CYCLOADDITION REACTIONS OF KETENES TO SULFUR DIIMIDES

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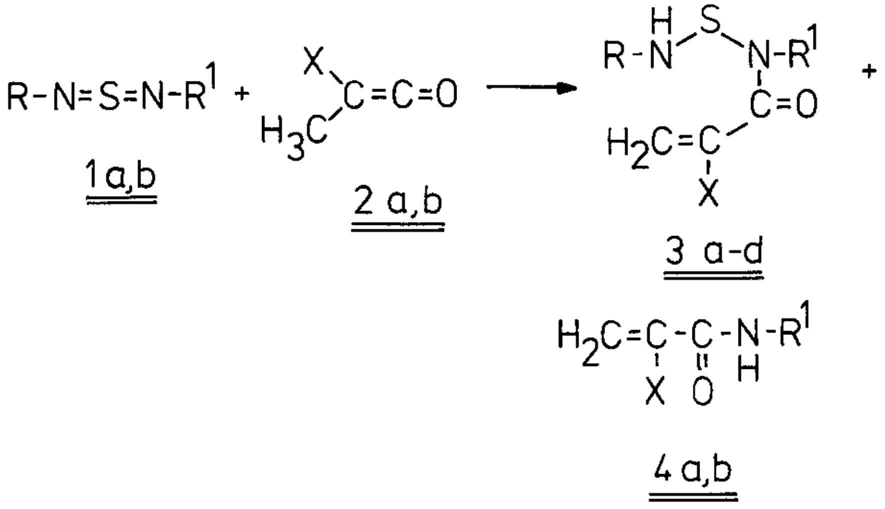
Abstract: The reactions of sulfur diimides **1** with substituted ketenes **2**, **5** were studied and the structures of the reaction products **3**, **4**, **6**, **7** were cleared up; the syntheses of new sulfur diimides **9a**, **9b** are described.

In the last few years we have studied the ractivities of sulfur diimides with bifunctional acid chlorides[1-9]. This led us to extend our investigations to reactions of sulfur diimides with halogenated ketenes which could be generated from the corresponding substituted acid halide in the presence of triethylamine[10]. Although there have been some examples of the reactions of sulfur diimides with ketenes in the literature[11-17], no reports with results appeared on the reactivities of halogenated ketenes towards sulfur diimides or of ketenes towards N-alkyl-N'-arylsulfur diimides like compounds **1a** or unsymmetrically substituted N,N'-diarylsulfur diimides **8**.

Now we have found that the reactions of sulfur diimides **1a**, **1b** with chloromethyl- or bromomethyl-ketenes **2a**, **2b** in benzene or n-hexane as solvent yielded the acylated diamino sulfanes **3a** - **3d**. In the case of the sulfur diimide **1a** the reactions occurred under formation of acrylic amides **4a**, **4b** as by-products. The reaction mechanism is maybe the same as already described by Minami et al.[15]; nevertheless, it was surprising that there was only an attack of the ketenes **2a**, **2b** at the aryl-substituted nitrogen atom of compound **1a**. Although we regarded this nitrogen atom as less hindered we expected also an attack at the alkylated nitrogen atom in respect to the inductive effect of the tert.butyl-group as it was already described for the reactions of ketenes with carbo-diimides[18]. But the reaction products indicated clearly that the steric effects predominated

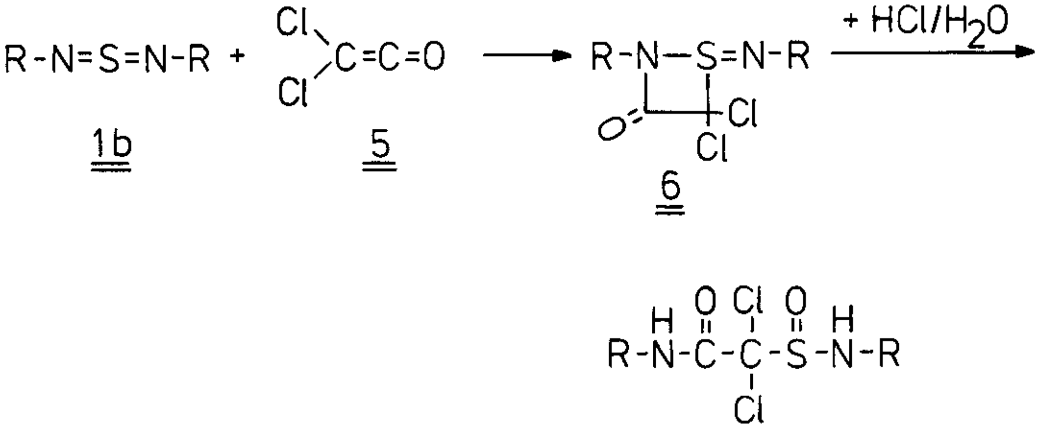


1a/2a/3a/4a : R = tert-C_4H_9; $R^1 = C_6H_5$; X = Cl

1a/2b/3b/4b : R = tert-C_4H_9; $R^1 = C_6H_5$; X = Br

1b/2a/3c : R = R^1 = tert-C_4H_9; X = Cl

1b/2b/3d : R = R^1 = tert-C_4H_9; X = Br



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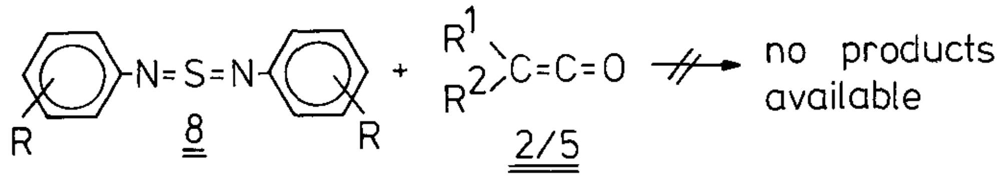
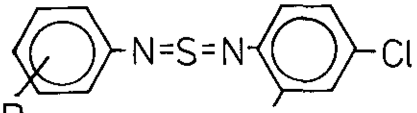
1b/6/7 : R = tert-C_4H_9



2a: $R^1 = CH_3$; $R^2 = Cl$
2b: $R^1 = CH_3$; $R^2 = Br$
5: $R^1 = R^2 = Cl$



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8a: $R = 4\text{-}J$

8b: $R = 3\text{-}CF_3$

leading to the compounds 3a, 3b. The formation of the acrylic acid amides 4a, 4b can be explained by hydrolytic or thermolytic decomposition of the compounds 3a, 3b during the reaction or isolation.

The reactions of dichloroketene 5 with the sulfur diimide 1b provided the 4,4-dichloro-1,2-thiazetidine-3-one 6 as a yellow oil which could not be purified neither by distillation nor by chromatographic methods. Compound 6 is very sensitive to moisture and could readily be hydrolized by dilute hydrochloric acid yielding the amide 7. The structure of 7 confirmed the structure of 6 which was already pointed out by ir spectroscopy.

The reactions of symmetrically or of unsymmetrically substituted N,N'-diarylsulfurdiimides 8 with halogenated ketenes 2, 5 did not proceed by the formation of heterocyclic compounds. All N,N'-diarylsulfurdiimides 8 having a substituent in the ortho- or meta position of the aryl group did not react with ketenes 2 or 5.

In many other cases the reactions occurred under formation of tarry reaction products which could not further be purified. Perhaps these tarry materials are produced by polymerization of ketenes 2, 5 because halogenated ketenes are known to undergo polymerization even at low temperatures[10]. In connection with these intended cycloaddition reactions some new unsymmetrically substituted N,N'-diaryl-sulfurdiimides 8a, 8b were synthesized. -

Table 1: Yields, Physical and Spectral Data of Compounds 3, 4, 6, 7, 8[a]

compounds	yield (%)	mp (°C)	ir (cm^{-1}), KBr or liquid films
3a	38	oil	3365 (NH), 1668 (C=O), 1650 (C=C)
3b	32	oil	3368 (NH), 1680 (C=O)
3c	56	88-89	3317 (NH), 1640 (C=O), 1616 (C=C)
3d	41.5	75-77	3315 (NH), 1635 (C=O), 1606 (C=C)
4a[19]	23	54	3300 (NH), 1676, 1540 (Amide I,II), 1625 (C=C)
4b[20]	21	90	3270 (NH), 1675, 1555 (Amide I,II), 1618 (C=C)
6	91	oil	1750 (C=O)
7	60	103-105	3405, 3220 (NH), 1682, 1520 (Amide I,II), 1096 (S=O)
8a	86	101	1100, 1070 (N=S=N)
8b	71	67-69	1098, 1067 (N=S=N)

	^{1}H-nmr (90 MHz, 60 MHz, $CDCl_3$)	ms, m/e (rel. int, %)
3a	1.33 (s, $C(CH_3)_3$), 5.53-5.72 ($C(Cl)=CH_2$ + NH), 6.98-7.26 (m, phenyl).	284 (M^+, 2), 228 (5), 208 (11), 192 (47), 123 (25), 106 (34), 93 (54), 61 (18), 57 (100).
3b	1.33 (s, $C(CH_3)_3$), ~5.70 (s, NH), 5.75, 5.97 (AB, J=2.2 Hz, $C(Br)=CH_2$, 6.96-7.24 (m, phenyl).	328 (M^+, 1), 272 (3), 252 (4), 196 (14), 192 (47), 150 (29), 133 (52), 105 (13), 57 (100).

Table 1 continued

3c	1.17, 1.50 (2s, 2 $C(CH_3)_3$), 3.73 (s, NH), 5.69, 5.77 (AB, J=1.8 Hz, $C(Cl)=CH_2$).	264 (M^+, 2), 208 (20), 152 (65), 106 (70), 89 (47), 61 (20), 57 (100).
3d	1.18, 1.50 (2s, 2 $C(CH_3)_3$), 3.70 (s, NH), 5.90, 6.15 (AB, J=2.2 Hz, $C(Br)=CH_2$).	307 (M^+, 4), 251 (15), 195 (38), 149 (20), 132 (11), 104 (3), 56 (100).
4a	5.88, 6.69 (AB, J=1.3 Hz, $C(Cl)=CH_2$), 7.06-7.64 (m, phenyl).	181 (M^+, 46), 146 (91), 89 (100), 61 (87).
4b	6.11, 7.09 (AB, J=1.6 Hz, $C(Br)=CH_2$), 7.14-7.63 (m, phenyl).	225 (M^+, 37), 146 (100), 133 (51), 105 (33).
6	1.37, 1.45 (2s, 2 $C(CH_3)_3$).	-.-.-
7	1.37, 1.45 (2s, 2 $C(CH_3)_3$), 4.05, 6.60 (2s, 2 NH).	-.-.-

a) Except of compound 6 satisfactory microanalyses were obtained for all compounds

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Experimental part:

mp: "Reichert"-micromelting apparatus, uncorrected.- ^{1}H-nmr: HX 90E Bruker-Physik AG., Karlsruhe-Forchheim, T 60 A Varian.- ms: MAT 311 A - Varian.- ir: Perkin-

Elmer 325.- The analyses were made by an automatic C,H,N - analysator - Heraeus, Hanau.-

N-tert-Butyl-N'-(2-chloro-2-propenoyl)-N'-phenyldiaminosulfane **3a** *and N-Phenyl-2-chloroacrylic acid amide* **4a**[19]: To a solution of 0.97 g (5 mM) sulfur diimide **1a** and 2.01 g (20 mM) of triethylamine in 20 ml benzene was dropped a solution of 0.64 g (5 mM) of 2-chloropropionyl chloride in 15 ml benzene at 70 °C. After boiling for 1 h the mixture was cooled to room temperature, the precipitate filtered off and the solvent removed under reduced pressure. Column chromatography provided three fractions (column: 3.5 x 70 cm; silica gel "Macharay and Nagel", eluent: dichloromethane):

1) unreacted sulfurdiimide **1a**
2) diaminosulfane **3a**
3) acrylic acid amide **4a**

Compound **3a** was purified by distillation in a micro-distillation-apparatus; light yellow oil.- Compound **4a** was sublimated (40 °C/$^{-2}$torr) and recrystallized from n-pentane; colourless crystals.-

N-tert-Butyl-N'-(2-bromo-2-propenoyl-)-N'-phenyldiaminosulfane **3b** *and N-Phenyl-2-bromo-acrylic acid amide* **4b**[20]: **3b**, **4b** were obtained analogously as described for compounds **3a** and **4a**. **3b** was purified by preparative tlc (silica gel "Merck", dichloromethane).-

N,N'-Di-tert-butyl-N-(2-chloro-2-propenoyl-)diaminosulfane **3c** *and N,N'-Di-tert-butyl-N-(2-bromo-2-propenoyl)diaminosulfane* **3d**: **3c**, **3d** were obtained analogously as described for compounds **3a**, **4a** at 40 - 50 °C from sulfur diimide **1b**. They were purified by sublimation (30 °C/1 torr) or recrystallization from ethanol/H_2O.-

1-tert-Butylimino-2-tert-butyl-4,4-dichloro-1,2-thiazetidin-3-one **6**: To a boiling solution of 1.74 g (10 mM) sulfur diimide **1b** and 1.50 g (15 mM) triethylamine in 40 ml n-hexane was dropped a solution of 1.47 g (10 mM) of dichloroacetyl chloride in 35 ml n-hexane. After 10 min the precipitate was filtered off, the solvent removed and under nitrogen atmosphere the residual oil was filtered; light yellow oil.

N-tert-Butyl-2,2-dichloro-2-(tert-butyl)sulfinylacetamide **7**: To a solution of

0.65 g (2.28 mM) of compound **6** in 20 ml ethanol were added 25 ml of 0.5 N HCl at room temperature. The solution was boiled for 10 min and filtered; the precipitated crystals were collected, washed with 60 ml of ethanol and dried.

N-2,4-Dichlorophenyl-N'-4-iodophenylsulfurdiimide **8a**: To a solution of 3.40 g (12.80 mM) of N-2,4-Dichlorophenylimidosulfurous dichloride[21] in 20 ml benzene was added a solution of 2.80 g (12.80 mM) of 4-iodoaniline and 2.60 g (25.60 mM) of triethylamine in 25 ml benzene with cooling. The mixture afterwards was stirred for 4 h, the precipitate filtered off and the residue recrystallized from benzene/petrolether; dark red crystals.-

N-2,4-Dichloro-N'-3-trifluoromethylphenyl-sulfurdiimide **8b**: **8b** was obtained analogously as described for compound **8a**; light red crystals.

References:

[+] Dedicated to Professor Tetsuji Kametani on the occassion of his retirement.

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