Ring Fragmentations of 2-Alkenyl- and 2-Benzyl-1,3-dithiolanes Induced by Bases. A Novel Method for the Preparation of 1,1-Bisalkylthio- or 1-Alkylthio-alk-1-enes and -alka-1,3-dienes

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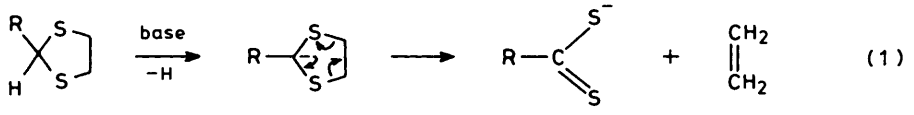
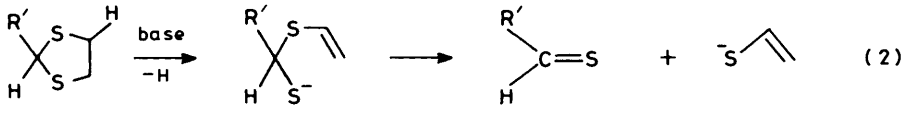
The reaction of 2-alkenyl- and 2-benzyl-1,3-dithiolanes with several bases and successive alkylation with alkyl halides has been investigated. In the reaction of 2-alk-1-enyl-1,3-dithiolanes with organolithium reagents and alkyl halides, deprotonation at C-2 and subsequent cycloelimination occurs to give α,β-unsaturated dithiocarboxylate anions; these readily undergo conjugate addition and/or enolation with bases followed by alkylation to afford 1,1-bisalkylthioalk-1-enes and/or 1,1-bisalkylthioalka-1,3-dienes, respectively. In contrast, when 2-alk-2-enyl-1,3-dithiolanes are submitted to an identical procedure, the reaction proceeds *via* ring-opening by attack of organolithium reagents at C-4 and subsequent elimination to afford 1-alkylthioalka-1,3-dienes. In the reaction of 2-benzyl-1,3-dithiolane with bases and methyl iodide in diethyl ether, β,β-bismethylthiostyrene is the major product; this is obtained *via* deprotonation at C-2 and subsequent cycloelimination. In contrast, in the same reaction sequence in tetrahydrofuran, base attack at C-4 gives ring-opening and 1-methylthiophenethyl vinyl sulphide and/or β-methylthiostyrene are produced preferentially. Since each of the above reaction courses is dependent both on the C-2 substituent and the reaction conditions (mainly the reaction medium) each of the products may be prepared selectively.

It is known that 1,3-dithiolanes[1-3] undergo deprotonation at C-2 by bases and subsequent cycloelimination[4] to give dithiocarboxylate anions and ethylene derivatives [equation (1)]; because of this ring-fragmentation, these reactions have



(1)

been little investigated in contrast with those of 1,3-dithianes[5] which are well known as examples of carbonyl umpolung. However, most of the 1,3-dithiolanes previously described possess an electron-withdrawing group at C-2[1,2] or four substituents at C-4 and C-5.[3] Recently it was reported by Wilson and his co-workers[6] and by us[7] that other 1,3-dithiolanes undergo ring-opening fragmentation by attack of bases at 4-H to afford the products derived from thioaldehydes or thioketones and vinyl thiolate anion [equation (2)]. It seems



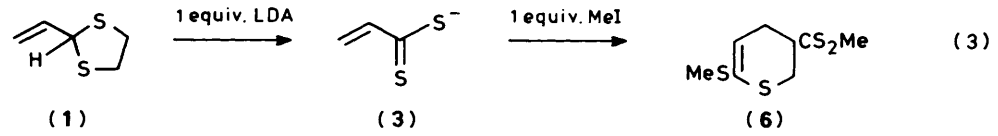
(2)

likely that these ring-fragmentations are influenced by the 1,3-dithiolane ring substituents or the reaction conditions.

We have investigated the ring-fragmentations of 2-alk-1-enyl- and 2-alk-2-enyl-1,3-dithiolanes involving regiospecific attack of organolithium reagents at 2-H or 4-H. We have also investigated the effect of reaction conditions (solvent, temperature, type of base, and deuterium effects) on product distribution in the reactions of 2-benzyl-1,3-dithiolane. We now describe the reactions which give rise to the preparation of 1,1-bisalkylthioalka-1-enes, 1,1-bisalkythioalka-1,3-dienes, 1-alkylthioalka-1,3-dienes, β,β-bismethylthiostyrene, 1-methylthiophenethyl vinyl sulphide, and β-methylthiostyrene.

Results and Discussion

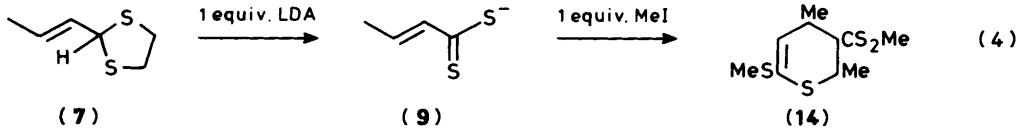
Ring-fragmentations of 2-Alkenyl-1,3-dithiolanes.—The reaction of 2-vinyl-1,3-dithiolane (**1**) with 2 molar equivalents of organolithium reagents and alkyl halides was carried out in tetrahydrofuran (THF) under nitrogen to give 1,1-bis(alkylthio)prop-1-ene derivatives (**5**). The results are summarized in Table 1 and a feasible pathway for the formation of (**5**) from (**1**) is outlined in Scheme 1. Deprotonation of (**1**) at C-2 with organolithium reagents followed by cycloelimination proceeds smoothly to afford the dithioacrylate anion (**3**) and ethylene. Surprisingly, (**3**) undergoes conjugate addition with organolithium reagents to give a dianion (**4**), which leads to (**5**) by trapping with alkyl halides. In the reaction, the red colour[8] of (**3**) initially appeared and then disappeared before the addition of alkyl haldies, indicating that (**3**) is an intermediate in the reaction, easily undergoing conjugate addition to afford (**4**) as shown in Scheme 1. When the reaction of (**1**) with an equimolar amount of lithium di-isopropylamide (LDA) was performed in THF, the disappearance of the red colour of (**3**) was not observed, and after trapping with methyl iodide, the 4*H*-thiopyran (**6**)[8], a dimer of methyl dithioacrylate, was obtained [equation (3)]. It is noteworthy that conjugate addition of organolithium reagents to (**3**) leading to (**5**) occurs even when an organolithium reagent of low nucleophilicity such as lithium 2,2,6,6-tetramethylpiperidide (LTMP)



(1) (3) (6)

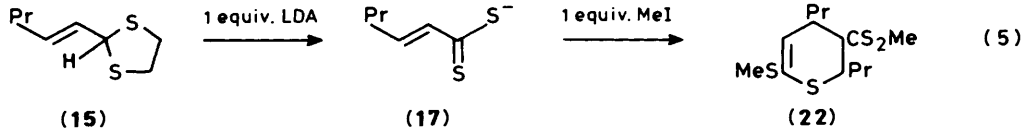
was used (run 9 in Table 1). This indicates that (3) undergoes remarkably facile conjugate addition with organolithium reagents, regardless of whether (3) is an anionic species.

When the same deprotonation–alkylation sequence was applied to 2-prop-1-enyl-1,3-dithiolane (7)* in THF, either 1,1-bisalkylthiobut-1-ene derivatives (12) or 1,1-bisalkylthiobuta-1,3-dienes (13) was obtained, depending on the choice of organolithium reagents (see Scheme 2 and Table 2). For reactions with butyl-lithium and phenyl-lithium which are moderately nucleophilic lithium reagents (runs 1 and 3 in Table 2), intermediary dithiocrotonate anion (9) smoothly undergoes conjugate addition with the lithium reagents to afford the dianion (10) which reacts with alkyl halides to give (12). In contrast, the employment of less nucleophilic organolithium reagents such as t-butyl-lithium, LDA, lithium hexamethyldisilazide (LHDS), or LTMP (runs 4—17 in Table 2) results in enolation of (9) to afford a dianion (11) from which (13) is derived after alkylation. These facts suggest that the nucleophilicity of organolithium reagents plays a dominant role in directing the reaction course which gives rise to (10) or (11) from (9); that is, with moderately nucleophilic organolithium reagents conjugate addition on (9) leading to (12) occurs preferentially, whereas enolation of (9) giving (13) proceeds predominantly when less nucleophilic organolithium reagents are used. The presence of an intermediate (9) is also confirmed by carrying out the reaction of (7) with an equimolar amount of LDA and methyl iodide in THF, as in the reaction of (3). As shown in the accompanying equation (4), the resulting methyl dithiocrotonate was isolated as the dimer (14).[8]



(7) (9) (14)

The same deprotonation–alkylation sequence for 2-pent-1-enyl-1,3-dithiolane (15) gave rise to 1,1-bisalkylthiohex-1-ene derivatives (20) and/or 1,1-bisalkylthiohexa-1,3-dienes (21), depending on the organolithium reagents employed (see Scheme 3 and Table 3). Even when LDA is used, which is less nucleophilic and hence causes only enolation of (9), conjugate addition with LDA to hex-2-enedithioate anion (17) occurs exclusively, no enolation of (17) being observed. The employment of weakly nucleophilic organolithium reagents such as LHDS or LTMP causes enolation of (17) to give a dianion (19) which upon alkylation gave (21). Also, the reaction of (15) with 1 equivalent of LDA and methyl iodide affords (22), the dimer of methyl hex-2-enedithioate [equation (5)].

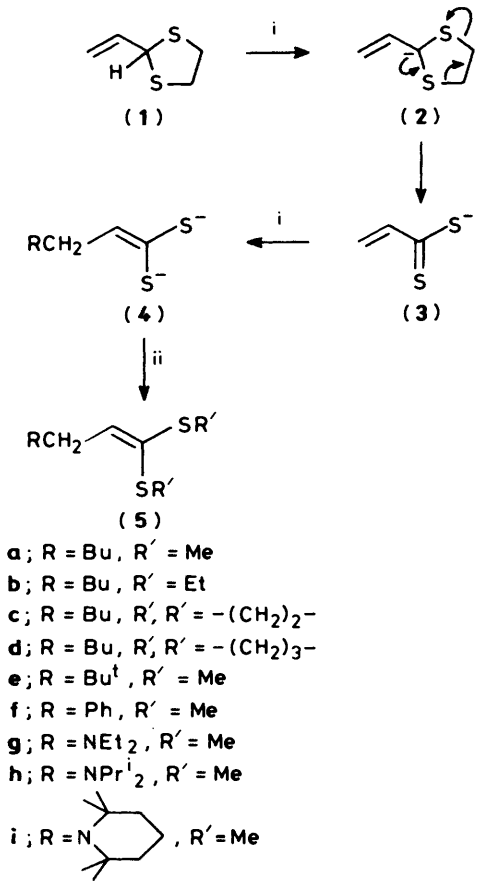


(15) (17) (22)

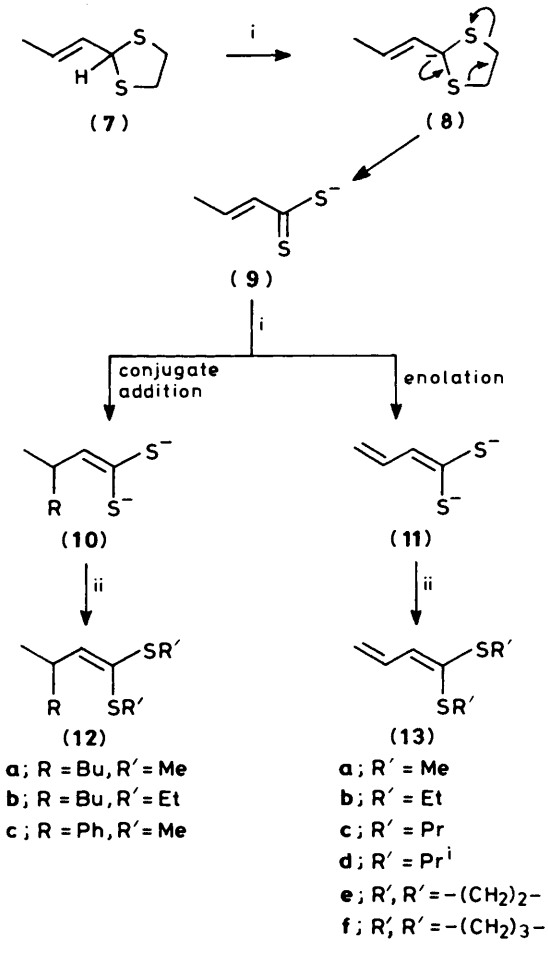
In the reaction of 2-alk-1-enyl-1,3-dithiolanes (1), (7), and (15) with organolithium reagents and alkyl halides, any products resulting from attack of the organolithium reagents at 4-H of the 1,3-dithiolane ring could not, in spite of careful analyses, be detected. It is suggested that deprotonation at C-2 of the 1,3-dithiolanes is facile because of the adjacent carbon–carbon double bond in the C-2 substituent. This prompted us to investigate the reactions with several organolithium reagents of 2-alk-2-enyl-1,3-dithiolanes (23), in which a methylene group is interposed between the double bond and the 1,3-dithiolane ring. The reaction of 2-prop-2-enyl-(23a; R″ = H) or 2-(2-methylprop-2-enyl)-1,3-dithiolane (23f; R″ = Me) with organolithium reagents and alkyl halides was carried out in THF under the same conditions as described previously to give 1-alkylthio- (27; R″ = H) or 1-alkylthio-3-methylbuta-1,3-dienes (27; R″ = Me), respectively, together with alkyl vinyl sulphides (28) (see Scheme 4 and Table 4). These observations have suggested that initial attack of organolithium reagents occurred at C-4 rather than C-2 of the 1,3-dithiolane ring of (23), resulting in ring-opening to give the anion (24). When the reaction of (23a) with 1 equivalent of LDA and ethyl iodide was carried out in the same manner the but-3-ene (29) was produced [see equation (6)]. This result demonstrates that an intermediary anion (24) is formed *via* ring-opening of (23) by attack of organolithium reagents at C-4, and that the fragmentation of (24) affords alka-1,3-dienethiolate anion (25) and ethenethiolate anion (26): the latter are transformed by alkylation into (27) and (28), respectively. Unlike similar reactions of other 1,3-dithiolanes[7] no reduction products derived from unstable 3-thiobutenal (3-methyl-3-thiobutenal) could be detected in the reaction mixture. This suggests that (25) is not formed *via* enolation of the thioaldehyde produced by elimination of (26) from (24). Although there is no direct evidence, it seems reasonable to assume that (25) is produced by elimination of (26) from a dianion, lithium 2-lithio-1-vinylthiobut-3-enethiolate, which was afforded by the reaction of (24) with organolithium reagents.

Considering these results together with those of earlier reports[1-3,6,7] it is proposed that the base-induced ring-fragmentations of 1,3-dithiolanes are influenced by the type of ring substituent present. Thus, 4,4,5,5-tetrasubstituted 1,3-dithiolanes or 1,3-dithiolanes possessing an electron-withdrawing group at C-2 predominantly suffer deprotonation at C-2 by bases and subsequent cycloelimination; in contrast other 1,3-dithiolanes preferentially undergo base-induced ring-opening at C-4. 2-Alk-1-enyl- and 2-alk-2-enyl-1,3-dithiolanes undergo either one of the ring-fragmentations of the above types, the position of the carbon–carbon double bond (whether or not

* When our experimental work was almost complete, formation of the dithiocrotonate anion was reported. Conjugate addition and enolation of the anion, however, have not been synthetically utilized: K. R. Lawson, A. Singleton, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1984, 859.



Scheme 1. *Reagents:* i, RLi in THF at −78 °C for 0.5 h and at 0 °C for 1 h; ii, R^1X at room temperature for 2 h.



Scheme 2. *Reagents:* i, RLi in THF at −78 °C for 0.5 h and at 0 °C for 1 h; ii, R′X at room temperature for 2 h.

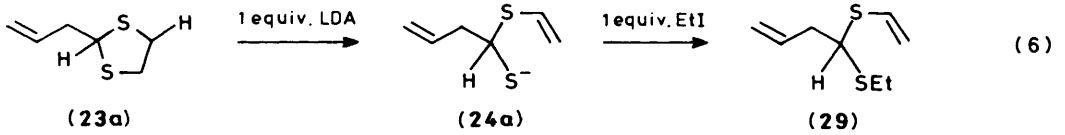
Table 1. Base-induced fragmentation of 2-vinyl-1,3-dithiolane (**1**)[a]

Run	RLi (2 equiv.)	R′X (2 equiv.)	Product[b]	Yield (%)[c]
1	BuLi	MeI	(**5a**)	74
2	BuLi	EtI	(**5b**)	83
3	BuLi	$\frac{1}{2}Br(CH_2)_2Br$	(**5c**)[d]	29
4	BuLi	$\frac{1}{2}Br(CH_2)_3Br$	(**5d**)[d]	53
5	Bu^{t}Li	MeI	(**5e**)	77
6	PhLi	MeI	(**5f**)	78
7	Et_2NLi	MeI	(**5g**)	85
8	LDA	MeI	(**5h**)	69
9	LTMP[e]	MeI	(**5i**)	53

[a] In the reaction, THF was used as solvent. [b] The products were isolated by distillation unless otherwise stated. [c] Yields of isolated products based on (**1**). [d] Isolated by chromatography on a short column of silica gel and following distillation. [e] Lithium 2,2,6,6-tetramethylpiperidide.

nucleophilicity of the organolithium reagents being the deciding factor. In particular, it is notable that conjugate addition smoothly proceeds even when less nucleophilic organolithium reagents are used. Also, the procedure presented above would provide a useful and selective method of preparing 1,1-bisalkylthioalk-1-enes [(**5**), (**12**), and (**20**)], 1,1-bisalkylthioalka-1,3-dienes [(**13**) and (**21**)], and 1-alkylthioalka-1,3-diene (**27**).

Ring-fragmentation of 2-Benzyl-1,3-dithiolane.—The reaction of 2-benzyl-1,3-dithiolane (**30**) with strong bases and subsequent methylation of the resulting anions with methyl iodide was carried out under nitrogen under various conditions to give β,β-bismethylthiostyrene (**34**), 1-methylthiophenethyl vinyl sulphide (**37**), and/or β-methylthiostyrene (**39**). The results are summarized in Table 5 and a reasonable pathway for the formation of (**34**), (**37**), and (**39**) from (**30**) is outlined in Scheme



(6)

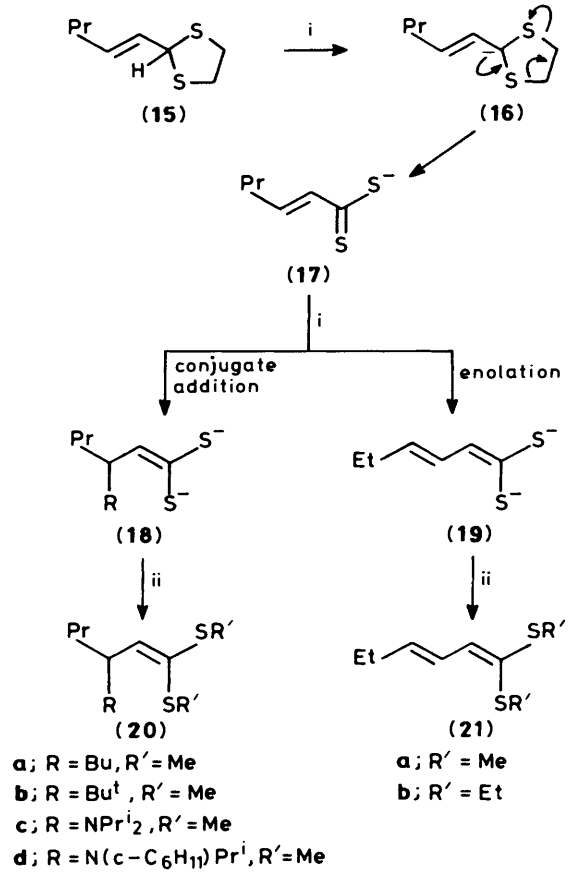
adjacent to the 1,3-dithiolane ring) of the C-2 substituent dictating which. The intermediary α,β-unsaturated dithiocarboxylate anions (**3**), (**9**), and (**17**) readily undergo either selective conjugate addition or enolation with organolithium reagents, the

5. The formation of the phenyldithioacetate anion (**32**) by deprotonation at C-2 with base and subsequent cycloelimination is easily understood by analogy with the reactions of other 1,3-dithiolanes:[1-3] subsequently (**32**) undergoes enolation to

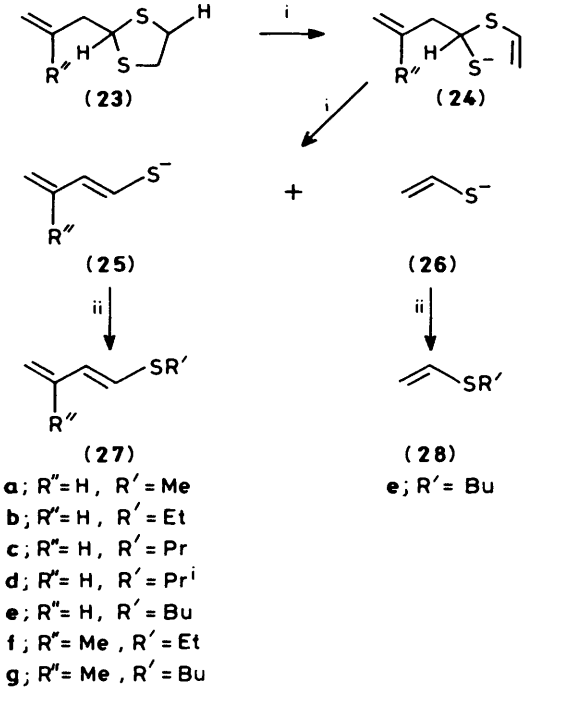
Table 2. Base-induced fragmentation of 2-prop-1-enyl-1,3-dithiolane (7)

Run	RLi (2 equiv.)	Solvent	Additive (2 equiv.)	R'X (2 equiv.)	Product[a], yield (%)[b]
1	BuLi	THF		MeI	(12a), 81
2	BuLi	THF		EtI	(12b), 86
3	PhLi	THF		MeI	(12c), 93
4	Bu^{t}Li	THF		EtI	(13b), (70)
5	LDA	THF		MeI	(13a), 76
6	LDA	THF		EtI	(13b), 73 (79)
7	LDA	THF	TMEDA	EtI	(13b), (41)
8	LDA	THF	HMPA	EtI	(13b), (43)
9	LDA	Ether		EtI	(13b), (8)
10	LDA	Ether	HMPA	EtI	(13b), (4)
11	LDA	THF		PrI	(13c), 79
12	LDA	THF		Pr^{i}I	(13d),[c] 27
13	LDA	THF		$\frac{1}{2}Br(CH_2)_2Br$	(13e), 73
14	LDA	THF		$\frac{1}{2}Br(CH_2)_3Br$	(13f), 88
15	LHDS[d]	THF		EtI	(13b), (23)
16	LHDS[d]	THF	HMPA	EtI	(13b), (69)
17	LTMP	THF		EtI	(13b), (73)

[a] The products were isolated by distillation unless otherwise stated. [b] The yields of the isolated products were based on (7). The values given in parentheses are referring yields obtained by g.l.c. analyses. [c] Isolated by chromatography on a short column of silica gel and following distillation. [d] Lithium hexamethyldisilazide.



Scheme 3. *Reagents:* i, RLi in THF at −78 °C for 0.5 h and at 0 °C for 1 h; ii, R'X at room temperature for 2 h



Scheme 4. *Reagents:* i, RLi in THF at −78 °C for 0.5 h and at 0 °C for 1 h; ii, R'X at room temperature for 2 h

afford the dianion (**33**) which reacts with methyl iodide to give (**34**) (course A). Attack of base at 4-H results in ring-opening to yield an anion (**36**) *via* the transition state (**35**): this involves the release of 4-H and synchronous bond cleavage between C-5 and S-1 (course B). Arguments in favour of the transition state (**35**) will be discussed later. Methylation of (**36**) affords (**37**) whilst further fragmentation gives the styrenethiolate anion (**38**) which upon methylation affords (**39**). The fragmentation of (**36**) should take place in a similar manner to that of (**24**). Failure to detect reduction products[7] derived from unstable phenylthioacetaldehyde make it unlikely that (**38**) is produced *via* enolation of phenylthioacetaldehyde.

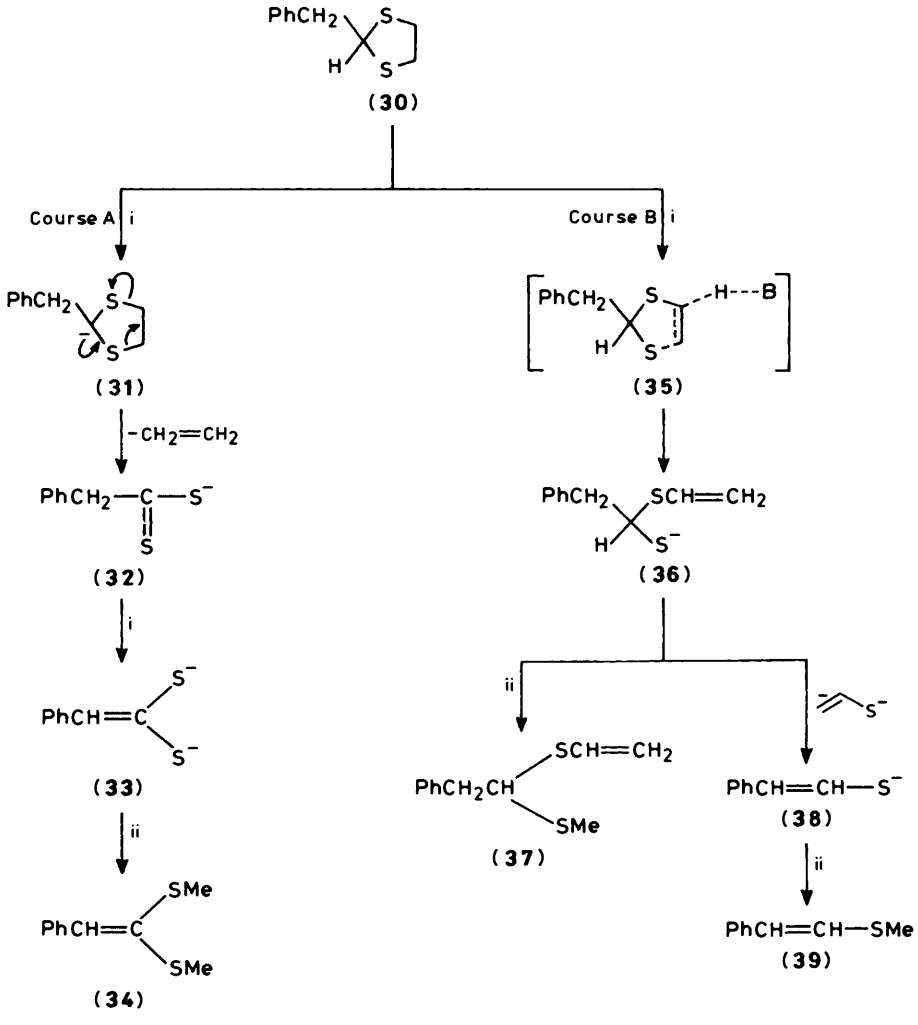
In Table 5, the ratio of (**34**):(**37**) + (**39**) is an indicator of the proportion of the reaction which goes *via* courses A and B respectively: that is, the ratio reflects the selectivity of the attack

Table 3. Base-induced fragmentation of 2-pent-1-enyl-1,3-dithiolane (**15**)[a]

Run	RLi (2 equiv.)	Additive (2 equiv.)	R'X (2 equiv.)	Product[b], yield (%)[c]
1	BuLi		MeI	(**20a**), 96
2	Bu'Li		MeI	(**20b**),[d] 35 (**21a**),[d] 21
3	LDA		MeI	(**20c**), 69
4	LDA	TMEDA	MeI	(**20c**), 84
5	LDA	HMPA	MeI	(**20c**), 80
6	LICA[e]		MeI	(**20d**), 83
7	LICA[e]	HMPA	MeI	(**20d**),[d] 41 (**21a**),[d] 36
8	$(c\text{-}C_6H_{11})_2NLi$		MeI	(**21a**),[d] 6
9	$(c\text{-}C_6H_{11})_2NLi$	HMPA	MeI	(**21a**), 39
10	LTMP		MeI	(**21a**), 70
11	LHDS		MeI	No reaction
12	LHDS	TMEDA	MeI	(**21a**), 13
13	LHDS	HMPA	MeI	(**21a**), 75
14	LHDS	HMPA	EtI	(**21b**), 69

[a] In the reaction, THF was used as solvent. [b] The products were isolated by distillation unless otherwise stated. [c] Yield of isolated product based on (**15**). [d] Isolated by chromatography on silica gel eluted by 20% benzene–hexane. [e] Lithium *N*-isopropylcyclohexylamide.

by base on (**30**) at C-2 and C-4. Of the reaction conditions the effect of solvent on the ratio is most significant (see Table 5). With diethyl ether as a solvent, only (**34**) was obtained without any regard to type of bases used: this indicated that the employment of diethyl ether as the solvent is favourable for reaction course A (see runs 8, 9, and 23 in Table 5). In contrast, with THF as the solvent, the reaction proceeded mainly *via* course B to give (**37**) and (**39**) as main products (see runs 1—5 and 19 in Table 5). In both cases, the addition of hexamethylphosphoric triamide (HMPA) resulted in an increase of of (**37**) and/or (**39**) (compare runs 2 *vs.* 6, 3 *vs.* 7, and 8 *vs.* 10 in Table 5). Although potassium t-butoxide is less basic, it reacted with (**30**) in refluxing THF to afford an excellent yield of (**39**) after methylation (see run 18 in Table 5). With butyl- or t-butyllithium in THF, the selectivity decreased significantly (compare runs 19 or 24 *vs.* 2 and 20 *vs.* 3 in Table 5). Among the lithium amides employed, lithium *N*-isopropylcyclohexylamide (LICA) and LTMP brought about a slight decrease in the selectivity under the same conditions (see runs 12 and 13 in Table 5). The selectivity is not sensitive to reaction temperature and slightly decreases at higher temperature (compare runs 3 *vs.* 4 and 20 *vs.* 21 in Table 5). The ratio of (**37**):(**39**) is greatly affected by the reaction temperature (see runs 1 and 3 in Table 5). When the reaction is carried out in THF at higher temperature, (**39**)



Scheme 5. *Reagents:* i, Base; ii, MeI

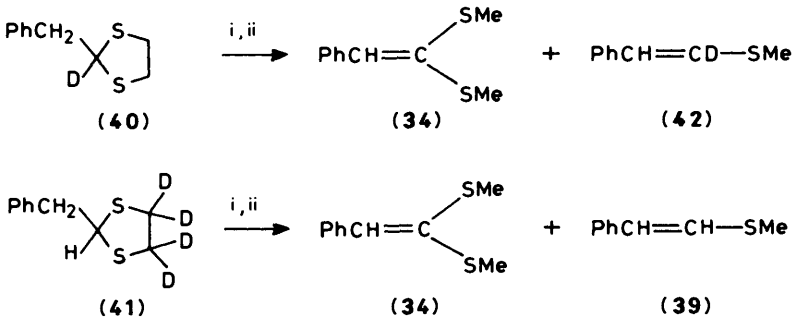
Table 4. Base-induced fragmentation of 2-alk-2-enyl-1,3-dithiolanes (**23**)

Run	Substrate	RLi (2 equiv.)	Solvent	Additive (2 equiv.)	R'X (2 equiv.)	Product[a], yield (%)[b]
1	(**23a**)	BuLi	THF		EtI	(**27b**), (28)
2	(**23a**)	Bu'Li	THF		EtI	(**27b**), (71)
3	(**23a**)	LDA	THF		EtI	(**27b**), 54 (89) (**13b**), (7)
4	(**23a**)	LDA	THF	TMEDA	EtI	(**27b**), (71)
5	(**23a**)	LDA	THF	HMPA	EtI	(**27b**), (48)
6	(**23a**)	LDA	Ether		EtI	No reaction
7	(**23a**)	LDA	THF		MeI	(**27a**), 52
8	(**23a**)	LDA	THF		PrI	(**27c**), 58
9	(**23a**)	LDA	THF		Pr'I	(**27d**), 59
10	(**23a**)	LDA	THF		BuI	(**27e**), 59 (**28e**), 38
11	(**23a**)	LHDS	THF		EtI	(**27b**), (9)
12	(**23a**)	LHDS	THF	HMPA	EtI	(**27b**), (49)
13	(**23f**)	LDA	THF		EtI	(**27f**), 64
14	(**23f**)	LDA	THF		BuI	(**27g**), 70 (**28e**), 35

[a] The products were isolated by distillation. [b] The yields of the isolated products based on (**23**). The values given in parentheses are referring yields obtained by g.l.c. analyses.

with LDA in ether results in a decrease of (**34**) and recovery of (**40**) (compare run 2 in Table 6 with run 9 in Table 5). Regardless of the recovery, (**39**) could not be detected; that is, attack at 4-H of (**40**) (course B) could not be observed. In the reaction of (**41**) in THF with HMPA, the attack of LDA at the C-4 deuterium of (**41**) (course B) is depressed by deuterium labelling at C-4 and results in a decrease of (**39**); the attack of LDA at 2-H (course A) proceeds mainly to afford (**34**) (compare run 3 in Table 6 with run 7 in Table 5). These results indicate that a significant deuterium effect is observed in these reactions. When (**30**) was treated with LDA in THF in a similar manner to that described in run 1 of Table 5 followed by trapping with D_2O instead of methyl iodide, a moderate amount of starting (**30**) was recovered in which no trace of (**40**) could be detected. Also, the products (**39**) and (**42**) obtained in runs 1 and 3 of Table 6 were pure and there was no cross-contamination. It suggests that there is no proton shift in the reactions. The above-mentioned facts indicate that in the ring-fragmentations of both courses A and B, the rate-determining steps are the initial steps involving base-induced bond cleavage between C-2 and H and between C-4 and H, respectively.

The results obtained suggest to us that the kinetic order of both base-induced ring-fragmentations of (**30**) to give (**32**) and (**36**) is second-order, but the reactions proceed by quite distinct



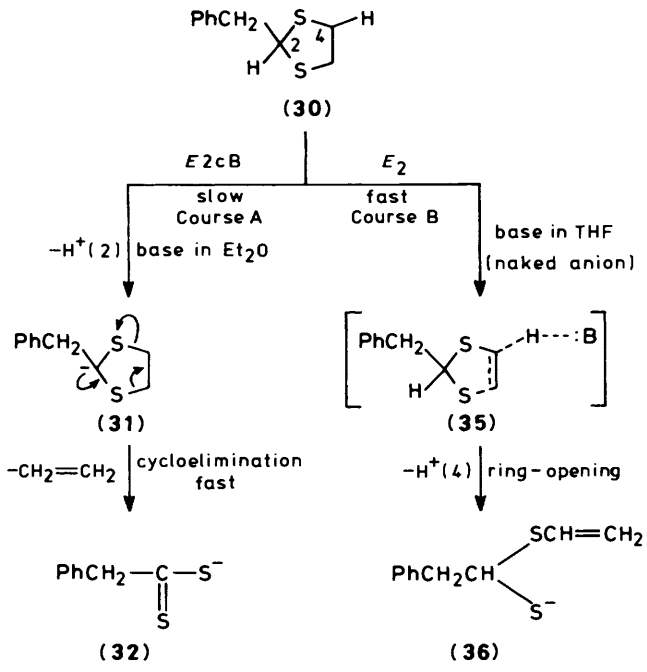
Scheme 6. *Reagents:* i, LDA at −78 °C for 0.5 h and at 0 °C for 1 h; ii, MeI at room temperature for 2 h

predominates. The above-mentioned procedure provides a useful method for preparing (**34**), (**37**), and (**39**) from (**30**), using LDA in ether at −78 °C, LDA in THF at −78 °C, and potassium t-butoxide in refluxing THF, respectively.

The results described cannot be discussed solely in terms of the estimated pK_a values of 2-H and 4-H in the dithiolane (**30**) and this suggests to us a considerable difference between the ring-fragmentations of courses A and B. Considering that the fragmentation of (**31**) to (**32**) (in course A) is cycloelimination, it has been assumed that the anion (**31**) is an intermediate in course A, and that attack of base at 4-H in (**30**) leading to (**36**) should proceed *via* a transition state (**35**) to result in ring-opening similar to β-elimination.

The reaction of 2-benzyl-2-deuterio- (**40**) and 2-benzyl-4,4,5,5-tetradeuterio-1,3-dithiolane (**41**) with LDA and methyl iodide was carried out in THF or ether for 0.5 h at −78 °C and for 1 h at 0 °C (Procedure C) to give (**34**), (**39**), and/or β-deuterio-β-(methylthio)styrene (**42**) (see Scheme 6 and Table 6). Under the conditions used, the formation of 1-deuterio-1-methylthiophenethyl vinyl sulphide and 1-methylthiophenethyl trideuteriovinyl sulphide which correspond to (**37**) were not observed. In the reaction of (**40**) with LDA in THF, the attack of LDA on the C-2 deuterium of (**40**) (course A) is suppressed, so that (**34**) was not detected in the reaction mixture (compare run 1 in Table 6 with run 3 in Table 5). Similarly, the reaction of (**40**) mechanisms. Considering the fact that (**31**) undergoes cycloelimination to afford (**32**),[4] it is certain that the anion (**31**) is an intermediate in the reaction of course A, which suggests that the ring-fragmentation of (**30**) in course A proceeds *via* an *E*2cB mechanism[9] involving deprotonation of (**30**) at C-2 and subsequent cycloelimination.* In contrast, a further base-induced ring-fragmentation of (**30**) (course B) may proceed by a different mechanism; this is an *E*2 mechanism[10] which involves release of 4-H and synchronous bond cleavage between C-5 and S-1. In THF, lithium amides or potassium t-butoxide, which mostly exist as a naked anion or a solvent-separated ion pair, attack 4-H more effectively than 2-H. This contrasts with the behaviour of an un-ionized molecule or a poorly solvated ion pair of bases such as butyl-lithium or lithium amides in ether which cannot undergo reaction *via* course B, instead attacking the more acidic 2-H. Thus, the selective preparations of (**34**), (**37**), and (**39**) from (**30**) have been accomplished.

* The reaction involving deprotonation at C-2 following cycloelimination of 1,3-dithiolanes having an electron-withdrawing group at C-2 seems to proceed *via* an *E*1cB mechanism. The reason is that 2-ethoxycarbonyl-2-lithio-1,3-dithiolane is trapped with Michael acceptor or acyl chloride: see, J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 1973, 2599; E. Vedejs, M. J. Arnost, J. M. Dolphin, and J. Eustache, *J. Org. Chem.*, 1980, **45**, 2601.



Scheme 7.

Experimental

^{1}H N.m.r. spectra were determined on a Varian EM-360 spectrometer in CCl_4 with $SiMe_4$ as an internal standard. ^{13}C N.m.r. spectra were recorded on a JEOL LNM FX-100 spectrometer in $CDCl_3$. Gas chromatography was carried out on a Shimadzu 4BM-PF apparatus, using PEG-6000 (25%)–Shimalite (100 × 0.3 cm) and EGSS-X (3% or 15%)–Chromosorb-W (100 × 0.3 cm) columns with nitrogen as carrier gas. THF was dried by distillation over sodium benzophenone ketyl. Other solvents such as ether were dried by distillation over lithium aluminium hydride. The amines used for the preparation of lithium amides as well as HMPA and TMEDA were distilled over calcium hydride. Butyl-lithium (in hexane), t-butyl-lithium, and phenyl-lithium (in cyclohexane–ether) were commercially available and the molarity of the organolithium reagents were determined by titration prior to their use.

Preparation of 2-*Vinyl*-(**1**), 2-*Prop*-1-*enyl*-(**7**), *and* 2-*Pent*-1-*enyl*-1,3-*dithiolane* (**15**).—These 2-alk-1-enyl-1,3-dithiolanes were prepared by a modification of the procedure of Dedieu and his co-workers.[11] To a solution of ethane-1,2-dithiol (9.5 g, 0.1 mol) and anhydrous toluene-*p*-sulphonic acid (0.2 g, 0.1 mmol) in benzene (80 ml) was added 0.1 mol of each of the following: acrolein diethyl acetal, crotonaldehyde diethyl acetal, and hex-2-enal diethyl acetal. The mixture was stirred under reflux for 8 h and then poured into 20% aqueous NaOH (100 ml). The

Table 5. Reaction of 2-benzyl-1,3-dithiolane (**30**) with bases and methyl iodide

Run	Base[a]	Solvent (Additive)[b]	Procedure[c]	Recovery of (**30**),[d] %	Product, yield (%) (**34**)[e]	(**37**)[e]	(**39**)[e]	Ratio (**34**) / (**37**) + (**39**)
1	LDA	THF	A	38.3	<1	49.7 (80.6)[f]	0	
2	LDA	THF	B	0	2.4	18.3	7.7	0.09
3	LDA	THF	C	0	3.2	0	43.1	0.07
4	LDA	THF	D	0	18.4	0	25.9	0.71
5	LDA	THF	E	0	3.1	0	56.8	0.05
6	LDA	THF (HMPA)	B	0	1.7	39.3	24.8	0.03
7	LDA	THF (HMPA)	C	0	1.2	0	89.2	0.01
8	LDA	Ether	B	24.7	61.7 (81.9)[f]	0	0	
9	LDA	Ether	C	0	46.4	0	<1	
10	LDA	Ether (HMPA)	B	0	<1	38.7	14.1	
11	LDA	Hexane	B	0	27.6	0	0	
12	LICA	THF	B	0	3.8	6.2	28.2	0.11
13	LTMP	THF	B	0	23.8	3.9	47.1	0.47
14	LHDS	THF	F	88.3	0	0	0	
15	LHDS	Benzene	F	99.2	0	0	0	
16	LHDS	THF (HMPA)	C	96.3	0	0	2.1	
17	LHDS	THF (HMPA)	F	0	0	0	84.9	
18	Bu^{t}OK	THF	F	0	3.0	0	96.8	0.03
19	BuLi	THF	B	0	27.9	30.4	21.6	0.54
20	BuLi	THF	C	0	35.6	0	31.0	1.15
21	BuLi	THF	D	0	36.8	0	20.5	1.80
22	BuLi	THF (HMPA)	B	0	2.1	14.3	58.9	0.03
23	BuLi	Ether	C	4.2	35.6	0	0	
24	Bu^{t}Li	THF	B	0	32.0	11.4	19.2	1.05
25	Bu^{t}Li	THF	D	0	33.4	0	15.4	2.17

[a] Molar ratio of (**30**) to bases was *ca.* 1:2. [b] Two molar equivalents of HMPA based on (**30**) was used. [c] See Experimental part. [d] Determined by g.l.c. analyses using 4-methylbenzophenone as an internal standard. [e] Determined by g.l.c. analyses using *p*-methoxyacetophenone as an internal standard. [f] The yield in parentheses based on consumed (**30**).

Table 6. Reaction of 2-benzyl-2-deuterio- (**40**) and 2-benzyl-4,4,5,5-tetradeuterio-1,3-dithiolane (**41**) with LDA and methyl iodide[a]

Run	Substrate	Solvent (Additive)	Recovery of substrate[b] (%)	Product, yield (%) (34)[c]	(39)[c]	(42)[c]	Ratio (34)/(39)
1	(**40**)	THF	0	0	—	51.4	
2	(**40**)	Ether	37.4	38.6 (61.7)[d]	—	<1	
3	(**41**)	THF (HMPA)[e]	0	40.5	26.3	—	1.5

[a] The reaction of (**40**) and (**41**) with 2 molar equivalents of LDA was carried out by Procedure C (see Experimental). [b] Determined by g.l.c. analyses using 4-methylbenzophenone as an internal standard. [c] Determined by g.l.c. analyses using 4-methoxyacetophenone as an internal standard. [d] Yield based on consumed (**40**). [e] Two molar equivalents of HMPA based on (**41**) was used.

benzene layer was separated, washed with 20% aqueous NaOH (80 ml × 3), dried ($MgSO_4$), and evaporated to give a residue which was distilled under reduced pressure to afford the product: (**1**), 69% yield; b.p. 88—91 °C/14 mmHg (lit.,[12] b.p. 46—48 °C/0.5 mmHg); δ_H 3.16 (4 H, s), 4.78 (1 H, d, *J* 9 Hz), 4.94 (1 H, dd, *J* 3 and 9 Hz), 5.10 (1 H, dd, *J* 3 and 17 Hz), and 5.79 (1 H, ddd, *J* 9, 9, and 17 Hz); (**7**), 90% yield; b.p. 84—85 °C/10 mmHg (lit.,[13] 60—61 °C/2 mmHg); δ_H 1.16 (3 H, d, *J* 5 Hz), 3.18 (4 H, s), 4.8—5.0 (1 H, m), and 5.3—5.7 (2 H, m); (**15**): 95% yield; 96—97 °C/5.5 mmHg; δ_H 0.88 (3 H, t, *J* 6 Hz), 1.1—1.8 (2 H, m), 1.8—2.2 (2 H, m), 3.15 (4 H, s), 4.7—5.1 (1 H, m), and 5.1—5.7 (2 H, m).

Preparation of 2-*Prop*-2-*enyl*-(**23a**; R″=H) *and* 2-(2-*Methylprop*-2-*enyl*)-1,3-*dithiolane* (**23f**; R″=Me).—At first, but-3-enal diethyl acetal and 3-methylbut-3-enal diethyl acetal were prepared by a modified Stetter's method.[14] To a solution of allylmagnesium chloride (0.1 mol) in THF (100 ml) was added diethyl phenyl orthoformate (25.5 g, 0.13 mol) at room temperature under nitrogen. The mixture was stirred under reflux for 1 h and then poured into aqueous NH_4Cl (150 ml). It was extracted with ether (50 ml × 2), and the combined ethereal extracts were washed with water (80 ml × 2) and with aqueous $NaHCO_3$ (80 ml), dried ($MgSO_4$), and concentrated under reduced pressure to give a residue, which was distilled to afford but-3-enal diethyl acetal (61% yield). Similarly, 3-methylbut-3-enal diethyl acetal was prepared by the reaction of methylallylmagnesium chloride with diethyl phenyl orthoformate (yield 46%). These acetals were converted into 2-alk-2-enyl-1,3-dithiolanes (**23**) in the same manner as described above: (**23a**; R″=H), 65% yield; b.p. 88—91 °C/14 mmHg; δ_H 2.49 (2 H, t, *J* 7 Hz), 3.13 (4 H, s), 4.38 (1 H, t, *J* 7 Hz), 4.8—5.3 (2 H, m), and 5.74 (1 H, ddt, *J* 9, 17, and 7 Hz); (**23f**; R″=Me), 94% yield; b.p. 110—112 °C/15 mmHg; δ_H 1.73 (3 H, s), 2.46 (2 H, d, *J* 7 Hz), 3.14 (4 H, s), 4.53 (1 H, t, *J* 7 Hz), and 4.74 (2 H, s).

General Procedure for the Base-induced Fragmentation of 2-*Alkenyl*-1,3-*dithiolanes* (**1**), (**7**), (**15**), *and* (**23**).—A solution of the desired organolithium reagent (4.6 mmol) in THF or ether (30 ml) was prepared under nitrogen in a usual manner. [if desired, HMPA or TMEDA (4.6 mmol) was added to this solution]. To the solution was added the 2-alkenyl-1,3-dithiolane (2.0 mmol) at −78 °C under nitrogen; the mixture was then stirred at −78 C for 30 min and at 0 °C for 1 h. The solution was cooled again to −78 °C, and the appropriate alkyl halide (5 mmol) was added with stirring. The mixture was gradually warmed to room temperature, stirred for 2 h, and poured into aqueous NH_4Cl

Table 7. B.p.s and ^{1}H n.m.r. spectral data of the products (**5**), (**12**), (**13**), (**20**), (**21**), (**27**), and (**28**)

Product	B.p. °C/mmHg (lit., b.p.)	^{1}H N.m.r. (δ)
(**5a**)	59—61/2 (52—54/0.2)[22]	0.7—1.6 (9 H, m), 2.1—2.5 (2 H, m), 2.16 (3 H, s), 2.20 (3 H, s), and 5.85 (1 H, t, *J* 7 Hz)
(**5b**)	68—71/1.5 (132/10)[23]	0.7—1.6 (9 H, m), 1.17 (6 H, t, *J* 7 Hz), 2.1—3.0 (6 H, m), and 6.11 (1 H, t, *J* 7 Hz)
(**5c**)	68—71/1.5	0.8—1.8 (9 H, m), 1.9—2.3 (2 H, m), 3.29 (4 H, s), and 5.40 (1 H, t, *J* 7 Hz)
(**5d**)	73—75/1.5	0.7—1.7 (9 H, m), 1.9—2.4 (4 H, m), 2.6—3.1 (4 H, m), and 5.77 (1 H, t, *J* 7 Hz)
(**5e**)	61—62/1.5	0.90 (9 H, s), 2.19 (2 H, d, *J* 8 Hz), 2.20 (6 H, s), and 5.94 (1 H, t, *J* 8 Hz)
(**5f**)	93—95/1.5	2.17 (3 H, s), 2.26 (3 H, s), 3.61 (2 H, d, *J* 8 Hz), 5.95 (1 H, t, *J* 8 Hz), and 7.08 (5 H, s)
(**5g**)	65—67/1.5	0.99 (6 H, t, *J* 7 Hz), 2.23 (3 H, s), 2.24 (3 H, s), 2.43 (4 H, q, *J* 7 Hz), 3.26 (2 H, d, *J* 6 Hz), and 5.85 (1 H, t, *J* 6 Hz)
(**5h**)	87—89/1.5	0.99 (12 H, d, *J* 6 Hz), 2.21 (3 H, s), 2.23 (3 H, s), 2.94 (2 H, sept, *J* 6 Hz), 3.26 (2 H, d, *J* 6 Hz), and 5.80 (1 H, t, *J* 6 Hz)
(**5i**)	95—99/1.5	1.00 (12 H, s), 1.4—1.6 (6 H, m), 2.23 (3 H, s), 2.24 (3 H, s), 3.33 (2 H, d, *J* 6 Hz), and 5.93 (1 H, t, *J* 6 Hz)
(**12a**)	55—56/1.5	0.94 (3 H, d, *J* 6 Hz), 0.9—1.5 (9 H, m), 2.17 (3 H, s), 2.21 (3 H, s), 2.4—3.2 (1 H, m), and 5.64 (1 H, d, *J* 10 Hz)
(**12b**)	71—72/2	0.7—1.5 (18 H, m), 2.4—3.0 (5 H, m), and 5.89 (1 H, d, *J* 9 Hz)
(**12c**)	90—92/1.5	1.31 (3 H, d, *J* 7 Hz), 2.16 (3 H, s), 2.20 (3 H, s), 4.15 (1 H, dq, *J* 9 and 7 Hz), 5.95 (1 H, d, *J* 9 Hz), and 7.19 (5 H, s)
(**13a**)	65—67/6 (41—46/0.07)*	2.29 (6 H, s), 5.04 (1 H, dd, *J* 2 and 10 Hz), 5.11 (1 H, dd, *J* 2 and 17 Hz), 6.23 (1 H, d, *J* 11 Hz), and 6.84 (1 H, ddd, *J* 10, 11, and 17 Hz)
(**13b**)	47—49/2	1.14 (3 H, t, *J* 8 Hz), 1.17 (3 H, t, *J* 8 Hz), 2.63 (4 H, q, *J* 8 Hz), 4.99 (1 H, dd, *J* 2 and 10 Hz), 5.07 (1 H, dd, *J* 2 and 17 Hz), 6.40 (1 H, d, *J* 11 Hz), and 6.80 (1 H, ddd, *J* 10, 11, and 17 Hz)
(**13c**)	72—73/2	0.99 (6 H, t, *J* 7 Hz), 1.2—1.9 (4 H, m), 2.68 (4 H, t, *J* 7 Hz), 4.95 (1 H, dd, *J* 2 and 10 Hz), 5.12 (1 H, dd, *J* 2 and 16 Hz), 6.45 (1 H, d, *J* 11 Hz), and 6.90 (1 H, ddd, *J* 10, 11, and 16 Hz)
(**13d**)	50—52/2	1.24 (12 H, d, *J* 6 Hz), 3.0—3.6 (2 H, m), 5.05 (1 H, dd, *J* 2 and 9 Hz), 5.12 (1 H, dd, *J* 2 and 16 Hz), 6.50 (1 H, d, *J* 10 Hz), and 6.85 (1 H, ddd, *J* 9, 10, and 16 Hz)
(**13e**)	59—61/2	3.29 (4 H, s), 4.6—5.2 (2 H, m), and 5.9—6.6 (2 H, m)
(**13f**)	69—71/2.5	1.7—2.4 (2 H, m), 2.6—3.1 (4 H, m), 4.98 (1 H, dd, *J* 3 and 9 Hz), 5.09 (1 H, dd, *J* 3 and 17 Hz), 6.24 (1 H, d, *J* 10 Hz), and 6.61 (1 H, ddd, *J* 9, 10, and 17 Hz)
(**20a**)	92—94/2	0.7—1.5 (16 H, m), 2.19 (6 H, s), 2.4—3.2 (1 H, m), and 5.60 (1 H, d, *J* 10 Hz)
(**20b**)	130—131/14	0.85 (9 H, s), 0.8—1.4 (7 H, m), 2.18 (6 H, s), 2.2—2.7 (1 H, m), and 5.70 (1 H, d, *J* 10 Hz)
(**20c**)	91—92/1.5	1.00 (12 H, d, *J* 7 Hz), 0.9—1.5 (7 H, m), 2.17 (3 H, s), 2.20 (3 H, s), 3.10 (2 H, sept, *J* 7 Hz), 3.6—4.1 (1 H, m), and 6.01 (1 H, d, *J* 9 Hz)
(**20d**)	112—115/2	0.99 (6 H, d, *J* 6 Hz), 0.7—2.1 (17 H, m), 2.15 (3 H, s), 2.20 (3 H, s), 2.2—2.7 (1 H, m), 2.7—3.4 (1 H, m), 3.6—4.2 (1 H, m), and 6.06 (1 H, d, *J* 9 Hz)

Table 7 (*continued*)

Product	B.p. °C/mmHg (lit., b.p.)	^{1}H N.m.r. (δ)
(**21a**)	62—63/1.5	0.99 (3 H, t, *J* 7 Hz), 1.9—2.6 (2 H, m), 2.22 (6 H, s), 5.2—5.9 (1 H, m), and 6.1—6.7 (2 H, m)
(**21b**)	60—63/1.5	1.02 (3 H, t, *J* 7 Hz), 1.21 (6 H, t, *J* 7 Hz), 1.8—2.5 (2 H, m), 2.72 (3 H, q, *J* 7 Hz), 5.2—6.0 (2 H, m), and 6.3—7.0 (1 H, m)
(**27a**)	51—52/42 (43—45/28)†	2.21 (3 H, s), 4.7—5.3 (2 H, m), and 5.6—6.6 (3 H, m)
(**27b**)	50—52/16 (46—47/14)†	1.27 (3 H, t, *J* 7 Hz), 2.64 (2 H, q, *J* 7 Hz), 4.7—5.2 (2 H, m), and 5.7—6.8 (3 H, m)
(**27c**)	65—68/15 (46.5—48/7)†	0.97 (3 H, t, *J* 6 Hz), 1.3—2.0 (2 H, m), 2.60 (2 H, t, *J* 6 Hz), 4.6—5.3 (2 H, m), and 5.7—6.6 (3 H, m)
(**27d**)	57—58/16 (54—54.5/3)†	1.28 (6 H, d, *J* 7 Hz), 2.7—3.4 (1 H, m), 4.7—5.2 (2 H, m), and 5.7—6.8 (3 H, m)
(**27e**)	54—55/4.5 (83—85/13)†	0.7—1.9 (7 H, m), 2.4—2.8 (2 H, m), 4.7—5.3 (2 H, m), and 5.8—6.6 (3 H, m)
(**27f**)	63—64/15 (67.5—70/15)‡	1.29 (3 H, t, *J* 7 Hz), 1.80 (3 H, s), 2.69 (2 H, q, *J* 7 Hz), 4.75 (2 H, s), and 6.06 (2 H, s)
(**27g**)	91—93/15	1.80 (3 H, s), 0.8—1.9 (7 H, m), 2.4—2.8 (2 H, m), 4.74 (2 H, s), and 6.04 (2 H, s)
(**28e**)	41—44/15 (30—33/15)§	0.98 (3 H, t, *J* 6 Hz), 1.1—2.0 (4 H, m), 2.64 (2 H, t, *J* 6 Hz), 4.99 (1 H, dd, *J* 1 and 17 Hz), 5.11 (1 H, dd, *J* 1 and 10 Hz), and 6.29 (1 H, dd, *J* 10 and 17 Hz)

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(100 ml). It was extracted with ether (50 ml × 2) and the combined extracts were washed with water (80 ml × 2) and brine (50 ml), dried ($MgSO_4$), and concentrated under reduced pressure to give a residue. The product was isolated by distillation or column chromatography from the residue. These are not cases when the yields were determined by g.l.c. The b.p.s and ^{1}H n.m.r. spectral data are summarized in Table 7. The elemental analyses of these products were in satisfactory agreement with calculated values (C ± 0.28%, H ± 0.21%, N ± 0.25%).*

Reaction of 2-Alkenyl-1,3-dithiolanes with an Equimolar Amount of LDA and Methyl Iodide (or Ethyl Iodide) in THF.—To a solution of LDA (8.2 mmol) in THF (70 ml) was added 8.0 mmol of each of compounds (**1**), (**7**), (**15**), and (**23a**) at −78 °C under nitrogen; each reaction mixture was then stirred at −78 °C for 2 h. Methyl iodide [or ethyl iodide in the case of (**23a**)] (10 mmol) was added to the cooled reaction mixture with continued stirring. The mixture was warmed to room temperature, stirred for 1 h, and then poured into water (100 ml) and extracted with ether (50 ml × 2). The extract was washed with water (50 ml × 2) and aqueous NH_4Cl (50 ml), dried ($MgSO_4$), and concentrated under reduced pressure to give a residue. The product (**6**), (**14**), (**22**), or (**29**) in the residue was isolated by chromatography on a short column of silica gel using 50% benzene–hexane as eluant and subsequent distillation under reduced pressure. If desired, the product was further purified by preparative t.l.c. using 30% chloroform–hexane as eluant: (**6**), 53% yield; b.p. 76—82 °C/1.5 mmHg (with decomp.) (Found: C, 40.4; H, 5.35. $C_8H_{12}S_4$ requires C, 40.64; H, 5.12%); δ_H 2.18 (3 H, s), 2.2—2.3 (2 H, m), 2.57 (3 H, s), 2.6—2.8 (2 H, m), 3.1—3.4 (1 H, m), and 5.75 (1 H, t, *J* 4 Hz); δ_C 14.036 (q), 16.843 (q), 36.727 (t), 37.975 (t), 60.666 (d), 131.002 (d), 134.745 (s), and 243.212 p.p.m. (s); (**14**), 62% yield; b.p. 80—86 °C/1.5 mmHg (with decomp.) (Found: C, 45.75; H, 6.17. $C_{10}H_{16}S_4$ requires C, 45.41; H, 6.01%); δ_H 1.04 (3 H, d, *J* 6 Hz), 1.25 (3 H, d, *J* 6 Hz), 2.24 (3 H, s), 2.54 (3 H, s), 2.3—2.6 (1 H, m), 3.0—3.9 (2 H, m), and 5.98 (1 H, s, *J* 6 Hz); δ_C 14.695 (q), 16.609 (q), 18.324 (q), 19.338 (q), 36.747 (d), 37.642 (d), 64.526 (d), 126.518 (s), 131.879 (d), and 236.662 p.p.m. (s); (**22**), 59% yield; b.p. 64—68 °C/1.5 mmHg (with decomp.) (Found: C, 52.3; H, 7.4. $C_{14}H_{24}S_4$ requires C, 52.45; H, 7.55%); δ_H 0.8—1.8 (14 H, m), 1.9—2.2 (1 H, m), 2.27 (3 H, s), 2.57 (3 H, s), 3.0—3.3 (1 H, m), 3.4—3.7 (1 H, m), and 5.98 (1 H, d, *J* 6 Hz); δ_C 13.841 (q), 14.133 (q), 17.350 (t), 19.884 (q), 20.469 (t), 21.054 (q), 32.165 (t), 37.526 (t), 41.328 (d), 46.884 (d), 64.331 (d), 127.688 (d), 130.320 (s), and 237.832 p.p.m. (s); (**29**), 38% yield; b.p. 88—91 °C/2 mmHg (Found: C, 55.35; H, 8.15. $C_8H_{14}S_2$ requires C, 55.12; H, 8.09%); δ_H 1.24 (3 H, t, *J* 7 Hz), 2.4—2.9 (4 H, m), 4.23 (1 H, t, *J* 7 Hz), 4.8—5.2 (4 H, m), 5.83 (1 H, ddt, *J* 9, 17, and 6 Hz), and 6.45 (1 H, dd, *J* 8 and 17 Hz); δ_C 14.625 (q), 23.986 (t), 40.483 (t), 51.365 (d), 117.473 (t), 117.824 (t), 130.051 (d), and 134.205 p.p.m. (d).

Preparation of 2-Benzyl-1,3-dithiolane (**30**).—This compound was prepared by the reaction of phenylacetaldehyde dimethyl acetal with ethane-1,2-dithiol in the same manner as above (95% yield); b.p. 142—144 °C/7 mmHg (lit.,[15] b.p. 122 °C/0.7 mmHg); δ_H 3.01 (2 H, d, *J* 7 Hz), 3.05 (4 H, s), 4.58 (1 H, t, *J* 7 Hz), and 7.13 (5 H, s).

Preparation of 2-Benzyl-2-deuterio-1,3-dithiolane (**40**).—By the method proposed by Ogura and his co-workers,[16] 1-methylsulphinyl-1-methylthio-2-phenylethylene was prepared. A solution of the ethylene (12.1 g, 57.1 mmol) in THF (20 ml) was added slowly to a suspension of lithium aluminium hydride (3.3 g, 87 mmol) in THF (80 ml) at room temperature under nitrogen, and the resulting mixture was stirred for 12 h at that temperature. After work-up, phenylacetaldehyde dimethyl dithioacetal (10.8 g, 96%) was obtained by distillation under reduced pressure. To a solution of the dithioacetal prepared (2.08 g, 10.5 mmol) in THF (50 ml) was added butyl-lithium (1.56M in hexane; 7.5 ml, 11.7 mmol) at −78 °C under nitrogen, and the resulting mixture was stirred for 0.5 h at −78 °C and for 1 h at 0 °C. The mixture was cooled again to −78 °C and a solution of D_2O (0.5 g, 25 mmol) in THF (20 ml) was added. The reaction mixture was stirred for 1 h at 0 °C, and then poured into aqueous NH_4Cl (100 ml), and extracted with ether (50 ml). The ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure to give crude 1-deuterio-phenylacetaldehyde dimethyl dithioacetal (2.1 g). The crude product was mixed with ethane-1,2-dithiol (1.46 g, 15.5 mmol) together with trifluoromethanesulphonic acid (0.1 g, 0.67 mmol) in benzene (20 ml). The mixture was stirred under reflux for 2 h and then poured into aqueous NaOH (50 ml). After work-up as above (**40**) (1.18 g, 57% based on the dithioacetal) was obtained, b.p. 116—119 °C/2 mmHg; δ_H 3.30 (2 H, s), 3.11 (4 H, s), and 7.16 (5 H, s).

Preparation of 2-Benzyl-4,4,5,5-tetradeuterio-1,3-dithiolane (**41**).—In the same manner as that described previously for the preparation of 1,3-dithiolanes, phenylacetaldehyde dimethyl acetal was treated with 1,1,2,2-tetradeuterioethane-1,2-dithiol, which was prepared from 1,2-dibromo-1,1,2,2-tetradeuterio-

* These have been treated as a Supplementary publication [SUP NO. 56650 (3 pp.)] For details of the Supplementary publications scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

ethane,[17] to give (**41**), b.p. 155—158 °C/15 mmHg; δ_H 3.07 (2 H, d, *J* 7 Hz), 4.74 (1 H, t, *J* 7 Hz), and 7.24 (5 H, s).

Reaction of 2-Benzyl-1,3-dithiolane (**30**) *with Bases and Methyl Iodide.—Procedure A.* To a solution of each base (0.71 mmol) [and HMPA (0.13 g, 0.73 mmol) if desired] in an appropriate solvent (10 ml) was added (**30**) (0.058 g, 0.30 mmol) at −78 °C under nitrogen; the resulting mixture was stirred at −78 °C for 0.5 h after which, at the same temperature, methyl iodide (0.11 g, 0.80 mmol) was added. The mixture was warmed to room temperature, stirred for 2 h, and then poured into aqueous NH_4Cl (50 ml) and extracted with ether (80 ml × 2). The ethereal extract was dried ($MgSO_4$) and submitted to g.l.c. analysis.

Procedure B. This procedure is the same as Procedure A except that, after addition of (**30**), the reaction mixture was stirred at −78 °C for 2 h.

Procedure C. This procedure is the same as Procedure A except that, after addition of (**30**), the reaction mixture was stirred for 0.5 h at −78 °C, for a further 1 h at 0 °C, after which it was cooled again to −78 °C before addition of methyl iodide.

Procedure D. To a solution of (**30**) (0.058 g, 0.30 mmol) in an appropriate solvent (7 ml) was added a solution of base (0.71 mmol) in the same solvent (3 ml) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 0.5 h. The other procedures involving addition of methyl iodide and work-up are identical with those described above.

Procedure E. This procedure is the same as Procedure D except that a solution of base was added to a solution of (**30**) at −78 °C, and the mixture was stirred for 0.5 h at −78 °C and for a further 1 h at 0 °C.

Procedure F. To a solution of base (0.71 mmol) [and HMPA (0.13 g, 0.73 mmol) if desired] in an appropriate solvent (10 ml) was added (**30**) (0.058 g, 0.30 mmol) at room temperature under nitrogen. The reaction mixture was refluxed under nitrogen for 3 h. After cooling to room temperature, the mixture was treated with methyl iodide and worked up as described above.

Reaction of 2-Benzyl-2-deuterio- (**40**) *or 2-Benzyl-4,4,5,5-tetradeuterio-1,3-dithiolane* (**41**) *with LDA and Methyl Iodide.*—To a solution of LDA (0.71 mmol) [and HMPA (0.13 g, 0.73 mmol) if desired] in THF or ether (10 ml) was added (**40**) or (**41**) (0.30 mmol) at −78 °C under nitrogen. The reaction mixture was stirred for 0.5 h at −78 °C and 0 °C for a further 1 h. After cooling to −78 °C, the mixture was treated with methyl iodide and then worked up as above.

Isolation of β,β-Bismethylthiostyrene (**34**).—To a cold (−78 °C) solution of LDA (10 mmol) in ether (50 ml) was added (**30**) (0.83 g, 4.2 mmol) under nitrogen. The mixture was stirred for 0.5 h at −78 °C and for 1 h at 0 °C. After the reaction mixture had been cooled to −78 °C, methyl iodide (1.6 g, 11 mmol) was added to it and the mixture stirred at room temperature for 2 h (same as Procedure C). The reaction mixture was poured into aqueous NH_4Cl (100 ml) and extracted with ether (50 ml × 2). The combined extracts were washed with aqueous NH_4Cl (100 ml), water (100 ml × 3), and brine (100 ml), dried ($MgSO_4$), and concentrated under reduced pressure to afford a residue which was purified by column chromatography (silica gel, 30 g; 30% benzene–hexane as an eluant) to give (**34**) (291 mg, 35%). All spectral data of the product were identical with those of authentic sample which was prepared by the known reaction[18] of phenylacetaldehyde dimethyl dithioacetal with butyl-lithium and 2,2′-dipyridyl disulphide, b.p. 84 °C/1.5 mmHg (lit.,[19] b.p. 105—107 °C/0.05 mmHg) (Found: C, 61.35; H, 6.3. Calc. for $C_{10}H_{12}S_2$: C, 61.18; H, 6.16%); δ_H 2.25 (3 H, s), 2.30 (3 H, s), 6.75 (1 H, s), and 7.1—7.5 (5 H, m).

Isolation of 1-Methylthiophenethyl Vinyl Sulphide (**37**).—To a cold (−78 °C) solution of LDA (10 mmol) and HMPA (1.8 g, 10 mmol) in THF (50 ml) was added (**30**) (0.81 g, 4.1 mmol) under nitrogen. After the reaction mixture had been stirred at −78 °C for 2 h, methyl iodide (1.6 g, 11 mmol) was added to it and the mixture stirred at room temperature for 2 h; it was then worked up in the same manner described above (Procedure B). The residue obtained was separated by column chromatography (silica gel, 80 g, 20% benzene–hexane as eluant) to afford (**37**) (278 mg, 32%) and a mixture of (**34**) and (**39**) (132 mg): (**37**), b.p 83—84 °C/2 mmHg (Found: C, 62.9; H, 6.7. $C_{11}H_{14}S_2$ requires C, 62.81; H, 6.68%); δ_H 2.08 (3 H, s), 3.08 (2 H, d, *J* 7 Hz), 4.00 (1 H, t, *J* 7 Hz), 5.25 (1 H, d, *J* 9 Hz), 5.26 (1 H, d, *J* 16 Hz), 6.43 (1 H, dd, *J* 9 and 16 Hz), and 7.16 (5 H, s).

Isolation of β-Methylthiostyrene (**39**).—To a cold (−78 °C) solution of LDA (10 mmol) and HMPA (1.8 g, 10 mmol) in THF (50 ml) was added (**30**) (0.82 g, 4.2 mmol) under nitrogen. The reaction mixture was stirred for 0.5 h at −78 °C and for a further 1 h at 0 °C. After the reaction mixture had been cooled to −78 °C again, methyl iodide (1.6 g, 11 mmol) was added to it. The resulting mixture was stirred at room temperature for 2 h and then worked up in the same manner as above (Procedure C). The residue obtained was purified by column chromatography (silica gel, 30 g; 30% benzene–hexane as an eluant) to afford (**39**) as a mixture of *trans* and *cis* isomer (*ca.* 10:1) (433 mg, 69%); b.p. 110—111 °C/8 mmHg (lit.,[20] b.p. 101.5 °C/5 mmHg) (Found: C, 71.8; H, 6.75. Calc. for $C_9H_{10}S$: C, 71.95; H, 6.71%); δ_H (*trans* isomer)[21] 2.29 (3 H, s), 6.19 (1 H, d, *J* 16 Hz), 6.72 (1 H, d, *J* 16 Hz), and 7.22 (5 H, s); (*cis* isomer)[21] 2.29 (3 H, s), 6.08 (1 H, d, *J* 11 Hz), 6.36 (1 H, d, *J* 11 Hz), and 7.22 (5 H, s).

Isolation of β-Deuterio-β-methylthiostyrene (**42**).—The reaction of (**40**) with LDA and methyl iodide was carried out in the same manner as that described in run 1 of Table 2. The residue obtained by evaporation of the ethereal extract was purified by preparative t.l.c. (silica gel, 20% benzene–hexane as an eluant) to give (**42**) (22 mg, 50%), δ_H 2.22 (3 H, s), 6.17 (1 H, s), and 7.11 (5 H, s).

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