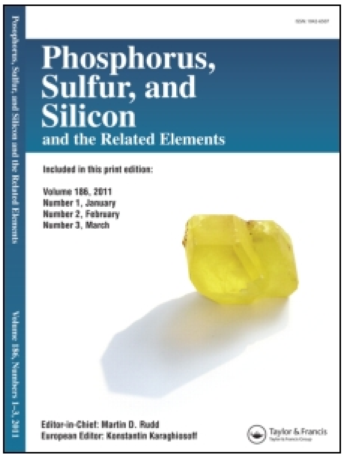

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α-ACYL-SULFINES BY REACTION OF ACETYLENES WITH N-SULFINYL-AMIDES[1]

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α-ACYL-SULFINES BY REACTION OF ACETYLENES WITH N-SULFINYL-AMIDES[1]

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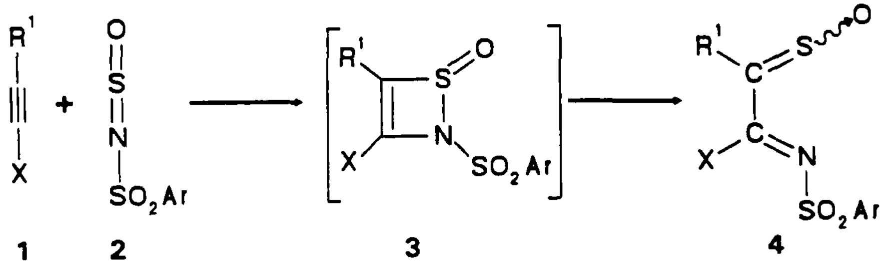
Abstract: Ynamines, ynethers and phenylacetylene react with N-sulfinyl-carboxamides to give 1,4,3-oxathiazines, which tend to devide by a retro Diels-Alder reaction into nitriles and 2-sulfinyl-amides, 2-sulfinyl-esters and sulfinylacetophenone, resp.

INTRODUCTION

Ynamines and Ynethers **1A**,**B** react with N-sulfinylarylsulfonamides **2** to give 2-sulfinyl-alkaneamidines[2] and 2-sulfinyl-alkanimidic esters[3] **4A**,**B**. These products are formed by regiospecific (2+2) cycloaddition between the C/C-triple bond of **1** and the cumulenic S/N double bond of **2** and by a spontaneous electrocyclic ringopening of the thereby formed 1,2-thiazetine derivatives.



RESULTS

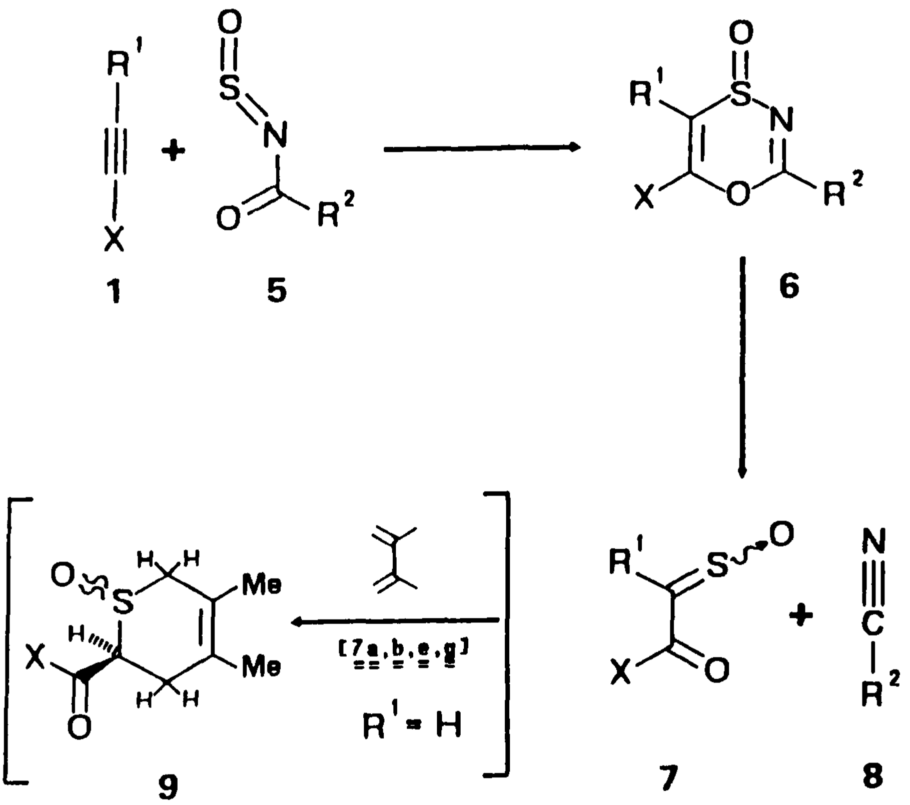
In contrast to this reaction mode, ynamines[1,4], ynethers[3] and arylacetylene[5] **1** react with N-sulfinyl-carboxamides **5** by (2+4) cycloaddition to give 1,4,3-oxathiazine derivatives **6**. These adducts are often isolable (s. **6a**-**e**,**g**), if the reaction temperature is low (-10°-

0°C) and if N-sulfinyl-p-toluamide 5a in diethylether is used. Under these conditions, the cycloadducts are obtained in crystalline form within a few minutes; they can be dried in vaccum at -40°C. In other cases (s.6f) and by using N-Sulfinyl-alkanamides 5b,c the adducts 6h-m cannot be isolated[6].

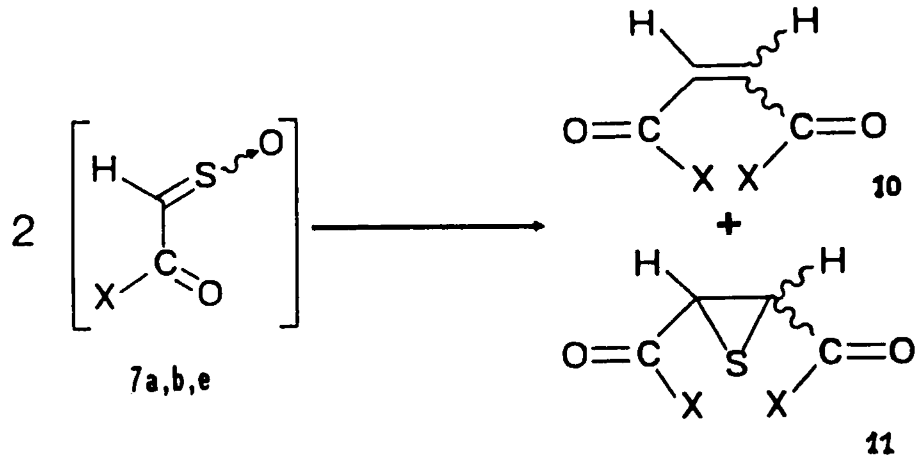
Unexpectedly, the crystalline adducts 6a-e[7] are rather unstable, they deliquesce within some hours at room temperature, even in solution this change can be monitored by spectroscopy[1]. The appearance of the ir-absorption of the nitriles 8 ($\tilde{\nu}$ = 2200 cm^{-1}) reveals the retro-Diels-Alder reactivity of 6. These adducts 6 tend to divide into the nitriles 8 and into the 2-sulfonyl-amides 7a-d, the 2-sulfinyl esters 7e,f and sulfinyl-acetophenone 7g, resp. The phenyl derivative 6g[5] seems to be more stable than the amino- and alkoxy-substituted 1,4,3-oxathiazines. In those cases, where the cycloadducts 6 are not isolated (not isolable?)[6], this change directly proceeds in the reaction mixture, according the scheme $1 + 5 \rightarrow [6] \rightarrow 7 + 8$.

While the thio ketone-S-oxides 7c,d,f,h-j can be isolated in good yields[7], the thio aldehyde-S-oxides 7a,b,e and g are much more unstable, as is generally known[8]; but in the presence of 2,3-dimethyl-1,3-butadiene these sulfines can be trapped as the Diels-Alder adducts 9[7].

Without any reaction partner 7a,b and e decompose to furnish maleic and/or fumaric acid derivatives 10 and in some cases an additional product to which we assign the structure of thiirane-2,3-dicarboxamides and -2,3-dicarboxylic acid esters 11, resp.[9]. The structure of 11 (e.g. X=NMePh) is confirmed by elemental analysis and by a 1H singlet at δ = 3.76 in the ^{1}H nmr spectrum and a doublet at δ = 35.37 with a coupling constant of 175.7 Hz in the ^{13}C nmr spectrum.



1	5 →	6 →	7 +	8	X	R^1	R^2
a	a	a^1	[a]	a	N(Me)Ph	H	p-Tolyl
b	a	b^1	[b]	a	Morpholino	H	"
c	a	c^1	c	a	N(Me)Ph	Ph	"
d	a	d^1	d	a	Morpholino	Ph	"
e	a	e	[e]	a	OEt	H	"
f	a	[f]	f	a	OEt	Me	"
g	a	g^5	[g]	a	Ph	H	"
h	b	[h]	h	b	N(Me)Ph	$SiPh_3$	tBu
i	b	[i]	i	b	N(Me)Ph	$SnPh_3$	"
d	b	[j]	j	b	N(Me)Ph	$P\ Ph_2$ N-Tos	"
e	b	[k]	d	b	Morpholino	Ph	"
f	c	[l]	[e]	b	OEt	H	Me
f	c	[m]	f	b	OEt	Me	"



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5. C. Carpanelli, G. Gaiani and F. Sancassan, Gazz. Chim. Ital. **115**, 265 (1985).
6. We didn't invest too much time in trying to isolate these compounds; but under the normally used conditions, the immediate occurence of **8** can be demonstrated ir-spectroscopically.
7. Some date of unpublished comounds: **6e**: 85%, colourless crystals, $\bar{\nu}$ = 1669vs, 1635m (C=N/C=C); ^1H nmr: (CD_2Cl_2,-50°C): δ = 5.37 (s, 1H, 5-H); ^{13}C nmr(CD_2Cl_2,-50°C): δ = 79.61 (d, J = 179.9 Hz, C-5), 155.76, 157.48 (2s, C-6, C-2); **7f**: quantitatively, light green oil, $\bar{\nu}$ = 1700vs cm^{-1}; ^{13}C nmr: δ = 163.62, 183.15 (2s, C=SO, COOEt); **7h**: 86%; mp = 132 °C (dec.), $\bar{\nu}$ = 1636s cm^{-1} (C=O); ^1H nmr $\delta(CDCl_3)$ = 3.21 and 3.17 (2 signals, 3:1, NMe of two isomers); **7i** : 67%, mp = 100 °C (dec.); **7j**: 97%, mp = 145 °C (dec.); **9e**: 78%, colourless oil; $\bar{\nu}$ = 1720vs (C=O); ^1H nmr: δ = 2.58, 2.74, 3.82 (ABX system, each 1H, J_{AB} = 17.3 Hz, J_{AX} = 4.5 Hz, J_{BX} = 7.9 Hz, 33-H_2, 2-H), 3.31, 3.50 (AB-System, J_{AB} = 16.8 Hz, each 1H, 6.6-H_2), 1.30, 4.26 (t,q, 3H, 2H, OCH_2CH_3).
8. Summaries: B. Zwanenburg, Recl. Trav. Chim. Pays-Bas **101**, 1 (1982); B. Zwanenburg, Phosphorus, Sulfur, Silicon Relat. Elem. **43**, 1 (1989); B. Zwanenburg and B. G. Lenz in Houben-Weyl-Müller: Methods of Organic Chemistry, vol. E11/1, Thieme, Stuttgart 1985, p.911.
9. These thiiranes are formally the "epithio" compounds of the isolated fumaric and maleic acid derivatives.