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Benzo[b]thiophenium S,C-Ylides: Preparation, Structure and Comparison with Thiophenium Analogues

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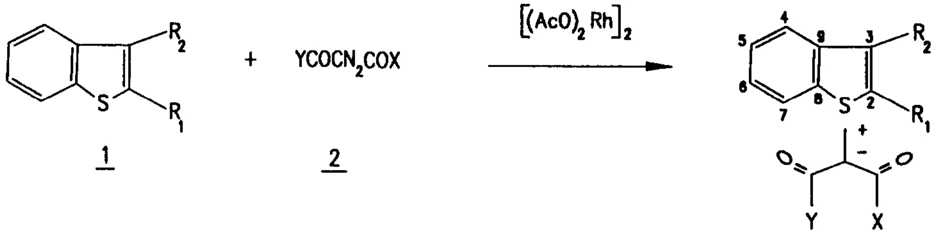
Abstract: A series of new S,C-ylides derived from benzo[b]thiophene and β-dicarbonyldiazocompounds were prepared and characterised NMR (^{1}H,^{13}C) studies revealed that ylides substituted additionally at position 2 of the thiophene ring can exist as pairs of diastereoisomers, not interchangeable at room temperature The slow exchange between two sites was attributed to the restricted rotation about the ylidic S-C bond The crystal structure determined for one ylide demonstrated different molecular environment for two parts of the β-dicarbonyl ylidic substituent with respect to the benzothiophene ring The prepared ylides were found to be much less reactive than the previously studied thiophenium S,C-ylides

We have recently reported[1] that substituted thiophenes react with diazocompounds in the presence of rhodium acetate giving, depending on the substrates used, stable S,C-ylides or the products of their further transformations. The scope of this reaction has been presented in a recent review.[2] The direct formation of the corresponding S,C-ylide from benzo[b]thiophene has been, to our knowledge, reported only in a single case [3] Other known, isolable S-substituted derivatives of benzo[b]thiophene include S-alkyl derivatives and S-mono- and dioxides [2,4] In this work we extended our studies on the S,C-ylides to the family of the benzo[b]thiophene derivatives, with the particular aim of comparing the properties of these products with those studied previously

RESULTS AND DISCUSSION

Five substituted benzo[b]thiophenes (1a-e), as well as the parent compound (1f), were prepared according to the literature procedures and were reacted with diazocompounds (2) derived from acetoacetate and malonate esters, and from dimedone in order to synthesise the corresponding S,C-ylides (3) (Equation 1)



(1)

3

1	R^1	R^2
a	Br	Br
b	Cl	Cl
c	COCl	Cl
d	CO$_2$Me	Cl
e	Me	H
f	H	H

2	Y	X
a	Me	OEt
b	Me	OtBu
c	OEt	OEt
d	OMe	OMe
e	CH$_2$CMe$_2$CH$_2$	

1c and **1d** failed to react with the diazocompounds, and **2e** gave **3** only with the unsubstituted substrate **1f** It is likely that steric effects are responsible for the failure to form products **3** congested at the ylidic function Eleven ylides, **3a-l**, and one ylide, **3m** (derived from dibenzo[b,d]thiophene) were synthesised according to Equation 1, and the results of these syntheses are summarised in Table 1 The structure of products **3a-m** was determined by spectroscopic techniques (IR, ^{1}H and ^{13}C NMR, and MS), the structure of **3l** was additionally determined by X-ray diffraction. IR spectroscopy demonstrated the lowering of the carbonyl frequency, similar to that observed before for other thiophenium methylides,[1,3] and consistent with the presence of an electron-rich centre in the α-position with respect to the carbonyl groups.

The detailed analysis of the NMR (^{1}H and ^{13}C) spectra of products **3** was carried out not only for the structure elucidation (which was relatively straightforward), but primarily in order to gain insight into the stereochemistry of this ylidic system The pyramidal nature of the sulfur atom in thiophenium ylides, as well as the orthogonal orientation of the substituents attached to the ylidic carbon with respect to the thiophene ring, are well established [2] These structural features lead to the stereoisomerism in suitably substituted ylides, which may result from restricted rotation about the ylidic S-C bond, and/or from slow inversion at the chiral sulfur atom The problem of the exchange processes at sulfur in thiphenium ylides was studied by NMR spectroscopy[5,6] and by MO calculations,[5] but no unequivocal conclusion about the relative importance of the two possible mechanisms was reached Theoretical calculations[5] pointed out at the rotation barrier as being significantly higher than the inversion barrier, while the NMR study[6] demonstrated the importance of the substituents in the thiophene ring for the magnitude of the energy barrier between the two stereoisomers From the point of view of the NMR analysis, ylides **3a-m** can be divided into two groups (i and ii)

(i) Ylides unsubstituted at C-2 (3a-d). No evidence for the stereoisomers was obtained at room temperature, as all hydrogen and carbon atoms gave rise to single set of signals in the ^{1}H and ^{13}C NMR spectra Only the diastereotopic methylene groups in **3b** and **3d** showed the nonequivalence of protons (ABX$_3$ and AB systems, respectively), heating the solution of **3b** to 60°C resulted in the collapse of the pair of quartets into a single quartet These results indicate that in the absence of a substituent at the C-2 position of

Table 1 Penzo[b]thiophenium and Dibenzo[b,d]thiophenium Ylides 3

3	R^1	R^2	X	Y	Yield (%)	React time (days)	Mp^a (°C)	$\delta_H(CDCl_3)^b$	$\delta_C(CDCl_3)$	IR (cm^{-1})	m/z/EI anal (%)/C,H
a	H	H	OMe	OMe	62	2	190(K) 182-184(m) (lit [3] 177-177 5)	3 58 (6H, s), 6 74 (1H, d, 5 8), 7 43-7 72 (5H, m)	51 0, 52 7, 123 7, 125 8, 127 1, 128 9, 130 8, 134 7, 136,7, 138 4, 165 7	1680, 1654	
b	H	H	Me	OEt	58	11	90-95(m)	1 00 (3H, t, 7 1), 2 45 (3H, s), 3 98 (two q, 7 1), 6 76 (1H, d, 5 8), 7 42-7 72 (5H, m)	14 1, 29 5, 59 4, 68 9, 123 7, 125 7, 126 7, 128 8, 130 5, 135 0, 136 7, 139 2, 165 5, 191 9	1668, 1590	262 (M^+, 5), 219 (76), 191 (100), 171 (45), 155 (34), 134 (86), 91 (80), 43 (38)
c	H	H	Me	OtBu	88	9	102-103(m)	1 54 (9H, s), 2 41 (3H, s), 6 75 (1H, m), 7 42-7 68 (5H, m)	18 2, 28 1, 29 3, 69 0, 79 5, 123 5, 125 6, 127 4, 128 5, 130 3, 134 6, 137 0, 139 0, 164 7, 192 1	1671, 1583	290 (M^+, 2), 247 (8), 217 (6), 191 (100), 174 (10), 147 (14), 134 (46), 57 (20), 43 (11)
d	H	H	$CH_2CMe_2CH_2$		29	7	oil	0 94 (6H, s), 2 19 (2H, s), 2 20 (2H, s), 6 64-7 59 (6H, m)	27 9, 30 7, 51 3, 80 4, 123 3, 124 1, 125 7, 128,6, 130 4, 134 6, 136 4, 139 7, 191 3	1720, 1633 1575	272 090^c (M^+, 70), 189 (35), 171 (27), 101 (51), 83 (49), 43 (100)
e	Cl	Cl	Me	OEt	84	2	105(K)	0 70, 1 32 (3H, two t, 7 1), 2 34, 2 57 (3H, two s), 3 67-3 77, 4 25-4 27 (2H, two m), 7 50-7 71 (4H, m)	13 5, 14 5, 29 3, 29 6, 59 3, 60 1, 67 0, 121 6, 122 0, 123 2, 124 2, 125 4, 125 8, 129 6, 129 7, 131 2, 131 5, 133 1, 134 8, 136 1, 136 4, 163 5, 166 7, 190 3, 194 2	1680, 1599	Calcd C, 51 1, H, 3 7 Found C, 51 4, H, 3 7
f	Br	Br	Me	OEt	71	3	151(K) 140-141 5(m)	0 66, 1 34 (3H, two t, 7 1), 2 35, 2 60 (3H, two s), 3 65-3 77, 4 26-4 30 (2H, 2q, 7 1), 7 49-7 73 (4H, m)	13 6, 14 6, 29 3, 29 6, 59 2, 60 1, 68 0, 69 1, 117 8, 120 1, 121 8, 123 1, 123 3, 124 2, 125 0, 125 1, 126 3, 129 4, 129 5, 131 2, 131 5, 135 0, 136 6, 138 4, 138 7, 163 6, 166 6, 190 2, 194 1	1694	Calcd C, 40 0, H, 2 9 Found C, 40 1, H, 2 4
g	Br	Br	Me	OtBu	41	7	176-177(K) 161-163(m)	0 88 (9H, s), 2 51 (3H, s), 7 56-7 61 (4H, m)	26 2, 26 9, 27 9, 66 5, 67 5, 77 8, 78 6, 119 6, 122 2, 123 2, 124 0, 127 7, 128 7, 129 6, 135 1, 136 7, 161 2, 164 5, 188 1, 192 5	1674	Calcd C, 42 9, H, 3 6 Found C, 42 9, H, 3 4
h	Br	Br	OMe	OMe	65	5	228(K) 225-226(m)	3 44, 3 81 (6H, two s), 7 50-7 74 (4H, m)	50 4, 50 8, 52 2, 119 9, 124 3, 124 6, 126 0, 129 9, 131 9, 135 5, 137 7, 163 0, 165 3^d	1685	Calcd C, 37 0, H, 2 4 Found C, 37 2, H, 2 3

Table 1, continued

i	Br Br OEt OEt	18	1	133-135(K) 133-134(m)	0 79, 1 34 (6H, two t, 7 0), 3 70-3 84, 4 23-4 34 (4H, two m), 7 50-7 72 (4H, m)	13 7, 14 5, 59 5, 60 3, 60 5, 120 9, 124 1, 124 9, 125 9, 129 6, 131 6, 136 4, 137 9, 163 2, 166 8	1682	405 (10), 377 (100), 349 (47), 292 (79)
j	Me H Me OEt	56	4	110(K) 111-113(m)	0 60, 1 14 (3H, two m), 2 14-2 44 (3H, two overlap br s), 3 63, 4 15 (2H, two m), 6 98 (1H, s), 7 25-7 49 (4H, m)	12 5, 13 3, 14.3, 29 1, 58 6, 59 2, 68.5, 69 6, 122 7, 123 5, 124 2, 127 2, 129 3, 130 1, 134 7, 136 2, 139 2, 139 5, 140 8, 163 9, 167 0, 189 3, 193 1	1667, 1583	276 (M$^+$, 6), 233 (81), 205 (100), 148 (39), 147 (60)
k	Me H Me OtBu	63	1 5	134-135(m)	1 13 (9H, br s), 2 21 (3H, s), 2 33 (3H, s), 7 36-7 69 (5H, m)[d]	11 7, 27 5, 28 4, 66 3, 77 9, 122 9, 124 3, 127 0, 129 3, 130 0, 135 7, 139 5, 140 3, 163 6, 189 3[d]	1667	304 (M$^+$, 3), 205 (100), 148 (20), 147 (29)
l	Me H OMe OMe	85	5	164(K) 163(m)	2 28 (3H, d, 1 6), 3 34, 3 80 (6H, two s), 7 05 (1H, br s), 7 36-7 51 (4H, m)	12 7, 50 9, 51 3, 53 6, 123 9, 124 6, 127 7, 129 2, 130 9, 135 9, 139 1, 140 6, 164 7, 167 4	1657	247 (4), 219 (100), 148 (18), 147 (29)
m	benzo OMe OMe	50	4	197-198(m)	3 77 (6H, br s), 7 40-7 92 (8H, m)	50 8, 56 9, 122 0, 124 5, 129 2, 131 0, 135 1, 136 7, 164 1, 167 7	1654	314 (M$^+$, 1), 283 (2), 255 (54), 184 (100)

[a] K - Kofler hot-stage, m - microscope hot stage

[b] J values in Hz

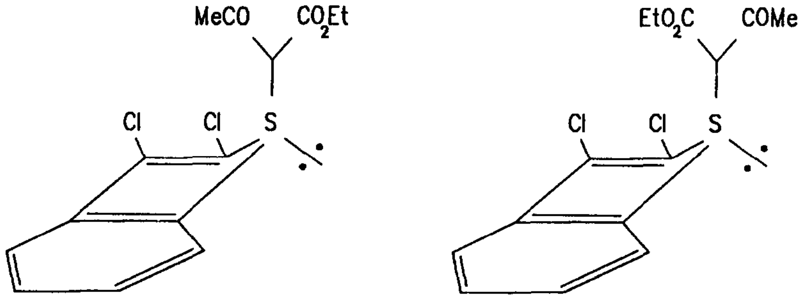
[c] accurate mass determined

[d] in DMSO-d_6

the thiophene ring the rotation about the S-C (ylidic) bond is, at room temperature, fast on the NMR scale, and that the inversion at sulfur is sufficiently fast at 60°C to remove the nonequivalence of the diastereotopic methylene hydrogens.

(ii) Ylides substituted at C-2. (a) Ylides derived from dialkyl diazomalonates (**3h,i,l,m**). All compounds of this group exhibited doubled signals for the ^1H and ^{13}C nuclei of the CO_2R groups of the malonate moiety (the effect is less clear for **3m**, but even in this case the ^{13}C NMR spectrum revealed two distinct signals for the carbonyl carbons, at 164.1 and 167.7 ppm). It is clear that the presence of a substituent at C-2 slows down significantly the exchange, so the two CO_2R groups are in a distinctly different molecular environment (*vide infra*). This result does not, however allow distinction between slow rotation or inversion as the mechanisms responsible for exchange.

(b) Ylides derived from alkyl diazoacetoacetates (**3e,f,g,j,k**). The results obtained for these compounds in which both, the thiophene, and the ylide parts are unsymmetrically substituted, were more informative. For the ethyl esters (**3e,f,j**), ^1H NMR spectra revealed that the acetyl methyl and ester ethyl groups give rise to pairs of signals (s,t, and q, respectively). Similarly, all six ^{13}C NMR signals of the $MeCOCCO_2Et$ fragment appeared doubled, and the benzothiophene part of the molecules yielded between eleven and seventeen signals in the aromatic range. At room temperature, two stereoisomers of **3** (e.g. **3e** and **3e'**, Figure 1) are present in solution, with the exchanges of the acetyl and the ethoxycarbonyl groups being slow on the NMR time scale. This result provides evidence for the restricted rotation about the ylidic S-C bond, since slow inversion at sulfur and fast S-C rotation would result in a single set for the signals of the MeCO and CO_2Et groups (except of the ^1H NMR signals of the diastereotopic methylene protons).[a]



3e **3e'**

Figure 1 Two stereoisomers of **3e**

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[a] Since the $\Delta G^{\dagger}$ values for the exchange in the ylides derived from dimethyl malonate and from dimedone are identical,[6] the restricted rotation within the ylidic substituents can be ruled out as a factor responsible for slow exchange.

^{1}H NMR spectra of **3e,f,j** are strongly temperature-dependent. For **3e** and **3f**, the pairs of triplets, singlets and quartets of the MeCOCCO$_2$Et moiety broadened upon heating in DMSO-d$_6$ solutions and coalesced into a single set of signals at *ca* 90°C (with some decomposition for **3f**). **3j**, when heated to 60°C showed the presence of one OEt group (0.93, t, 3.90, q) and one acetyl group (2.17, s), cooling back to room temperature resulted in the recovery of the initial spectrum containing three pairs of the respective signals (0.60, 1.14, 2.14-2.44; 3.63, 4.15). The coalescence temperatures are higher than those reported[6] for some chlorothiophenium S,C-ylides, and confirm earlier observation[6] about the effect of substituents in positions 3,4(β) of the thiophene ring on the free energy of activation for the exchange process.

The t-butyl esters (**3g**,**3k**) exhibited more ambiguous spectroscopic properties. ^{1}H NMR spectra of both ylides revealed only one set of signals (t-Bu and Me for **3g** and t-Bu and two Me for **3k**) for each compound. The existence of two stereoisomers of **3g** could be, however, seen clearly from its ^{13}C NMR spectrum which contained two sets of signals for all carbon nuclei of the MeCOCCO$_2$t-Bu group, as well as more than eight signals for the aromatic carbons. ^{13}C NMR spectrum of **3k** contained, however, like the corresponding ^{1}H NMR spectrum, only one set of signals for the ylide and ring atoms. In view of the observed stereoisomerism of **3j** (*vide supra*), it is very unlikely that the exchange in **3k** should be fast on the NMR time scale. It seems therefore that in this case the synthesis (Equation 1) leads to the formation of a single stereoisomer, probably the one with the bulky CO$_2$t-Bu group located away from the benzothiophene ring (Figure 1).

The differences in the shielding of the individual ^{1}H and ^{13}C nuclei of the 1,3-dicarbonyl fragment in **3e-m**, resulting from slow exchange between the two sites with respect to the aromatic part, are large. For example, in **3l** the $\Delta\delta_H$ value for the methyl ester groups is 0.36 ppm, while the $\Delta\delta_C$ values for the ester methyl and carbonyl carbons are 0.42 and 2.77 ppm, respectively. Such differences are comparable with the typical $\Delta\delta$ values observed for rigid molecules, in which the nuclei differ significantly in their spatial relation to a π-electron system.[7] The crystal structure of the unsubstituted, symmetrical ylide - thiophenium bismethoxycarbonylmethylide (**4**) was determined by Porter *et al*,[8] who first established the geometry of the system responsible for the nonequivalence of the two CO$_2$Me groups. In order to confirm the ylide geometry for the benzo[b]thiophene derivatives **3** and to demonstrate different shielding environments of the ylidic substituents, we determined the crystal structure of one of the ylides **3**. Compound **3l** was chosen as a natural extension of the earlier crystallographic study.[8]

Crystal and molecular structure of 3l The projection of the molecule is shown in Figure 2, while Table 2 contains selected molecular parameters for **3l**, the corresponding values reported[8] for **4** are included for comparison. Although the general structural features of both ylides are similar, a noticeable difference involves shorter ylidic and longer S-C(ring) bonds in **3l**. This implies greater electron density shift from the malonate group, hence higher barrier for the rotation about the S-C ylidic bond. The malonate moiety deviates slightly, but not significantly, from planarity, and adopts a conformation in which one carbonyl group points towards the thiophene ring and the other away from it. Such conformation was found to be typical of other systems of related structure.[9] Figure 2 shows that the orientation of the malonate group with respect to the benzothiophene skeleton is not far from orthogonal, the corresponding values of the dihedral angles C(11)-S-C(8)-C(9), C(11)-S-C(2)-C(3), and C(11)-S-C(2)-C(10) are 123.5°, -125.3°, and 57.6°, respectively. In consequence, the molecular environment of two methoxycarbonyl groups is very different, also with respect to the diamagnetic anisotropic effect of the aromatic part of the molecule. We believe that the slow exchange observed for all systems **3** substituted at position C-8, and responsible for the stereoisomerism of **3e,f,g,j,k**, is a result of the restricted rotation about the ylidic bond. Variable temperature NMR study of S-ylides derived from thioxanthones[10] also provided strong evidence for the restricted rotation in those closely related systems

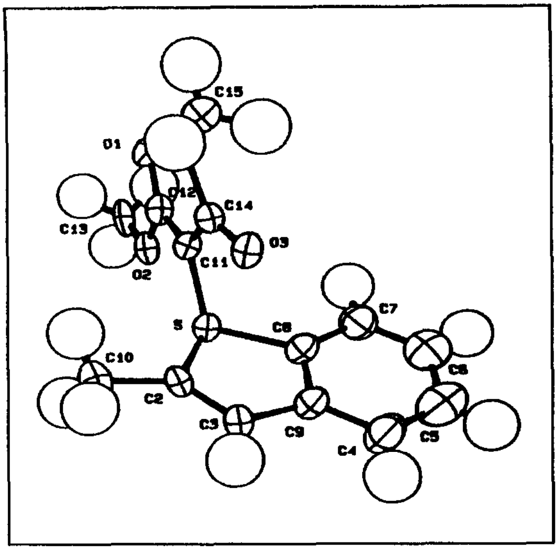


Figure 2 A perspective view of 3l with atomic numbering

Table 2. Molecular Parameters of 3l and 4

Bond lengths (Å)	3l	4
Ylidic S-C	1.708(2)	1.711(4)
S-C(8)	1.772(2)	1.745(7)
S-C(2)	1.791(2)	1.743(4)
C(ylidic)-C(carbonyl)	1.445(2)	1.441(6)
	1.440(2)	1.431(6)
Valence angles (°)		
C(8)-S-C(11)	113.1(1)	116.8(2)
C(2)-S-C(11)	111.1(1)	114.7(2)
C(2)-S-C(8)	91.6(1)	92.2(3)

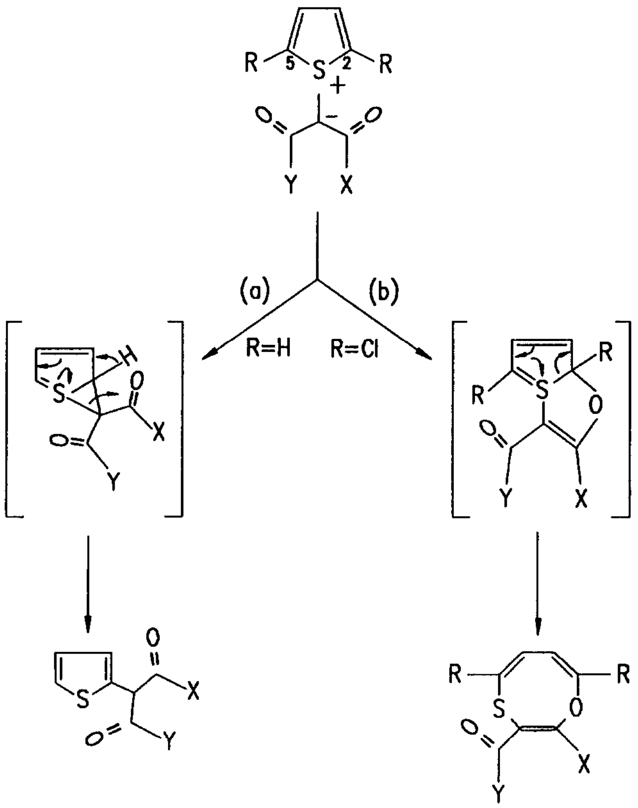
Reactivity All ylides 3 studied in this work showed remarkable thermal stability, strongly contrasting with thermal behaviour of the thiophene-derived ylides reported before [1] This property is clearly indicated by the very similar values of the melting points recorded for compounds 3 with faster (Kofler) or slower (microscope) rates of heating (Table 1) In no case could we achieve for ylides **3a-m** their thermal rearrangement to the 1,4-oxathiocines or any other products observed previously for thiophenium ylides For the ring-unsubstituted substrates, thermally induced S-C shift of the ylidic group (Equation 2, pathway a) was reported,[2] ylides substituted at positions 2,5 by chlorine atoms rearrange thermally to the corresponding oxathiocines (Equation 2, pathway b).[1] The postulated mechanism of both reactions, presented in Equation 2, involves intermediates for which in case of the benzo[b]thiophenium structure of the ylidic substrate, the aromaticity of the fused benzene ring would be lost It seems that this structural factor increases the activation energy of the first step of the rearrangements to the degree that makes ylides 3 thermally stable at the temperature range applied in this work

EXPERIMENTAL

Melting points were recorded on a Reichert hot-stage microscope and Reichert Kofler hot stage apparatus, and are uncorrected IR spectra were recorded on a Perkin-Elmer 883 spectrometer as liquid films or Nujol mulls Mass spectra were recorded using a Varian MAT 188 spectrometer Mass spectra of haloderivatives indicate only the major peaks of the clusters of isotopic peaks. NMR spectra were recorded on a Bruker AM 300 spectrometer and the chemical shifts are given relative to TMS as internal standard Silica gel Merck Kieselgel 60 was used for column chromatography, and silica gel Merck Kieselgel 60F-254 plates were used for TLC and preparative TLC. A laboratory sonication bath was used for sonication experiments

The following substituted benzo[b]thiophenes **1** were prepared according to the literature procedures **1a**, 57%, mp 52-54°C (from MeOH, lit.[11] mp 57 5°C); **1b**, purified by column chromatography (hexane), 55%, mp 55°C (lit.[12] mp 55-56°C), **1c**, 52%, mp 116°C (lit.[13] 114-116°C), **1d**, 75%, mp 80°C (lit [13] mp 81-82°C); **1e**, 89%, mp 51-52°C (lit.[14] mp 51-52°C). Diazocompounds used for the preparation of **3** were prepared as described before.[1]

Preparation of ylides 3 General procedure Diazocompound (0 005 mol) was added dropwise at room temperature, under dry nitrogen, with or without sonification, to the mixture of **1** (0 025 mol), tetrakis(acetato)dirhodium(II) (5 mg), and 1,2-dichloroethane (2-4 mL) The mixture was stirred at room temperature for several days, solvent was evaporated, and hexane (*ca* 20 mL) was added. The insoluble material was collected by filtration and the crude product was purified as indicated below **3a,b,c,e,f,g,h,i**, were purified by column chromatography by first eluting the unreacted **1** with pet. ether (bp 60-80°C), followed by elution with pet. ether/ether (1.1), and, finally, with chloroform **3d,j,k,l,m**, were purified by column chromatography using elution with pet ether, followed by pet ether/ether (1 1), chloroform, and, finally, methanol The last fraction containing mostly **3** was additionally purified by preparative TLC using chloroform/methanol (19 1) The yields and other data on products **3** are given in Table 1



(2)

Crystal structure determination. Data were measured at room temperature with a CAD4 diffractometer, using graphite monochromated MoKα radiation (λ = 0.71073 Å). Accurate cell dimensions were obtained from the setting angles of 25 standard reflections in the range $18 \leq \Theta \leq 22°$. An ω-scan was used. Both, the horizontal, and the vertical apertures were fixed at 1.3 and 4.0 mm, respectively. The crystal was tested for decay every hour and the orientation matrix every 200 reflections. Essential crystal data are summarised in Table 3. The structure was solved with MULTAN80[15] and completed with subsequent Fourier analysis. All hydrogen atoms were located. A full-matrix least squares method with SHELX76[16] converged to R = 4.2% and wR = 3.7%. Non-hydrogen atoms were refined anisotropically, the H-atoms with a common isotropical temperature factor, U = 0.097 (2) Å^2. A $^1/\sigma^2(F)$ weighting scheme was used.[17]

Table 3. Experimental Data for the X-ray Diffraction Study on **31**

Formula	$C_{14}H_{14}O_4S$
MW (g mol^{-1})	278.3
Space group	$P\bar{1}$
a (Å)	8.3269 (8)
b (Å)	8.5056 (6)
c (Å)	11.0114 (4)
α (°)	98.193 (5)
β (°)	99.576 (6)
γ (°)	113.541 (7)
V (Å^3)	685.9 (0.2)
Z	2
μ (cm^{-1})	1.97
F (ooo)	292
d_{calc} (g cm^{-3})	1.35
scan range (°)	$3 \leq \Theta \leq 30$
scan mode	ω-scan
h	0 11
k	-11·11
l	-15·15
vertical aperture (mm)	4.0
horizontal aperture (mm)	1.3
$\Delta\omega$ (°)	0.42 + 0.34 tan (Θ)
reflections measured	3969
reflections used ($I \geq 2\sigma(I)$)	3399
variables refined	215
R_{int}	0.000
R	0.0420
wR	0.0370

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