THE RETRO-DIELS-ALDER-REACTIVITY OF 1,4,3-OXATHIAZIN-4-OXIDES

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Summary : 1,4,3-oxathiazin-4-oxides **3** and **8**, formed by (4+2) cycloaddition of ynamines **1a-d** or phenylacetylene **7** with N-sulfinyl-p-toluamide **2**, furnish p-tolunitrile **5** and the acyl-sulfines **4** and **9** by a retro-Diels-Alder reaction.

Ynamines react with N-sulfinyl-<u>tosylamide</u> by (2+2) cycloaddition to give 1,2-thiazetin derivatives, which spontaneously isomerize to 2-sulfinyl-alkaneamidines.¹⁻³ Now, we became interested in the reaction of ynamines with N-sulfinyl-<u>carboxamides</u>; thus, ynamines **1a-d**, bearing hydrogen atoms or phenyl groups in their β -position (Scheme 1) react with N-sulfinyl-p-toluamide 2 to furnish crystalline 1:1 adducts to which the structure of the 1,4,3-oxathiazin-4-oxides **3a-d** is assigned.⁴ These heterocycles **3** exhibit an unexpectedly low stability: the crystalline products deliquesce within some hours at room temperature; also in solution, a change can be monitored by spectroscopy. By proving that p-tolunitrile **5** is formed to a high extent, the obvious supposition is that the heterocycles **3** furnish **5** and the **«**-sulfinyl-alkaneamides **4** by the retro-Diels-Alder reaction indicated by the dotted arrows (Scheme 1).

And indeed, after separation of 5 by column chromatography, both the phenylated sulfinylacetamides 4c and 4d can be isolated.⁵ Their structure is confirmed by analytical and spectroscopic means.⁶ Under analogous reaction conditions, the thioaldehyde-S-oxides 4a and 4b (\mathbb{R}^3 =H) cannot be isolated; in the absence of suitable reaction partners they decompose to furnish butene-1,4-diamides. In the presence of 2,3-dimethyl-1,3-butadiene, however, the sulfinyl-acetamides 4a and b can be trapped as the Diels-Alder adducts 6a and b.⁶ The constitution of these adducts 6 is confirmed by their spectroscopic data⁷ and by the comparison with those of published derivatives.^{2,6} Assuming that this trapping reaction is very fast and that no subsequent isomerization occurs, we assign the E-configuration to the isolated compounds 6a and b.

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1,3,4,6	R ¹	R ²	R ³	1,3,4	R ¹	R ²	R ³
٩	CH3	C ₆ H ₅	н	c	CH 3	C ₆ H ₅	C ₆ H ₅
Þ	(CH ₂) ₂	0(CH ₂)2	H	đ	(CH ₂) ₂ 0(CH ₂) ₂		C 5 H 5

In the light of these observations the question came up whether the adducts of 2 with simple acetylenes would display an analogous reactivity. The Italian authors⁸ report on the appearance of p-tolunitrile 5 as a thermai decomposition of N-sulfinyl-p-toluamide 2 formed by the "leading-back" retro-Diels-Alder reaction (Scheme 2). However, by heating up the cycloadduct⁸ 8 from 2 and 7 in the presence of 2,3-dimethylbutadiene, the adduct⁹ 10 has been isolated in 96% yield. That means that **8**, even though it is thermally more stable than the ynamine adducts **3**, also undergoes the retro-Diels-Alder reaction to give **5** and the sulfinyl-acetophenone **9**, and not the one leading back to the starting materials.



Thus, the sequences of the reactions $1 + 2 \longrightarrow 3 \longrightarrow 4 + 5$ as well as $7 + 2 \longrightarrow 8 \longrightarrow 9 + 5$ represent a new synthesis of acyl-sulfines, whereby the N-sulfinyl-p-toluamide 2 transfers its components (SO and O) to the acetylene derivatives 1 and 7.

Literature and Footnotes

- [1] S. Kosack, G. Himbert, G. Maas, Angew. Chem. 98 (1986) 443; Angew. Chem. Int. Ed. Engl. 25 (1986) 459.
- [2] S. Kosack, G. Himbert, Chem. Ber. 121 (1988) 833.

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- [3] H. Gotthardt, T. Löhr, Liebigs Ann. Chem. 1987, 189.
- [4] A solution of 2 (5 mmol) in 10 ml diethyl ether is added dropwise to a solution of ynamine 1 (5 mmol) in 10 ml diethyl ether within 5 min at -10 $^{\circ}$ C to 0 $^{\circ}$ C. Thereby yellow crystalline adducts (80-94%) are formed: 3a: ir (KBr): \vec{v} [cm⁻¹] = 1637, 1065, 1053 (C=N, S=O); ¹³C nmr (CD₂Cl₂, -50 $^{\circ}$ C): δ = 78.05 (d, J = 178.2 Hz, C-5), 152.63, 155.50 (2s, C-6, C-2); 3b: ir (KBr): \vec{v} [cm⁻¹] = 1624, 1115, 1064 (C=N, S=O); ¹H nmr (CD₂Cl₂, -50 $^{\circ}$ C): δ = 5.17 (s, 1H, 5-H); 3c: ir (KBr): \vec{v} [cm⁻¹] = 1632, 1148, 1121, 1070 (C=N, S=O); ¹³C nmr (CD₂Cl₂, -50 $^{\circ}$ C): δ = 107.02 (s, C-5), 150.26, 158.21 (2s, C-6, C-2); 3d: ir (KBr): \vec{v} [cm⁻¹] = 1628, 1134, 1112, 1081 (C=N, S=O).
- [5] These adducts **3a-d** are rather stable at low temperature, but at room temperature they deliquesce within 24 h. Column chromatography (SiO₂, first CH₂Cl₂, than diethyl ether) of the resulting products (**3c,d**) furnishes first p-tolunitrile 5, than the sulfines 4c and 4d. 4c: green-yellow oil 96%; ir (film): $\overline{\nu}$ [cm⁻¹] = 1649, 1145, 1123, 1103 (C=O, C=S=O); 4d: colourless crystals (82%), mp. 103-104 °C (dec.); ir (KBr): $\overline{\nu}$ [cm⁻¹] = 1638, 1137, 1110 (C=O, C=S=O); ¹³C nmr (CDCl₃): δ = 160.91 (s, C=O), 179.15 (s, C=SO).
- [6] Reviews: Syntheses and spectroscopy of sulfines: a) B. Zwanenburg, J. Strating, Q. Rep. Sulfur Chem. 5 (1970) 79; b) E. Block in R. K. Freidlina, A. E. Skorova (edts): Organic Sulfur Chemistry (IUPAC), Pergamon Press, Oxford 1981, S. 15ff; c) B. Zwanenburg, Recl. Trav. Chim. Pays-Bas 101 (1982) 1; d) B. Zwanenburg, B. G. Lenz in Houben-Weyl-Müller: Methods of Organic Chemistry, vol. E 11/1, Thieme, Stuttgart 1985, S. 911; e) B. Zwanenburg, Phosphorus, Sulfur Silicon Relat. Elem. 43 (1989) 1.
- [7] The pronounced character of sulfines as dienophiles is known and is used very often in trapping unstable sulfines.⁶ 6a: 70%, colourless crystals, mp. 131~132 °C; ¹H nmr (CDCl₃): δ = 2.35, 2.67, 3.82 (ABX-system, each 1H, 3,3-H₂, 2-H), 3.19, 3.50 (AB-system, 6,6-H₂), 1.61, 1.66, 3.36 (3s, each 3H); **6b**: 72%, colourless crystals, mp. 162-163 °C; ir (KBr): $\bar{\nu}$ [cm⁻¹] = 1644, 1637 (C=O).
- [8] C. Carpanelli, G. Gaiani, F. Sancassan, Gazz. Chim. Ital. 115 (1985) 265.
- [9] B. G. Lenz, H. Regeling, H. L. M. van Rozendaal, B. Zwanenburg, J. Org. Chem. 50 (1985) 2930.

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