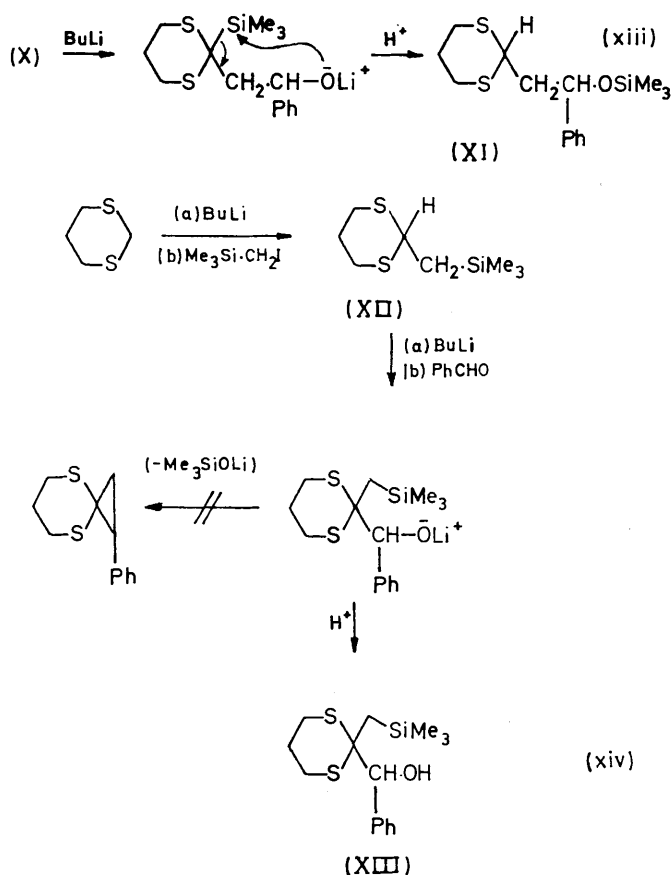
with epoxides or 1,2-dihalides [equation (xi)].⁴ Since Wittig reagents (*e.g.*, Ph₃P·CH·CO₂Et) may react with epoxides to yield cyclopropane derivatives,¹⁷ the possibility of (VII) providing a simplified alternative was examined. However, from styrene oxide the 2- β -hydroxyalkyl-2-trimethylsilyl-1,3-dithian (X) was obtained [equation (xii)]. This compound did not cyclise upon heating.

An attempt to provide more forcing conditions (BuLi) for the cyclisation is believed to have promoted a molecular rearrangement into (XI) [equation (xiii)]. Evidence for compound (XI) is incomplete and rests on i.r. [ν (SiO)] and ¹H n.m.r. spectra. Resistance to cyclisation, even upon heating, may be steric in origin.

An alternative cyclopropanone synthesis was therefore designed [equation (xiv)]. However, the final cyclisation step was again not achieved; use of more forcing



¹⁷ D. B. Denney, J. J. Vill, and M. J. Boskin, *J. Amer. Chem. Soc.*, 1962, **84**, 3944.



conditions (thermal or BuLi) provided no evidence that cyclisation or rearrangement had occurred.

A preliminary survey was made of the possibility of attaching the 2-trimethylsilyl-1,3-dithian ligand through C_2 to a transition metal, using the lithio-derivative (VII). With 2 moles of the latter per mole of *cis*-[PtCl₂(PPh₃)₂], only one chlorine atom was displaced.

EXPERIMENTAL

1,3-Dithian and its 2-trimethylsilyl derivative (VIII) were prepared by published procedures.^{16,18} *n*-Butyllithium (1.3M-solution in hexane, obtained commercially) was estimated by Gilman's double titration method.¹⁹ Tetrahydrofuran (THF) was dried over sodium and was distilled immediately before use. All reactions were carried out under an atmosphere of oxygen-free dry nitrogen.

N.m.r. spectra were recorded on a Varian T60 spectrometer with tetramethylsilane as internal reference. Molecular weights were determined by use of an A.E.I. MS9 mass spectrometer. M.p.s. were measured on a Kofler hot-stage apparatus. Microanalyses were carried out by Mr. A. G. Olney of this Department.

General Technique for Wittig Reactions.—(a) *From 2-trimethylsilyl-1,3-dithian* (VIII). Reactions were carried out in a flame-dried, three-necked, 100 ml flask, equipped with a rubber septum, a nitrogen inlet, and a magnetic stirrer; the system was evacuated *in vacuo* and was then filled with nitrogen. The lithium reagent (VII) was prepared by injection of an equivalent of butyl-lithium into

a solution of (VIII) in THF, cooled to -23° . After stirring at -23° for 1 h, a solution of an equimolar amount of the carbonyl compound (or an excess, if volatile) in THF was added dropwise at -23° . The resulting mixture was then allowed to attain room temperature and was stirred for the time stated. Following hydrolysis with 5% hydrochloric acid and extraction with ether, the organic layer was dried (Na_2SO_4) and the solvent was removed.

By essentially this procedure, the following compounds were prepared: (i) 2-diphenylmethylene-1,3-dithian (IVa) (18 h) (2.61 g, 75%), m.p. $131\text{--}133^\circ$ ($\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$); the analytical sample had m.p. $138\text{--}139^\circ$ (MeOH) (lit.,⁴ $134.5\text{--}135^\circ$) (Found: C, 71.9; H, 5.8%; M^+ , 284. Calc. for $\text{C}_{17}\text{H}_{16}\text{S}_2$: C, 71.8; H, 5.7%; M , 284), δ (CCl_4) 7.30 (10H, s, Ph), 3.16—2.83 (4H, m, CH_2S), and 2.42—1.76 (2H, m, $\text{CH}_2\text{-CH}_2\text{S}$); (ii) 2-(1-phenylethylidene)-1,3-dithian (IVb) (32 h) (2.00 g, 67%), b.p. 116° at 0.001 mmHg (Found: C, 65.0; H, 6.6%; M^+ , 222. Calc. for $\text{C}_{12}\text{H}_{14}\text{S}_2$: C, 64.8; H, 6.4%; M , 222), δ (CCl_4) 7.40—7.06 (5H, m, Ph), 3.13—2.62 (4H, m, CH_2S), 2.32—1.83 (2H, m, $\text{CH}_2\text{-CH}_2\text{S}$), and 2.16 (3H, s, CMe); (iii) 2-(isopropylidene)-1,3-dithian (IVc) (18 h) (1.18 g, 45%), b.p. $64\text{--}67^\circ$ at 0.7 mmHg, contaminated with starting (VIII) (6% recovered material); a pure sample of (IVc), m.p. $38\text{--}39^\circ$, was obtained by preparative g.l.c. (Found: C, 52.8; H, 7.6%; M^+ , 160. Calc. for $\text{C}_7\text{H}_{12}\text{S}_2$: C, 52.45; H, 7.6%; M , 160), δ (CDCl_3) 3.00—2.73 (4H, m, CH_2S), 2.33—1.86 (2H, m, $\text{CH}_2\text{-CH}_2\text{S}$), and 1.96 (6H, s, CMe); (iv) 2-(3-phenylprop-2-enylidene)-1,3-dithian (IVd) (18 h) (1.53 g, 66%), m.p. $81\text{--}82^\circ$ ($\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$); the analytical sample had m.p. $84\text{--}85^\circ$ (MeOH) (lit.,¹ $85\text{--}86^\circ$) (Found: C, 66.7; H, 6.2%; M^+ , 234. Calc. for $\text{C}_{13}\text{H}_{14}\text{S}_2$: C, 66.6; H, 6.0%; M , 234), δ (CDCl_3) 7.52—7.10 (5H, m, Ph), 7.00—6.30 (3H, m, olefinic), 3.10—2.66 (4H, m, CH_2S), 2.35—1.72 (2H, m, $\text{CH}_2\text{-CH}_2\text{S}$); (v) 2-butyldiene-1,3-dithian, (IVe) (1.54 g, 67%), b.p. $72\text{--}74^\circ$ at 0.04 mmHg (M^+ , 174. Calc. for $\text{C}_8\text{H}_{14}\text{S}_2$: M , 174), δ (CCl_4) 5.97 (1H, t, J 7 Hz, C=CH), 3.16—2.76 (4H, m, CH_2S), and 2.76—0.83 (9H, 3 overlapping m, $\text{CH}_2\text{-CH}_2\text{S} + \text{Pr}$); (vi) 2-(2-methylpropylidene)-1,3-dithian (IVf) (18 h) (1.39 g, 69%), b.p. $62\text{--}63^\circ$ at 0.35 mmHg; an n.m.r. spectrum indicated contamination with (VIII) (3% recovered material); a pure sample was obtained by preparative g.l.c. (lit.,¹⁰ b.p. $84\text{--}89^\circ$ at 1.5 mmHg) (Found: C, 55.3; H, 8.4%; M^+ , 174. Calc. for $\text{C}_8\text{H}_{14}\text{S}_2$: C, 55.1; H, 8.1%; M , 174), δ (CCl_4) 5.67 (1H, d, J 8 Hz, C=CH), 3.00—2.66 (4H, m, CH_2S), 2.66—1.67 (3H, m, $\text{CH}_2\text{-CH}_2\text{S} + \text{CHMe}_2$), and 0.99 (6H, d, J 6 Hz, CHMe_2); (vii) 2-ethylidene-1,3-dithian (IVg) (20 h) (0.99 g, 45%), b.p. $48\text{--}52^\circ$ at 0.3 mmHg; an n.m.r. spectrum indicated contamination with (VIII) (5% recovered material); attempted separation by g.l.c. (7 ft column; 20% SE 52; 135°) caused decomposition; δ (CCl_4) 5.88 (1H, q, J 7 Hz, C=CH), 3.03—2.63 (4H, m, CH_2S), 2.50—1.97 (2H, m, $\text{CH}_2\text{-CH}_2\text{S}$), and 1.76 (3H, d, J 7 Hz, CMe).

(b) *From 1,3-dithian*. With the foregoing equipment, a solution of 1,3-dithian in THF, cooled to -23° , was treated with butyl-lithium (1 equiv.). The solution was stirred at -23° for 1 h, then an equimolar amount of chlorotrimethylsilane was added in a single portion. The mixture was stirred at -23° for 30 min and then at room temperature for 30 min. It was again cooled to -23° , a further equivalent of butyl-lithium was added, and stirring at

¹⁸ P. R. Jones and R. West, *J. Amer. Chem. Soc.*, 1968, **90**, 6978.

¹⁹ H. Gilman and J. W. Morton, *Org. Reactions*, 1954, **8**, 258.

—23° was continued for 1 h. The carbonyl compound was then added and the foregoing work-up procedure was followed.

2-Diphenylmethylene-1,3-dithian (IVa) from 1,3-Dithian.—A solution of 1,3-dithian (1.35 g, 0.0113 mol) in THF (50 ml) was treated successively with butyl-lithium (8.7 ml, 0.0113 mol), chlorotrimethylsilane (1.44 ml, 0.0113 mol), butyl-lithium (8.7 ml), and a solution of benzophenone (2.04 g, 0.0113 mol) in THF (20 ml). After 85 h, work-up gave (IVa) (2.39 g, 75%), m.p. 138—139° (MeOH).

2-Cyclohexylidene-1,3-dithian (IVi).—A solution of 1,3-dithian (1.53 g, 0.0127 mol) in THF (50 ml) was treated successively with butyl-lithium (9.8 ml, 0.0127 mol), chlorotrimethylsilane (1.63 ml, 0.0127 mol), butyl-lithium (9.8 ml), and a solution of cyclohexanone (1.25 g, 0.0127 mol) in THF (10 ml). After 22 h, work-up gave the olefin (IVi) (1.77 g, 70%), m.p. 95—96° (MeOH) (lit.,⁴ 93.6—94°) (Found: C, 59.9; H, 8.1%; M^+ , 200. Calc. for $C_{10}H_{16}S_2$: C, 59.9; H, 8.1%; M , 200), δ (CCl_4) 3.0—2.66 (4H, m, CH_2S), 2.66—2.00 (6H, 2 overlapping m, $CH_2\cdot CH_2S$ and $C=C\cdot CH_2$), and 1.83—1.33 (6H, m, $[CH_2]_3$).

2-Benzylidene-1,3-dithian (IVj).—A solution of 1,3-dithian (1.86 g, 0.0155 mol) in THF (50 ml) was treated successively with butyl-lithium (11.9 ml, 0.0155 mol), chlorotrimethylsilane (2.0 ml, 0.0155 mol), butyl-lithium (11.9 ml), and a solution of benzaldehyde (1.65 g, 0.0155 mol) in THF (10 ml). After 18 h, work-up and distillation gave the olefin (IVj) (2.19 g, 68%), b.p. 120—122° at 0.01 mmHg (lit.,¹ 142—145° at 0.1 mmHg) (Found: C, 63.4; H, 6.0%; M^+ , 208. Calc. for $C_{11}H_{12}S_2$: C, 63.4; H, 5.8%; M , 208), δ ($CDCl_3$) 7.66—7.10 (5H, m, Ph), 6.86 (1H, s, $C=CH$), 3.16—2.83 (4H, m, CH_2S), and 2.42—1.90 (2H, m, $CH_2\cdot CH_2S$).

Dimethylaminomethylene-1,3-dithian (IVh).—*NN*-Dimethylformamide (0.80 ml, 0.0104 mol) was added to an equimolar amount of the lithium reagent (VII) in THF (50 ml). After 20 h, work-up gave a yellow liquid (1.44 g). G.l.c. and n.m.r. showed two products: (IVh) (corresponding to 0.86 g, 45%) and an unidentified silylhydrocarbon (0.58 g); preparative g.l.c. proved difficult but sufficient pure (IVh) (as judged by n.m.r.) was isolated, as an oil, for spectroscopic examination; ν_{max} , 1595 cm^{-1} (C=C), δ ($CDCl_3$) 6.58 (1H, s, vinyl), 3.33—1.73 (6H, m, $S[CH_2]_3S$), and 2.87 (6H, s, NMe_2).

Reaction of Acetyl Chloride with the Lithium Reagent (VII).—Excess of acetyl chloride (2.10 ml, 0.0312 mol) was added to a solution of the lithium reagent (VII) (0.0209 mol), prepared from the dithian (VIII) (4.01 g) and butyl-lithium (16.1 ml) in THF (100 ml). After 17 h, work-up gave a product (4.01 g) contaminated with the dithian (VIII). Distillation gave a fraction (0.75 g), b.p. 62—64° at 0.04 mmHg, which after redistillation partially solidified. The solid was identified as 2-(1-acetoxyvinyl)-2-trimethylsilyl-1,3-dithian (IX) (Found: C, 47.9; H, 8.0. $C_{11}H_{20}O_2S_2Si$ requires C, 47.8; H, 7.3%; ν_{max} (CCl_4) 1760 (C=O), 1620 (C=C), and 1250 cm^{-1} ($SiMe_3$), δ ($CDCl_3$) 5.62 (1H, d, J 1.5 Hz, vinyl), 5.07 (1H, d, J 1.5 Hz, vinyl), 2.16 (s, 3H, Ac), 3.40—1.00 (6H, m, $S[CH_2]_3S$), and 0.20 (9H, s, $SiMe_3$). G.l.c. of the crude mixture (4.01 g) revealed three compounds: (VIII) (27.5%), (IX) (22.3%), and an unidentified silylhydrocarbon (50.2%).

Reaction of Styrene Oxide with the Lithium Reagent (VII).—The oxide (1.20 ml, 0.01052 mol) was added to an equimolar amount of the lithium reagent (VII) in THF (50 ml). After 17 h, work-up gave a yellow oil (0.82 g), which

afforded crystals of 2-(β -hydroxyphenethyl)-2-trimethylsilyl-1,3-dithian (X) (0.60 g, 17%), m.p. 109—111° (MeOH) (Found: C, 57.5; H, 7.6. $C_{15}H_{24}OS_2Si$ requires: C, 57.6; H, 7.7%; ν_{max} (CCl_4) 3500—3320 (OH) and 1250 and 945 cm^{-1} ($SiMe_3$), δ (CCl_4) 7.4—7.1br (5H, s, Ph), 5.0 (1H, dd, J 5 Hz, $CHPh$), 3.86br (1H, s, OH), 3.50—1.67 (8H, m, $S[CH_2]_3S\cdot C\cdot CH_2$), and 0.33 (9H, s, $SiMe_3$). When compound (X) (0.10 g) was heated at 150° and 5 mmHg for 3 h there was no change in either i.r. or n.m.r. spectrum.

To compound (X) (0.060 g, 0.19 mmol) in THF (*ca.* 6 ml) was added a solution of butyl-lithium in hexane (0.18 ml, 0.23 mmol) and the mixture was set aside for 15 min. Solvent was removed and the residue was heated (2.5 h) at 140° and 5 mmHg. The usual work-up gave a wax, tentatively formulated as (XI) contaminated with (X); ν_{max} (film) 3600—3140 (OH), 1250 and 855 ($SiMe_3$), and 1015 and 1025 cm^{-1} ($OSiMe_3$), δ (CCl_4) 7.25 (s, Ph), 4.8 (t, J 6 Hz, $CH\cdot OSiMe_3$), 4.1 (t, J 7 Hz, $S[CH_2]_3\cdot S\cdot CH$), 3.0—1.0 (m, $S[CH_2]_3S\cdot C\cdot CH_2$), and 0.05 (s, $SiMe_3$).

2-Trimethylsilylmethyl-1,3-dithian (XII).—Butyl-lithium (32 ml, 0.0416 mol) was added to a solution of 1,3-dithian (5.0 g, 0.0416 mol) in THF (100 ml) at -23° . The mixture was stirred at -23° for 2 h, and a solution of iodomethyltrimethylsilane (8.8 g, 0.0416 mol) in THF (50 ml) was added. After 16 h at 20°, work-up and distillation gave 2-trimethylsilylmethyl-1,3-dithian (XII) (5.68 g, 66%) (Found: C, 47.1; H, 8.7. $C_8H_{18}S_2Si$ requires C, 46.5; H, 8.8%), b.p. 78—80° at 0.6 mmHg; δ (CCl_4) 4.07 (1H, t, J 8 Hz, SCHS), 3.0—2.67 (4H, m, CH_2S), 2.33—1.67 (2H, m, $CH_2\cdot CH_2S$), 1.77 (2H, d, J 8 Hz, CH_2Si), and 0.17 (9H, s, $SiMe_3$).

Reaction of Benzaldehyde with the Lithium Reagent from Compound (XII).—Butyl-lithium solution in hexane (6.1 ml, 0.00785 mol) was added to compound (XII) (1.62 g, 0.00785 mol) in THF (20 ml) at -23° . The mixture was stirred at -23° for 2 h, and a solution of benzaldehyde (0.84 g, 0.00785 mol) in THF (10 ml) was added. After 16 h at 20°, work-up gave an oil. Addition of methanol caused the precipitation of the carbinol (XIII), m.p. 98—102°. A further 0.53 g (total 0.79 g, 32%), m.p. 88—98°, was recovered from the mother liquor by partial evaporation. Recrystallisation (MeOH) gave 2-(α -hydroxybenzyl)-2-trimethylsilylmethyl-1,3-dithian (XIII) (Found: C, 57.4; H, 7.6. $C_{15}H_{24}OS_2Si$ requires C, 57.6; H, 7.7%), m.p. 101—102°, ν_{max} (CCl_4) 3450 (OH) and 1240 cm^{-1} ($SiMe_3$), δ (CCl_4) 7.67—7.15 (5H, m, Ph), 5.03 (1H, s, $CHPh$), 3.53—1.67 (7H, m, OH and $S[CH_2]_3S$), 0.95 (2H, ABq, CH_2Si), and 0.13 (9H, s, $SiMe_3$). When compound (XIII) (0.09 g, 0.28 mmol) was heated at 150° and 5 mmHg for 3 h there was no change in the i.r. or n.m.r. spectrum.

Compound (XIII) (1.17 g, 0.00374 mol) in THF (6 ml) was added to a solution of butyl-lithium in hexane (3.7 ml, 0.0048 mol), and the mixture was set aside for 20 min at 20°. Solvent was removed and the residue was heated (2.5 h at 140° and 5 mmHg). The usual work-up gave a brown oil, which was not identified.

Reaction of cis-Dichlorobis(triphenylphosphine)platinum(II) with the Lithium Reagent (VII).—The platinum complex (0.85 g, 0.00108 mol) was added to a solution of the lithium reagent (VII) in hexane (0.00166 mol) in ether at -23° . After 1 h at 0°, then 2 h at 20°, ether was removed *in vacuo*. Benzene was added. The filtrate was evaporated to *ca.* 5 ml. Hexane was added dropwise and a dark yellow

solid precipitated. This was recrystallised (C₆H₆-C₆H₁₄) to give pale yellow crystals, believed to be cis -[PtCl{C(SiMe₃)·S[CH₂]₃·S}(PPh₃)₂] (Found: C, 54.3; H, 4.9. C₄₃H₄₅ClP₂PtS₂Si requires C, 54.5; H, 4.8%).

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