

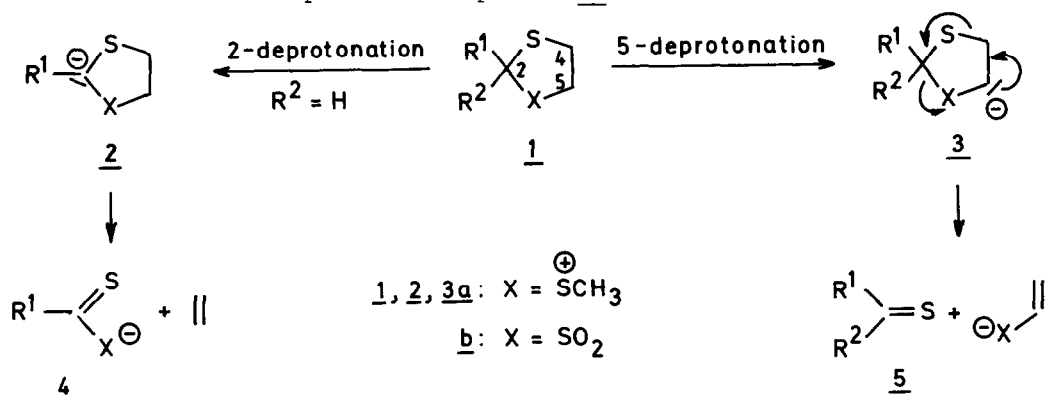
FRAGMENTATION OF 1,3-DITHIOLANE-DERIVED SULFUR YLIDES.
 A CONVENIENT THIOALDEHYDE SYNTHESIS

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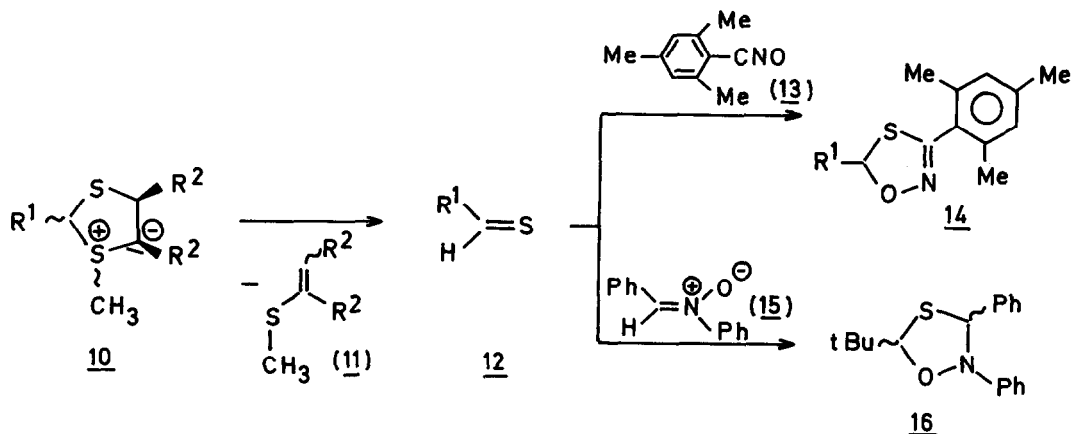
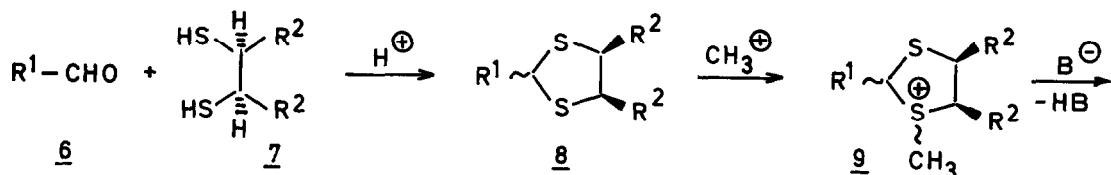
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Summary: S-Ylides 10, which are generated by regioselective deprotonation of 1,3-dithiolanium salts 9 with electron-withdrawing groups in the 4,5 positions, fragment under mild conditions to generate thioaldehydes 12.

The fragmentation of 1,3-dithiolane carbanions is synthetically useful, if one of the sulfur atoms is part of an efficient leaving-group. Thus, 2-oxo-dithiocarboxylates are obtained starting from 1a ($R^1 = \text{acyl}$) via 2-deprotonation¹ and the route 1b→3b→5 allows convenient access to thioketones or thioketenes². Thioaldehydes were virtually inaccessible till very recently, but are now emerging as synthetically useful species³ and so constitute another attractive target of dithiolane fragmentation. However, generation of thioaldehydes from 1 ($R^2 = \text{H}$) requires selective deprotonation to give 3 rather than 2. Moreover, in an exploitation of the particularly efficient fragmentation route from 1a, deprotonation of the methyl group on sulfur must also be excluded. We envisaged that the presence of electron-withdrawing groups in the 4,5 positions of the heterocyclic ring would lead to selective generation of the 5-deprotonated species 3a.



Synthesis of dithiolanes 3 with the desired substitution pattern is achieved via thioacetalization of aldehydes 6 with dithiols 7b⁴ or c⁵. Starting from formaldehyde (6, $R^1 = \text{H}$), reaction with the commercially available acid 7a and subsequent ester formation (MeOH, H_2SO_4 , 20°C, 7 days) is advantageous.



7a: R² = COOH ; 7b: R² = COOMe ; 7c: R² = Ph

8 - 10, 14 : see Table

Methylation of 8 can be carried out with methyl fluorosulfonate ("magic methyl", 3 eq. in CH₂Cl₂ or 1 eq. in MeNO₂, 20°C, 18 hrs; for R² = COOMe) or with trimethyloxonium tetrafluoroborate (in CH₂Cl₂; for R² = Ph); alternatively, methyl trifluoromethylsulfonate can be employed. Without purification, the solutions containing the sulfonium salt 9 are concentrated *in vacuo* and, in THF, treated with lithium diisopropylamide (LDA), Hünig base, or sodium hydride (Table) to afford ylides 10, which undergo spontaneous fragmentation of the type 3a → 5 generating vinylsulfide 11 apparently along with thioaldehydes 12.

By analogy with other thiocarbonyl compounds⁷, products 12 can be efficiently trapped with added mesitronitrile oxide (13) in a 1,3-dipolar cycloaddition to give 1,4,2-oxathiazoles 14. Similarly, benzylidenaniline N-oxide (15) can be used and, with thiopivalaldehyde (12, R¹ = tBu) furnishes heterocycle 16 (Table). On heating in toluene, 16 gives a (3+2) cycloreversion regenerating the thioaldehyde which, in the presence of 2,3-dimethylbutadiene, is intercepted as the Diels-Alder adduct (oil, 39 %).

At 0-20°C, in the absence of a trapping agent, thiopivalaldehyde (12, R¹ = tBu) forms a polymer (49 %). This thermally formed polymer seems to be identical with the known photopolymer⁸ as, on heating, it is cleaved to monomeric thioaldehyde. Generation of the thioaldehyde at 110°C leads to the trimer⁹

as is the case for thiobenzaldehyde (12, $R^1 = \text{Ph}$) independent of temperature.

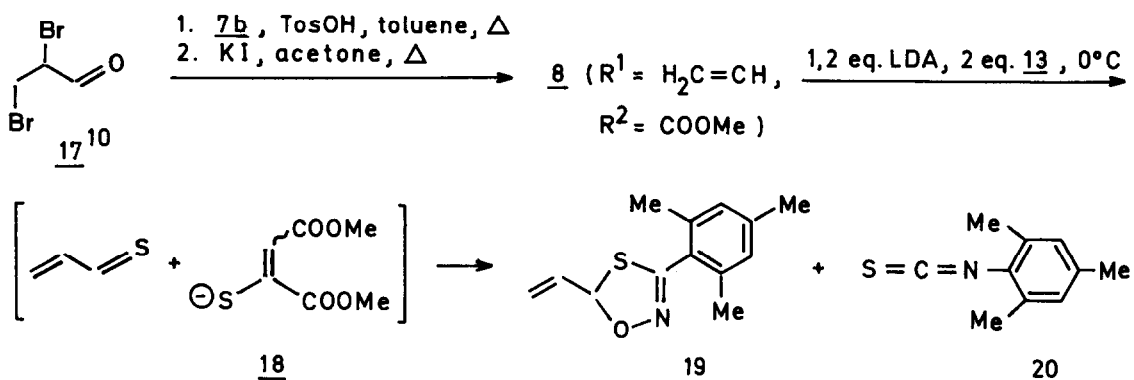
Dithiolane 8 ($R^1 = \text{CH}=\text{CH}_2$, $R^2 = \text{COOMe}$), the precursor of thioacrolein, gives no clean methylation product. However, the thioaldehyde can be generated and trapped by 13 on treatment of 8 with base. The anionic fragment 18 is

Table. Isolated yields and physical data of the new compounds^{a)}

R^1	Dithiolanes <u>8</u>		Trapping products <u>14</u> , <u>16</u> , <u>19</u>			
	R^2	Yield [%]	m.p. [$^{\circ}\text{C}$]	Reagent	yield [%]	m.p. [$^{\circ}\text{C}$]
H	COOH	65 ⁶	210			
	COOMe	43	37-38	<u>13</u>	24 ^{b)} , 27 ^{c)}	75
Me	COOMe	80 ^{g)}	71 ^{e)}	<u>13</u>	63 ^{b)}	69-71
tBu	COOMe	81 ^{f)} , 87 ^{g)}	34	<u>13</u>	65 ^{b)} , 63 ^{c)}	oil
				<u>15</u>	59 ^{b)}	61
Ph	Ph	91 ^{f)}	75	<u>13</u>	47 ^{c)} , 46 ^{d)}	oil (as above)
	COOMe	96 ^{f)} , 45 ^{g)}	59-60 ^{e)}	<u>13</u>	46 ^{d)} , 48 ^{c)}	80-81
$\text{H}_2\text{C}=\text{CH}$	COOMe	68 ^{f)}	84	<u>13</u>	34 ^{c)}	oil

a) Satisfactory microanalytical data and IR, ^1H NMR, and ^{13}C NMR data in accord with expectations were obtained. - b) EtNiPr_2 as base, 0°C . - c) LDA as base, 0°C . - d) NaH as base, 20°C . - e) Mixture of diastereomers; m.p. after recrystallization from dichloromethane/petroleum ether. - f) Toluene, TosOH, water separator, reflux. - g) Methanol, gaseous HCl, 0°C .

deactivated by using an excess of trapping agent 13 to give mesityl isothiocyanate (20, 39 %) via an unstable heterocyclic intermediate.



In conclusion, it has been demonstrated that dithiolanes 8 are convenient precursors of highly reactive thioaldehydes 12 in a one-pot reaction. Considering the mild reaction conditions, the approach nicely complements the photochemical^{3a} or thermal^{3b} routes to 12 and is more variable in R^1 than the base-induced 1,2-elimination methods^{3c}. In comparison with the fluoride-induced cleavage of α -silyldisulfides^{3d}, the ready accessibility of pre-

cursors 8 is advantageous.

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