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THE USE OF SULFINES IN NUCLEOPHILIC ACYLATION REACTIONS[1]

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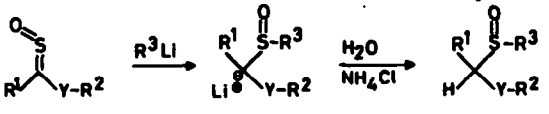
Abstract—The thiophilic addition of MeLi and BuLi to aromatic alkylthio- and arylthio sulfines has been studied. The resulting dithioacetal monoxides are isolated in high yields. Reactions of MeLi with aromatic arylsulphinyl- and arylsulfonyl sulfines give the corresponding dithioacetal di- and trioxides. Acid treatment of dithioacetal monoxides results in aromatic aldehydes. The nucleophilic acylation of the acylanion equivalents obtained from sulfines is investigated. Alkylation of the dithioacetal monoxide anions, prepared *in situ* from MeLi and sulfines of the type Ar(RS)C=S=O, with primary alkyl halides leads to dithioketal monoxide which upon acidolysis under anhydrous conditions are converted into vinylsulfides. The mechanism of the formation of the vinyl sulfides is discussed. The acylanion equivalents are acylated with benzoylchloride, CO_2 and benzaldehyde. The use of Cu^I and 18-crown-6 as a catalyst appears to be crucial in some reactions. Michael additions of the dithioacetal monoxides to acrylonitrile are described.

Sulfur substituted carbanionic species are frequently used as masked acyl anions in nucleophilic acylation processes.[2] In this paper the applicability of sulfines (thione S-oxides) as substrates for nucleophilic acylation reactions will be described.

In the course of our efforts to explore the chemistry of sulfines we prepared a series of sulfines by stepwise oxidation of dithiocarboxylic esters.[3] Reactions of these types of sulfines with alkyl lithium at the sulfine S atom will lead to dithioacetal mono-, di- and trioxides as shown in Scheme 1.



1 (Y = S, SO, SO_2) 2 3

Scheme 1.

The monoxides 3 (Y = S) are of particular interest in connection with the objective of this study, since they are masked carbonyl compounds whose anions, *viz.* 2 (Y=S) may serve as acyl anion equivalents.[4] Accordingly, reaction of these anions with suitable electrophilic reagents and a subsequent demasking procedure leads to carbonyl compounds.[4,5] Therefore, sulfines of the type 1 (Y=S) can be considered as potential substrates in nucleophilic acylation reactions in the manner as outlined in Scheme 2.

Support for the first step in this concept is the thiophilic reaction of diarylsulfines with alkyl lithium to produce alkyl sulfoxides.[6] It should be noted, however, that carbophilic attack by nucleophiles has been observed for chlorosulfines[7] and aryl arylthio sulfines[8] (1, Y=S).

RESULTS AND DISCUSSION

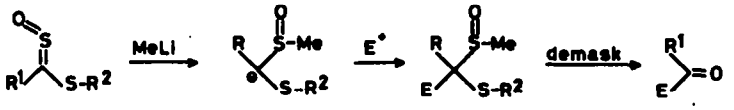
Treatment of *E*-phenyl phenylthio sulfine 1a with one equivalent of MeLi in THF at −78° gave after quenching with aqueous ammonium chloride the anticipated S-methylated product 3a, i.e. α-(phenylthio)benzyl methyl sulfoxide, in 83% yield, as a 1:1 mixture of diastereomers. The spectral data are in full accordance with structure 2a, namely an IR absorption at 1045 cm^{-1} (ν_{SO}) and two singlets for the Me protons (2.05, 2.18) and methine proton (4.82, 4.90) in the NMR spectrum. Demasking of 3a to benzaldehyde was accomplished by treatment with 70% $HClO_4$.

The sulfines 1b–h similarly gave with MeLi the dithioacetal monoxide 3b–h as mixtures of diastereomers. The acidolytic conversion to the aldehydes 4, was performed with $HClO_4$ (70%), gaseous HCl in Et_2O, 6N HCl as well as with 1N HCl. In every case almost the same (high) yields were obtained (Table 1).

Reaction of diphenyl trithiocarbonate S-oxide (1l) with MeLi gave the unstable sulfoxide 3l. Acidolysis of 3l led to thiophenol, which arises from the decomposition of the intermediate phenyl thioformate (PhSCHO).[9]

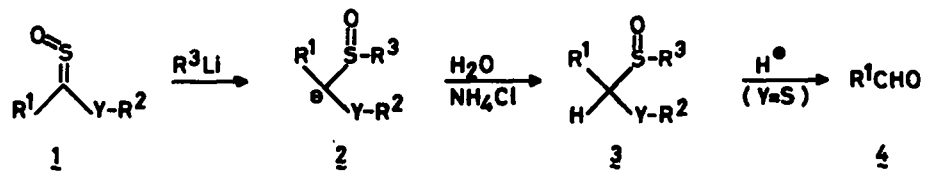
Treatment of the sulfines 1j, d and k with n-BuLi under similar conditions gave the alkylated products 3j, k and l in good yields. Since the isolation and purification of the butyl sulfoxides appeared to be more laborious than that of the corresponding methyl sulfoxides, it was decided to use the latter for further investigations.

Sulfonyl sulfines 1l and m as well as sulfinyl sulfine 1n reacted very smoothly with MeLi to yield the corresponding dithioacetal trioxides 3m and n and the dithioacetal dioxide 3o. The structure of these products



Scheme 2.

Table 1. Conversion of sulfines to dithioacetal mono-, di and trioxides and aldehydes



1 2 3 4

sulfine	R_1	R_2	Y	R_3	product	yield(%) 3	aldehyde 4
1a	Ph	Ph	S	Me	3a	83	88
b	Tol	Ph	S	Me	b	78	90
c	Tol	Et	S	Me	c	63	
d	An	Tol	S	Me	d	84	91
e	Mes	Ph	S	Me	e	46	44[a]
f	Mes	Mes	S	Me	f	74	64[a]
g	Mes	Et	S	Me	g	51	
h	2-$CH_3OC_{10}H_6$	Me	S	Me	h	70	80
i	PhS	Ph	S	Me	i	b	b
j	Ph	Et	S	n-Bu	j	65	85
d	An	Tol	S	n-Bu	k	79	
k	An	Et	S	n-Bu	l	58	
l	Ph	Ph	SO_2	Me	m	80	
m	An	Tol	SO_2	Me	n	84	
n	Ph	Ph	S(O)	Me	o	90	

Tol = p-$CH_3C_6H_4$; An = p-$CH_3OC_6H_4$; Mes = 2,4,6-$Me_3C_6H_4$

[a] Product isolated as the DNPH of mesityl aldehyde; the NMR spectrum of the crude reaction mixture indicated the presence of the aldehyde in almost quantitative yield.

[b] Product unstable (see text)

was based on spectral data (Experimental) and elemental analysis (3a). Furthermore, 3m and e were oxidized with *m*CPBA to the same bis-sulfones (*p*-$MeOC_6H_4(SO_2Me)SO_2C_6H_4Me$-*p*).

The results shown sofar demonstrate that the addition of MeLi to aromatic alkylthio or arylthio sulfines and subsequent protonation offers an efficient route to the dithio-acetal monoxides. The alternative, oxidation of a dithioacetal, has been shown[10] to be less useful, since the corresponding aromatic aldehydes are usually formed by concomitant acidolysis during the oxidation.

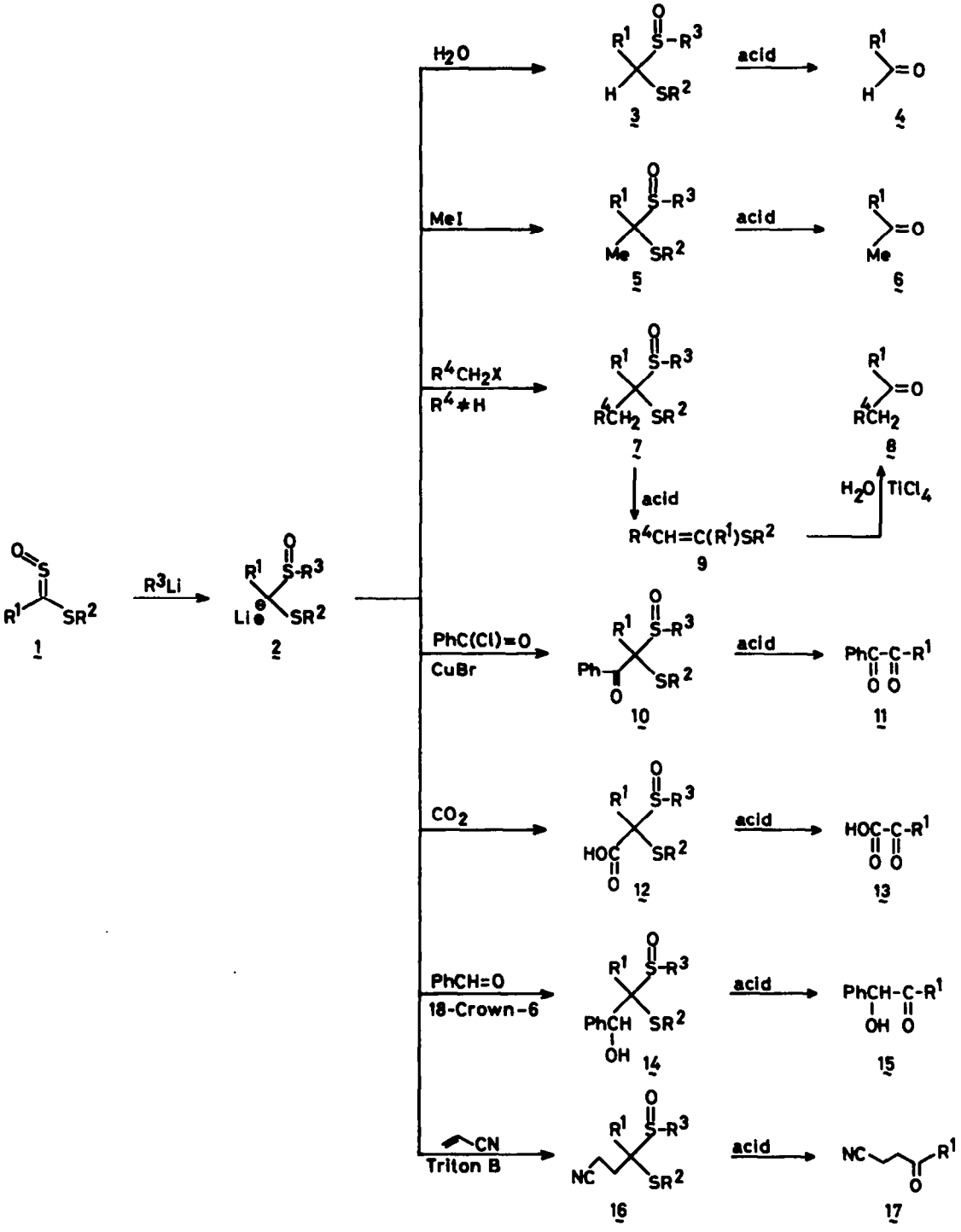
The methylation of sulfinyl and sulfonyl sulfines represent an attractive synthesis of higher oxidized asymmetrically substituted dithioacetals.[10,11]

The alkylation of the acylanion equivalent 2 was investigated with several primary alkylhalides. Treatment of 2a, b, d and j with MeI for 3–5 hr at 20° gave in a smooth reaction the methylated products 5. Subsequent demasking of 5 with an acid catalyst gave the corresponding methyl ketones 6 in good yields (Scheme 3 and Table 2). The intermediate products 5, which consisted of a mixture of diastereomers, were rather unstable, however isolation before demasking turned out to be unneccesary. Reaction of 2b and d with other alkyl halides in the presence of hexamethyl phosphoric triamide (HMPA) gave the alkylated compounds 7, which again were—without insolation—subjected to acid treatment.

When ethereal HCl was used as a demasking agent, the expected ketones 8 were not obtained, but the vinylsulfides 9 were isolated instead. When the deprotection was performed with aqueous acid, the ketones 8 admixed with the vinylsulfides 9 were formed (Table 2). The structure of the vinylsulfides was based on spectral data and on the hydrolysis to the ketones 8 by means of $TiCl_4/H_2O$, according to the procedure of Mukaiyama.[12] The formation of vinylsulfides from dithioketal monoxides under acidic conditions had not been previously observed.

To explain this behaviour of the dithioketal monoxides 7 the mechanism as put forward by Kuhn[11] and Louw[10] may be used when modified as indicated in Scheme 4. Cleavage of the carbon sulfur bond by loss of methanesulfenic acid from the protonated substrate 7, yields a thia-oxonium ion, which upon deprotonation gives rise to the isolated vinylsulfides.

The intermediate thia-oxonium ion also may account for the formation of the ketones 8 when using aqueous demasking conditions (Scheme 4). Remarkably, when methyl iodide is used as the electrophilic quenching reagent for the anions 2, aqueous as well as non-aqueous demasking conditions lead to methyl ketones only. The formation of ketones under non-aqueous acidic condi-



Scheme 3.

tions can be rationalized by assuming a reaction of the sulfenic acid with the thia-oxonium ion and a subsequent spontaneous fragmentation of the thus formed sulfenic ester (Scheme 4).

The alkylation of 2i with beazyl bromide and ethyl iodide gave, after demasking under anhydrous conditions, the ketene dithioacetals 9c and h and trithioorthoester 18. The structure of 9c and h was in accordance with spectral data. Furthermore, the oxidation of the dithioacetal function with one equiv. of *m*CPBA to the corresponding ketene dithioacetal monoxides, and subsequent ethanolysis[13,14] gave ethyl phenylacetate and ethyl propionate, respectively. An authentic sample of 18 was prepared by a thiophilic methylation of diphenyl trithiocarbonate with MeLi.[15]

To account for the deoxygenated product 18 it is suggested that an intramolecular oxidation reduction process of the intermediate O-alkylated product takes place (Scheme 5).

A similar deoxygenation process was proposed during the alkylation of β-oxo-sulfinyl anions[16] and vinylsulfenate anions.[14]

Table 2. Nucleophilic acylation using sulfines

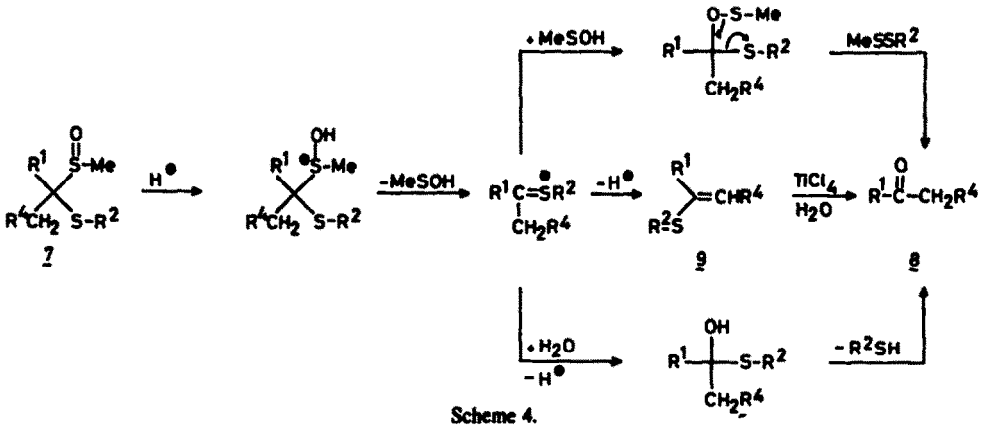
Electrophile	Sulfine (Y=S)	R^1	R^2	R^3	Catalyst	Acidolysis reagent	Products after acidolysis (yield)[a,b]
MeI	1a	Ph	Ph	Me	-	70% $HClO_4$	PhCOMe (66%)
	b	Tol	Ph	Me	-	6N HCl	TolCOMe (65%)
	d	An	Tol	Me	-	6N HCl	AnCOMe (70%)
	j	Ph	Et	n-Bu	-	70% $HClO_4$	PhCOMe (60%)
$PhCH_2Br$	b	Tol	Ph	Me	HMPA	HCl/Et_2O	Tol(PhS)C=CHPh (9a, 90%) [$TolCOCH_2Ph$, 8a, 70%][c]
	d	An	Tol	Me	HMPA	70% $HClO_4$	An(TolS)C=CHPh (9b, 70%) [$AnCOCH_2Ph$, 8b, 61%][c]
	i	PhS	Ph	Me	HMPA	HCl/Et_2O	$(PhS)_2C$=CHPh (9c, 24%) + $(PhS)_2CHSMe$ (18, 52%)
n-BuBr	b	Tol	Ph	Me	HMPA	HCl/Et_2O	Tol(PhS)C=CHPr-n (9d, 78%) [TolCOBu-n, 8c, 63%][c]
	d	An	Tol	Me	HMPA	HCl/Et_2O	An(TolS)C=CHPr-n (9e, 78%) [AnCOBu-n, 8d, 73%][c]
$Br(CH_2)_4Br$	d	An	Tol	Me	HMPA	HCl/Et_2O	An(TolS)C=CH$(CH_2)_3$Br (9f, 80%) [$AnCO(CH_2)_4Br$, 8e, 68%][c]
	d	An	Tol	Me	HMPA	9N HCl	9f (17%) + 8e (58%) [64%][c]
n-HexBr	d	An	Tol	Me	HMPA	HCl/Et_2O	An(TolS)C=CHC_5H_{11}-n (9g, 84%) [AnCOHex-n, 8f, 74%][c]
	d	An	Tol	Me	HMPA	9N HCl	9g (20%) + 8f (62%) [72%][c]
EtI	i	PhS	Ph	Me	HMPA	HCl/Et_2O	$(PhS)_2C$=CHMe (9h, 17%) + 18 (76%)
PhCOCl	a	Ph	Ph	Me	Cu^I	HCl/Et_2O	PhCOCOPh (11a, 54%)
	b	Tol	Ph	Me	Cu^I	HCl/Et_2O	TolCOCOPh (11b, 60%)
CO_2	a	Ph	Ph	Me	-	6N HCl	PhCOCOOH (13a, 72%)
	b	Tol	Ph	Me	-	6N HCl	TolCOCOOH (13b, 66%)
	d	An	Tol	Me	-	6N HCl	AnCOCOOH (13c, 77%)
PhCHO	a	Ph	Ph	Me	18-crown-6	HCl/Et_2O	PhCOCHOHPh (15a, 48%) + $PhCH_2OH$ (40%)
	b	Tol	Ph	Me	18-crown-6	HCl/Et_2O	TolCOCHOHPh (15b, 52%) + $PhCH_2OH$ (42%)
CH_2=CHCN	a	Ph	Ph	Me	Triton B	6N HCl	$PhCOCH_2CH_2CN$ (17a, 49%)
	b	Tol	Ph	Me	Triton B	6N HCl	$TolCOCH_2CH_2CN$ (17b, 60%)

Tol = p-$CH_3C_6H_4$; An = p-$CH_3OC_6H_4$; n-Hex = n-C_6H_{13}; n-Bu = n-C_4H_9

[a] All yields are based on starting sulfine

[b] Yield after acidolysis

[c] Yield of ketone 8 after hydrolysis of vinylsulfide 9

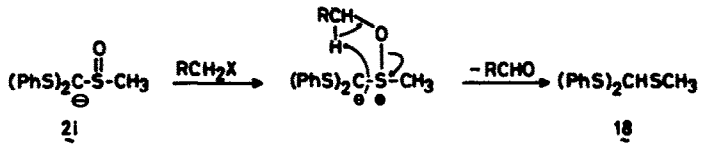


Scheme 4.

The alkylation of the anions 2 with reactive halides such as α-haloketones, α-haloesters and α-halocyanides were unsuccessful. This reluctance is probably caused by a proton exchange between the anion 2 and the activated methylene groups.

By using an acylating agent as the electrophile in the nucleophilic acylation α-functionalized carbonyl compounds are expected to arise (Scheme 3).

Treatment of anions 2a and b with benzoyl chloride at −30° in the presence of CuBr gave the acylated products 10a and b. Acidolysis of the crude products 10a and b gave the corresponding diketones 11a and b in reasonable yields (Table 2). Purification and characterization of 10 was impossible because of the slow spontaneous demasking to the benzils 11a and b. A possible side reaction, viz. the interaction of benzoyl chloride and the



Scheme 5.

sulfoxide group[17] in 2, was suppressed by performing the reaction at low temperature (−30°). Under these conditions the presence of Cu^{I} ions to catalyse the C-acylation turned out to be crucial.

With other acylhalides, however (e.g. acetyl chloride, pivaloyl chloride, ethyl chloroformate, isobutylchloroformate), no acylation was observed, only decomposition of 2 took place.

Quenching of **2a, b** and **d** with CO_2 as the electrophile gave the corresponding carboxylated products **12a, b** and **c**, which after acidolysis resulted in the expected aromatic glyoxylic acids **13a, b** and **c** in good yields (Table 2). Except for **12c** the intermediate acids **12a** and **b** decarboxylated rapidly at room temparature. Therefore, isolation of **12a** and **b** was impossible and immediate acidolysis is recommendable.

Aldehydes, ketones and esters reacted very sluggishly with the anions **2a** and **b**. With aromatic aldehydes a Cannizzaro reaction was observed. Complexing agents like DABCO, TMEDA and HMPA did not enhance the reactivity of the anions **2a** and **b** towards this type of carbonyl compounds. However, in the presence of 18-crown-6 addition of **2a** and **b** to benzaldehyde was achieved. Demasking of the addition products **14a** and **b** with ethereal HCl gave the benzoins **15a** and **b** in reasonable yield (Table 2). The role of the crown ether is 2-fold. Firstly, complexation of the action makes the anion **2** more reactive[18] and secondly, the Cannizzaro reaction is suppressed.[19]

Michael acceptors were also investigated in this context. Conjugate addition of the carbonylanion equivalent **2** to electrondeficient olefins will lead to 1,4-difunctionalized systems (Scheme 3).

Treatment of **3a** and **b** with a large excess of acrylonitrile in the presence of a trace of Triton B gave the expected 1,4-addition products **16a** and **b**, which were isolated in 68 and 73%, respectively. Characterisation of the Michael adducts was based on spectral data and an elemental analysis. Furthermore, demasking with aqueous HCl gave the corresponding γ-keto-cyanides **17a** and **b** in high yields (Table 2). Efforts to add the anions **2** to α,β-unsaturated aldehydes, ketones and esters were not successful; in most cases only polymerisation of the Michael acceptor was observed.

In summary, nucleophilic methylation at the S atom of aromatic arylthio and alkylthio sulfines and subsequent quenching with an electrophile at the sulfine C atom offers a useful extension of nucleophillic acylation via dithioacetal monoxides.

EXPERIMENTAL

IR spectra were taken on a Perkin–Elmer 257 grating spectrometer. NMR spectra were recorded on a Varian T60 or EM 360 spectrometer, using TMS as internal standard. The mass spectral measurements were performed on a Varian MS IB mass spectrometer. Elemental analyses were carried out in the micro analytical department of our laboratory by Mr. J. Diersmann. All m.ps are uncorrected and were determined on a Kofler hot stage.

Assistance during some of the preparations was provided by Miss E. M. M. van Rens, Mr. L. P. L. Kleintjes and Mr. M. H. Janssens.

Sulfines. Syntheses of the sulfines were performed as described in Ref. 3 by stepwise oxidation of the corresponding dithiobenzoates. The oxidation was performed with *m*-chloroperbenzoic acid (*m*CPBA). The sulfines **1a**[20], **d**[21], **e**[20], **f**[22]**g**[22], **i**[23], **k**[21]**l**[20], **m**[21] and **n**[20] have been described previously.

Phenylthio p-tolyl sulfine (**1b**), yield 78%. *E–Z* ratio 6:1. Crystallization from ether afforded the pure *E*-isomer, m.p. 62–64°. IR (KBr) ν(CSO) 1110, 1010, 1000 cm^{-1}. NMR ($CDCl_3$) *E*-isomer δ 2.31 (s, 3H, CH_3), 7.11, 8.15 (ABq, 4H, C_6H_4, J = 8 Hz) 7.38 (s, 5H, C_6H_5); Z-isomer 2.32 (s, 3H, CH_3), 7.38 (m, 9H, aromatic protons) ppm. (Found: C, 64.6; H, 4.7; S, 24.6. $C_{14}H_{12}OS_2$ requires: C, 64.58; H, 4.65; S, 24.63%).

Ethylthio p-tolyl sulfine (**1c**), yield 71%, *E–Z* ratio 1:1. IR (neat) ν(CSO) 1100, 1000 cm^{-1}. NMR ($CDCl_3$) *E*-isomer δ 1.20 (t, 2H, CH_3, J = 7 Hz), 2.45 (s, 3H, CH_3), 2.70 (q, 2H, CH_2), 7.90, 8.30 (ABq, 4H, C_6H_4, J = 8 Hz); *Z*-isomer 1.42 (t, 3H, CH_3), J = 7 Hz), 2.45 (3, 3H, CH_3), 3.21 (q, 2H, CH_2), 7.95 (s, 4H C_6H_4) ppm.

2-Methoxynaphtyl methylthio sulfine (**1h**), yield 68%. *E–Z* ratio 1:1. IR (neat) ν(CSO) 1090, 1000 cm^{-1}. NMR ($CDCl_3$) δ 1.88, 2.33 (s, 3H, SCH_3, *E*-, *Z*-isomer, respectively), 3.89 (s, 3H, CH_3O), 7.20–8.02 (m, 6H, aromatic protons) ppm.

Ethylthio phenyl sulfine (**1j**), yield 74%. *E–Z* ratio 5:4. IR (neat) ν(CSO) 1110, 995 cm^{-1}. NMR ($CDCl_3$) δ 1.12, 1.36 (t, 3H, CH_3, J = 7 Hz, *E*-, *Z*-isomer), 2.58, 3.19 (q, 2H, CH_2, *E*-, *Z*-isomer, respectively), 7.45 (m, 3H, aromatic protons), 8.10–8.31 (m, 2H, aromatic protons, *E*-isomer) ppm.

Alkylation of sulfines. (General procedure). To a stirred solution of the sulfine of choice (~2 mmol) in 25 ml of THF at −78° and under an inert atmosphere was added 1.0 equiv. of alkyllithium soln in hexane or ether. After 10 min at −78° the mixture was poured on 50 ml of sat NH_4Cl aq. The aqueous layer was extracted with ether, the combined organic layers were dried over $MgSO_4$ and the solvents were removed. The residue was recrystallized from ether.

Reaction of MeLi

With phenyl phenylthio sulfine (**1a**). Product **3a**, yield 83%, m.p. 81–82°. IR (KBr) ν(SO) 1045 cm^{-1}. NMR ($CDCl_3$) δ 2.05, 2.18 (s, ratio 1:1, 3H, $S(O)CH_3$), 4.83, 4.90 (s, ratio 1:1, 1H, CH), 7.25 (s, 10H, C_6H_5) ppm.

With phenylthio p-tolyl sulfine (**1b**). Product **3b**, yield 78%, m.p. 119–120°. IR (KBr) ν(SO) 1050 cm^{-1}. NMR ($CDCl_3$) δ 2.35 (s, 3H, $S(O)CH_3$), 2.40 (s, 3H, CH_3), 4.82, 4.90 (s, ratio 1:3, 1H, CH), 7.00–7.25 (m, 9H, aromatic protons) ppm.

With ethylthio p-tolyl sulfine (**1c**). Product **1c**, yield 63%. IR (neat) ν(SO) 1035 cm^{-1}. NMR ($CDCl_3$) δ 1.28, 1.30 (t, ratio 1:2, 3H, CH_2CH_3, J = 7 Hz), 2.22, 2.42 (s, ratio 1:2, 3H, $S(O)CH_3$), 2.30 (s, 3H, CH_3), 2.70, 2.90 (1, ratio 2:1, 2H, CH_2), 4.76, 4.88 (s, ratio 1:2, 1H, CH), 7.30 (s, 4H, C_6H_4) ppm.

With p-methyloxyphenyl p-tolylthio sulfine (**1d**). Product **3d**, yield 84%, m.p. 112–114°. IR (KBr) ν(SO) 1035 cm^{-1}. NMR ($CDCl_3$) δ 2.20, 2.32 (s, ratio 1:1, 3H, $S(O)CH_3$), 2.28 (s, 3H, CH_3), 3.78 (s, 3H, CH_3O), 4.82, 4.95 (s, ratio 1:1, 1H, CH), 6.88, 7.42 (ABq, 4H, $CH_3OC_6H_4$, J = 9 Hz), 7.19, 7.36 (ABq, 4H, $CH_3C_6H_4$, J = 8 Hz) ppm.

With mesityl phenylthio sulfine (**1e**). Product **3e**, yield 46%. IR (neat) ν(SO) 1050 cm^{-1}. NMR ($CDCl_3$) δ 2.24, 2.42 (s, ratio 2:3, 3H, $S(O)CH_3$), 2.36 (s, 3H, CH_3), 2.53 (s, 6H, CH_3), 5.35, 5.50 (s, ratio 3:2, 1H, CH), 6.95 (s, 2H, C_6H_2), 7.50–7.80 (m, 5H, C_6H_5) ppm.

With mesityl mesitylthio sulfine (**1f**). Product **3f**, yield 74%.

m.p. 148–149°. IR (KBr) ν(SO) 1030 cm^{-1}. NMR ($CDCl_3$) δ 2.35 (s, 3H, S(O)CH_3), 2.06, 2.54, 2.70 (s, ratio 1:3:2, 18H, CH_3), 5.20(s, 1H, CH), 7.03 (s, 4H, C_6H_2) ppm.

With ethylthio mesityl sulfine (1g). Product 3g, yield 51%. IR (neat) ν(SO) 1055 cm^{-1}. NMR ($CDCl_3$) δ 1.35 (t, 3H, CH_2CH_3, J = 7 Hz), 2.36 (s, 3H, S(O)CH_3), 2.50 (s, 9H, CH_3), 2.93 (q, 2H, CH_2), 5.05 (s, 1H, CH), 6.98 (s, 2H, C_6H_2) ppm.

With 2-methoxynaphtyl methylthio sulfine (1h). Product 3h, m.p. 102–105°. IR (KBr) ν(SO) 1035 cm^{-1}. NMR ($CDCl_3$) δ 2.16 (s, 3H, S(O)CH_3), 2.57 (s, 3H, SCH_3), 3.88 (s, 3H, CH_3O), 5.42 (s, 1H, CH), 7.04–7.98 (m, 6H, aromatic protons) ppm.

With diphenyl trithiocarbonate-S-oxide (1i). Product 2i is labile and cannot be isolated in pure state. IR (neat) ν(SO) 1055 cm^{-1}. NMR ($CDCl_3$) δ 2.68 (s, 3H, S(O)CH_3), 5.13 (s, 1H, CH), 7.35 (s, 10H, C_6H_5) ppm.

With phenyl phenylsulfonyl sulfine (1l). Product 3m, yield 80%, m.p. (ethanol) 152–154°. IR (KBr) ν(SO) 1050, ν(SO_2) 1320, 1140 cm^{-1}. NMR ($CDCl_3$) δ 2.34, 2.38 (s, ratio 3:5, 3H, S(O)CH_3), 4.85, 5.13 (s, ratio 5:3, 1H, CH), 7.36–7.57 (m, 8H, aromatic protons), 7.73–7.91 (m, 2H, aromatic protons) ppm. Oxidation of 3m with 1 equiv. of *m*CPBA gave the corresponding bis-sulfone, yield 72%, m.p. 180–181° (ethanol). IR (KBr) ν(SO_2) 1320, 1140 cm^{-1}. NMR ($CDCl_3$) δ 3.45 (s, 3H, SO_2CH_3), 5.49 (s, 1H, CH), 7.45 (s, 8H, aromatic protons), 7.69–7.82 (m, 2H, aromatic protons) ppm. (Found: C, 54.2; H, 4.6. $C_{14}H_{14}O_4S_2$ requires: C, 54.18; H, 4.56; S, 20.56%).

With p-methoxyphenyl p-tolylsulfonyl sulfine (1m). Product 3n, yield 84%, m.p. 149–150° (EtOH). IR (KBr) ν(SO) 1055, ν(SO_2) 1320, 1145 cm^{-1}. NMR ($CDCl_3$) δ 2.30 (s, 3H, CH_3), 2.40, 2.49 (s, ratio 1:3, 3H, S(O)CH_3), 3.72 (s, 3H, CH_3O), 4.96, 5.21 (s, ratio 3:1, 1H, CH), 6.80, 7.30 (ABq, 4H, $CH_3OC_6H_4$, J = 9 Hz), 7.15, 7.53 (ABq, 4H, $CH_3C_6H_4$, J = 8 Hz) ppm. (Found: C, 56.9; H, 5.4; S, 18.9. $C_{16}H_{16}O_4S_2$ requires: C, 56.78; H, 5.36; S, 18.95%).

With phenyl phenylsylphinyl sulfine (1n). Product 3o, yield 90%. IR (neat) ν(SO) 1050 cm^{-1}. NMR ($CDCl_3$) δ 2.50, 2.72, 2.80 (s, ratio 2:1:1, 3H, S(O)CH_3), 4.48, 4.51, 4.84, 5.03 (s, ratio 1:1:1:1, 1H, CH), 7.24–7.58 (m, 10H, C_6H_5) ppm. Oxidation of 3o with *m*CPBA gave a product, which appeared to be identical with the bis-sulfone obtained from 3m upon oxidation.

Reactions of BuLi

With ethylthio phenyl sulfine (1j). Product 3j, yield 65%, m.p. 65–68°. IR (KBr) ν(SO) 1030 cm^{-1}. NMR ($CDCl_3$) δ 0.83–2.0 (m, 7H, S(O)$CH_2C_3H_7$), 1.30, 1.35 (t, ratio 4:1, 3H, SCH_2CH_3, J = 7 Hz), 2.38, 2.62 (m, ratio 4:1, 2H, S(O)CH_2), 2.94, 2.97 (q, ratio 1:4, 2H, CH_2S), 4.78, 5.85 (s, ratio 4:1, 1H, CH), 7.44 (s, 5H, C_6H_5) ppm.

With p-methoxyphenyl p-tolylthio sulfine (1d). Product 3k, yield 79%, m.p. 84–85°. IR (KBr) ν(SO) 1025 cm^{-1}. NMR ($CDCl_3$) δ 0.82–1.90 (m, 7H, C_3H_7), 2.30 (s, 3H, CH_3), 2.56 (m, 2H, S(O)CH_2), 3.74 (s, 3H, CH_3O), 4.80, 4.91 (s, ratio 1:1, 1H, CH), 6.83, 7.42 (ABq, 3H, $CH_3OC_6H_4$, J = 9 Hz), 7.12 (s, 4H, $CH_3C_6H_4$) ppm. (Found: C, 65.6; H, 6.9; S, 18.3. $C_{19}H_{24}O_2S_2$ requires: C, 65.48; H, 6.94; S, 18.40%).

With ethylthio p-methoxyphenyl sulfine (1k). Product 3l, yield 58%, m.p. 68–69°. IR (KBr) ν(SO) 1030 cm^{-1}. NMR ($CDCl_3$) δ 0.86–1.90 (m, 7H, C_3H_7), 1.28, 1.32 (t, ratio 3:1, 3H, SCH_2CH_3, J = 7.5 Hz), 2.48 (m, 2H, S(O)CH_2), 2.83, 2.95 (q, 2H, SCH_2), 3.70 (s, 3H, CH_3O), 4.93, 5.08 (s, ratio 1:3, 1H, CH), 6.78, 7.32 (ABq, 4H, C_6H_4, J = 9 Hz) ppm.

Acidolysis of the dithioacetal monoxides 3 (General procedure). The dithioacetal monoxide 3(a–l), dissolved in ether–CH_2Cl_2 1:1, was treated with a small amount of the acidic catalyst. After stirring for 1 hr at 0° sat NH_4Cl aq was added. The aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% $NaHCO_3$ aq, with water, dried over $MgSO_4$ and concentrated. The aldehyde was isolated by column chromatography. In some cases the aldehyde was isolated from the crude mixture as its corresponding DNPH (see Table 1). The following catalysts were employed: 70% $HClO_4$ (0.1–0.2 ml), 1N HCl (3–5 ml), 6N HCl (3–5 ml), ethereal HCl (2–4 ml). The results obtained with different catalysts were nearly identical.

Alkylation of dithioacetal monoxide anions 2. (General procedure). The soln obtained after the addition of MeLi to the sulfines 1 (~2 mmol) was concentrated *in vacuo* to about 1/5 of its original volume. Then HMPA (~2 ml) and 1.1–1.8 equiv. of the appropriate alkyl halide were added. (No HMPA was required when CH_3I was used). This mixture was stirred for 2.5–18 hr at 20°. When the alkylation was complete, the intermediate disubstituted dithioacetal monoxide was demasked immediately by treatment with an acidic catalyst (Table 2). After stirring for 3–4 hr at 20° in the presence of the acidic catalyst, the mixture was worked up to as described above.

The crude mixture was chromatographed on preparative tlc Development with benzene and elution with ether afforded the ketones 6 and 8. The vinylsulfides 9 were obtained after development with CCl_4 and elution with ether.

The vinylsulfides 9 were characterized by hydrolysis to the corresponding ketones 8. To a soln of the vinylsulfide 9 (~2 mmol) in 25 ml of acetonitrile was added 2 equiv. of $TiCl_4$ and after 0.3 hr 4 equiv. of H_2O. After stirring for 16 hr at 20° NH_4Cl aq was added, the aqueous layer was extracted twice with ether. The organic layer was washed with water, dried over $MgSO_4$ and the solvents were removed. Column chromatography of the residue afforded the ketones 8.

Alkylation with MeI. Treatment of the anions 2a, b, d and j with 1.1–1.3 equiv. of MeI for 3–5 hr at 20° gave after demasking with 70% $HClO_4$, 6N HCl or anhydrous HCl in ether the corresponding methylketones in 60–70% (Table 2).

Alkylation with benzyl bromide

Anion 2b (1.54 mmol) was alkylated with 0.30 g (1.75 mmol, 1.1 equiv.) of benzyl bromide. After 5 hr at 20° 3 ml of ether containing a trace of anhyd HCl was added. Chromatography gave 0.44 g (90%) of 9a (ratio of isomers 5:2). NMR (CCl_4) δ 2.30, 2.34 (s, ratio 5:2, 3H, CH_3), 3.96, 4.30 (s, ratio 5:2, 1H, =CH), 6.80–7.60 (m, 14H, aromatic protons) ppm. Treatment of 9a with $TiCl_4$–H_2O gave ketone 8a (0.23 g, 70%), m.p. 109–110° (EtOH) (lit.[24] 109–110°).

Anion 2d (1.72 mmol) was alkylated with 0.32 g (1.85 mmol, 1.1 equiv.) of benzyl bromide. After 25 hr at 20° 0.3 ml of 70% $HClO_4$ was introduced. Isolated was 0.39 g (70%) of 9b, (ratio of isomers 6:1). NMR (CCl_4) δ 2.11, 2.20 (s, ratio 6:1, 3H, CH_3), 3.62 (s, 3H, OCH_3), 6.68 (s, 1H, =CH), 6.80–7.50 (m, 8H, aromatic protons) ppm. Hydrolysis of 9b with $TiCl_4$–H_2O gave 8b (0.25 g, 61%), m.p. 74–76° (lit.[25] 77°); semi-carbazone m.p. 144–146° (lit.[26] 148–149°).

Anion 2i (1.81 mmol) was treated with 0.55 g (3.25 mmol, 1.80 equiv) of benzyl bromide. After 5 hr at 20° 5 ml of ethereal HCl was added to give 0.14 g (24%) of 9c. [m.p. 42–44° (pentane). NMR (CCl_4) δ 7.10 (s, 1H, =CH), 7.23–7.40 (m, 15H, C_6H_5) ppm. M^+ 320.0702. $C_{20}H_{16}S_2$ requires: 320.0692] and 0.23 g (52%) of the trithio-orthoester 10. NMR (CCl_4) δ 2.35 (s, 3H, CH_3), 5.18 (s, 1H, CH), 7.18–7.64 (m, 10H C_6H_5) ppm. Product 9c (0.15 g, 0.63 mmol) in 20 ml of ether was oxidized with 1 equiv. (0.13 g) of *m*CPBA. After 5 hr at 20° 5 ml of ethanol and 5 ml of ethereal HCl was added. After 2 hr the acids were removed by 5% $NaHCO_3$ soln. Chromatography gave 67 mg (65%) of ethyl phenylacetate.

Alkylation with n-butyl bromide

Anion 2b (1.54 mmol) was treated with 0.35 g (2.56 mmol, 1.6 equiv) of n-BuBr for 16 hr at 20°. Acidolysis with ethereal HCl gave 0.04 g (16%) of *p*-tolualdehyde and 0.33 g (78%) of 9d (ratio of isomers 3:2). NMR (CCl_4) δ 0.98 (t, 3H, CH_3, J = 7.5 Hz), 1.38 (m, 2H, CH_2CH_3), 2.10, 2.50 (*q*, ratio 2:3, 2H, $CH_2CH_2CH_3$), 2.20 (s, 3H, CH_3), 6.04, 6.30 (t, ratio 2:3, 1H, =CH, J = 7.5 Hz), 6.90–7.42 (m, 9H, aromatic protons) ppm. Hydrolysis of 9d with $TiCl_4$–H_2O gave ketone 8c (0.17 g, 63%), n_D^{20} 1.5295 (lit.[27], n_D^{20} 1.5287). Semicarbazone m.p. 198–200° (lit.[27] 199–201°).

Anion 2d (1.72 mmol) was alkylated with 0.40 g (2.9 mmol, 1.7 equiv.) of n-BuBr. After 18 hr at 20° etheral HCl was added to give 9e (78%), ratio of isomers 1:2. NMR (CCl_4) δ 0.89, 0.96 (t, ratio 2:1, 3H, CH_2CH_3, J = 7 Hz), 1.26, 1.40 (m, ratio 2:1, 2H, $CH_2CH_2CH_3$), 2.10, 2.33 (*q*, ratio 2:1, 2H $CH_2C_2H_5$, J = 7 Hz), 2.20, 2.23 (s, ratio 1:2, 3H, CH_3), 3.71 (s, 3H, CH_3O), 5.98, 6.28 (t, ratio 1:2, 1H, =CH, J = 7 Hz), 6.90–7.40 (m, 8H, aromatic pro-

tons) ppm. Hydrolysis of **9e** with $TiCl_4$–H_2O gave 0.24 g (73%) of ketone **8d**, m.p. 27–28° (lit.[28] 26°). DNPH m.p. 154–155° (lit.[28] 157°).

Alkylations with other alkyl halides

Anion **2d** (1.72 mmol) was treated with 0.45 g (2.12 mmol, 1.2 equiv) of *1,4-dibromobutane*. After 15 hr at 20° 4 ml of 9N HCl was introduced. Chromatography gave 0.26 g (58%) of **8e** and 0.11 g (17%) of **9f**. Demasking with ethereal HCl gave **9f** in 80% yield, as a 5:1 mixture of isomers. NMR (CCl_4) δ 2.25, 2.30 (s, ratio 5:1, 3H, CH_3), 2.30 (m, 2H, CH_2), 2.72, 2.85 (*q*, ratio 5:1, 2H, $=CHCH_2$, J = 7 Hz), 3.45 (t, 2H, CH_2Br, J = 7 Hz), 3.79 (s, 3H, CH_3O), 6.28, 6.84 (t, ratio 1:5, 1H, =CH), 6.78–7.50 (m, 8H, aromatic protons) ppm. Hydrolysis of **9f** with $TiCl_4$–H_2O gave 0.30 g (64%), 0.32 g (68%) of **8e** respectively m.p. (CCl_4) 68–70°. DNPH m.p. 159–160°. NMR ($CDCl_3$) δ 1.90 (m, 4H, CH_2), 2.94 (t, 2H, CH_2CO, J = 7 Hz), 3.34 (t, 2H, CH_2Br, J = 7 Hz), 3.82 (s, 3H, CH_3O), 6.92, 7.94 (ABq, 4H, C_6H_4, J = 9 Hz) ppm. M^+ = 270.0258: $C_{12}H_{15}O_2Br$ requires: 270.0250.

Anion **2d** (1.72 mmol) was treated with 0.30 g (1.83 mmol, 1.1 equiv.) of *n-hexyl bromide*. After 16 hr at 20° 5 ml of 9N HCl was added. Chromatography gave 0.24 g (62%) of **8f** and 0.12 g (20%) of **9g**. Demasking with ethereal HCl gave the **9g** in 84% yield. NMR (CCl_4) δ 0.90 (t, 3H, CH_3, J = 7 Hz), 1.38 (m, 6H, CH_2), 2.23 (s, 3H, CH_3), 2.48 (q, 2H, $=CHCH_2$, J = 7 Hz), 3.76 (s, 3H, CH_3O), 6.31 (t, 1H, =CH), 6.74–7.50 (m, 8H, aromatic protons) ppm. Hydrolysis of **9g** with $TiCl_4$–H_2O gave **8f** in 72 and 74%, respectively. M.p. (ethanol) 41–43° (lit.[29] 43°), semicarbazone m.p. 127–129° (lit.[29] 130°).

Anion **2i** (1.81 mmol) was treated with 0.50 g (3.25 mmol, 1.8 equiv.) of *ethyl iodide*. After 16 hr at 20° 5 ml of ethereal HCl was added. Chromatography gave 0.35 g (76%) of **1f** and 0.080 g (17%) of **9h**. NMR (CCl_4) δ 2.10 (d, 3H, CH_3, J = 7 Hz), 6.48 (q, 1H, =CH), 7.12–7.28 (m, 10H, C_6H_5) ppm (M^+: 257.9744. $C_{15}H_{14}S_2$ requires: 257.9758). Oxidation of **9h** with *m*CPBA and subsequent ethanolysis gave ethyl propionate in 46%.

Acylation with benzoylchloride. To a cooled (−78°) solution of **2b** (1.54 mmol) in 25 ml of THF was added 0.10 g (0.70 mmol) of CuBr. After 30 min the temp was raised to −30° and 0.20 g (1.43 mmole, 0.9 equiv.) of benzoylchloride in 5 ml of THF was slowly introduced. After stirring for 6.5 hr at −30° the mixture was poured on sat NH_4Cl aq. The aqueous layer was extracted twice with ether. The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated. Preparative tlc of the residue (development with ether, elution with MeOH) gave 0.46 g of the acylated **10b**. IR (KBr) ν(CO) 1700, ν(SO) 1065 cm^{-1}. Treatment of **10b** with HCl/ether (15 ml) for 3 hr at 20° gave after the usual work up, chromatography and crystallization from EtOH 0.19 (60%) of **11b**, m.p. 30–31° (lit.[30] 31°).

Anion **3a** (1.60 mmol) gave under the same conditions as described for **3b** upon treatment with CuBr (0.13 g), benzoylchloride (0.20 g, 1.43 mmol) and subsequent acidolysis with ethereal HCl benzil (**11a**, 54%).

Reaction with CO_2. To a soln of **3d** (1.72 mmol) in 25 ml of THF was added an excess (~5 g) of CO_2 (solid). After 3 hr the mixture was extracted twice with 25 ml of water. The aqueous layer was carefully acidified with 4N HCl. The white ppt was filtered off, washed with water and dried to give 0.41 g (68%) of **12e**, m.p. 104–105°. IR (KBr) ν(COOH) 3000–2300, ν(SO) 995 cm^{-1}. NMR ($CDCl_3$) δ 2.10, 2.12 (s, ratio 1:1, 3H, $S(O)CH_3$), 2.28 (s, 3H, CH_3), 3.67 (s, 3H, CH_3O), 5.88–6.73, 8.12 (m, 8H, aromatic protons), 8.70 (s, 1H, COOH) ppm. Treatment of the crude mixture with 10 ml of 6N HCl for 2 hr at 20° gave after base-acid separation and crystallisation from CCl_4 0.24 g (77%) of *p*-methoxyphenyl glyoxylic acid (**13e**), m.p. 91–92° (lit.[31] 90°).

In the same way as described above phenyl glyoxylic acid (**13a**) was obtained in 72% from **2a**. Treatment of **2b** with CO_2 gave after acidolysis *p*-tolyl glyoxylic acid (66%). The intermediate carboxylic acids **12a** and **b** were too unstable to permit their isolation.

Reactions with benzaldehyde

Anion **2b** (1.54 mmol) in 5 ml of THF was treated at 20° with 0.25 g (2.36 mmol of benzaldehyde and 0.40 g of 18-crown-6. After 2 days at 20° the mixture was quenched with sat NH_4Cl aq. The aqueous layer was extracted twice with 35 ml of ether. The combined organic layers were washed with water, dried over $MgSO_4$ and the solvents were partially removed. The resulting soln was treated with 5 ml of ethereal HCl. After stirring for 2 hr at 20° the reaction was worked up in the usual way. Chromatography on prep tlc (developed with $CHCl_3$, eluted with ether) gave 0.07 g (42%) of benzyl alcohol and 0.18 g (52%) of benzoin **15b**, m.p. 106–108° (lit.[30] 110–111°). Oxidation of **15b** with I_2 and $NaOMe$[32] gave the diketone **11b**.

Anion **2a** (1.60 mmol) was treated with 0.25 g (2.36 mmol) of benzaldehyde and 0.40 g of 18-crown-6. After 2 days the adduct **14a** was demasked with ethereal HCl and after work up and chromatography 0.16 g (48%) of benzoin (**15a**) and 0.07 g (40%) of benzyl alcohol was isolated.

Reactions with acrylonitrile

A mixture of 0.27 g (1.0 mmol) of **3b**, 0.2 ml of Triton B (40% in MeOH) and 0.28 g (5.3 mmol) of acrylonitrile in 15 ml of THF was kept for 3 days at 20°. The mixture was quenched with sat NH_4Cl aq. The aqueous layer was extracted twice with $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$ and the solvents were removed. Crystallisation from ether gave 0.25 g (73%) of **16b**, m.p. 115–116°. IR (KBr) ν(CN) 2260, ν(SO) 1060 cm^{-1}. NMR ($CDCL_3$) δ 2.10, 2.14 (s, ratio 1:1, 3H, $S(O)CH_3$), 2.28 (s, 3H, CH_3), 2.0–2.8 (m, 4H, CH_2), 7.0–7.5 (m, 9H, aromatic protons) ppm. Acidolysis of **16b** with 5 ml of 6N HCl gave, after crystallisation from CCl_4, ketone **17b**, yield 81%, m.p. 74–76° (lit.[33] 76°). IR (KBr) ν(CN) 2265, ν(CO) 1680 cm^{-1}. NMR ($CDCl_3$) δ 2.32 (s, 3H, CH_3), 2.70 (t, 2H, CH_2, J = 7 Hz), 3.36 (t, 2H, CH_2), 7.18, 7.80 (ABq, 4H, C_6H_4, J = 8 Hz) ppm.

Treatment of **3a** (0.26 g, 1.0 mmol) with 0.27 g (5.0 mmol) of acrylonitrile and 0.2 ml of Triton B gave, in same way as described above, 0.21 g (68%) of adduct **16a**, m.p. 97–98°. IR (KBr) ν(CN) 2260, ν(SO) 1055 cm^{-1}. NMR ($CDCl_3$) δ 2.15 (s, 3H, $S(O)CH_3$), 2.0–2.9 (m, 4H, CH_2), 7.00–7.25 (m, 10H, C_6H_5) ppm. (Found: C, 64.6; H, 5.4; N, 4.8. $C_{17}H_{17}NOS_2$ requires: C, 64.73; H, 5.43; N, 4.44%). Acidolysis of **16a** with 6N HCl gave after crystallisation from CCl_4 the γ-keto cyanide **17a** (70%), m.p. 75–76° (lit.[34] 76°). IR (KBr) ν(CN) 2270, ν(CO) 1680 cm^{-1}. NMR ($CDCl_3$) δ 2.76(t, 2H, CH_2, J = 7 Hz), 3.35 (t, 2H, CH_2), 7.0–7.8 (m, 5H, C_6H_5) ppm.

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