

## Unsaturated Hetero Chains -VII. The Synthesis of 1-Thioacyl-Oligonitriles<sup>1</sup>

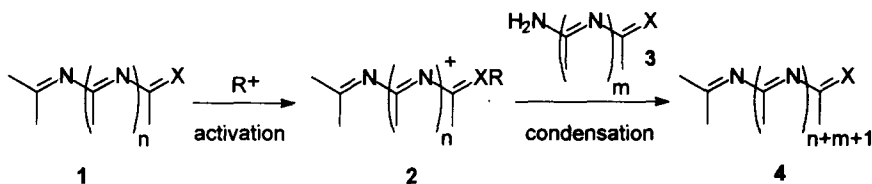
Anke Beckmann, Roland Fröhlich and Ernst-Ulrich Würthwein\*

Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster  
 Corrensstrasse 40  
 D-48149 Münster, Germany

**Abstract:** 1-Thioacyl substituted oligonitriles **7**, **8**, **10** are prepared by nucleophilic ring opening reactions of 1-thia-3,5-diazinium salt **5**. Alkylation of **8** with oxonium salts furnishes the corresponding azavinyllogous iminium salts **11**, which may be converted to 1,5-diamino-2,4-diazapentamethinium salts **12** by reaction with secondary amines. Alkylation of **10c** and subsequent condensation with thiobenzamide lead to the new oligonitrile **13** with a 12 $\pi$ -system, the longest oligonitrile derivative known so far. © 1997 Elsevier Science Ltd.

In contrast to polyacetylenes,  $-(CH=CH)_n-$ , which found ample interest due to their electricity conducting properties,<sup>2</sup> only little is known about the isoelectronic polynitriles,  $-(CR=N)_n-$ . Wöhrle obtained polymeric products from the thermolysis of triazine in the presence of metal halides for which he attributed a polynitrile structure.<sup>3</sup> As part of an ongoing project we are investigating possibilities for the selective synthesis of polynitriles of definite chain length.<sup>1,4,5</sup>

Recently, we reported on a synthetic strategy for the repetitive preparation of monodisperse oligonitriles starting from 1-oxa-3-aza-butadienes (**1**,  $n=0$ ,  $X=O$ ) or its longer homologue (**1**,  $n=1$ ).<sup>1,5</sup> The activation of **1** with alkylating reagents (e.g. oxonium salts) furnished the cationic intermediates **2**, which were condensed with nitrogen nucleophiles **3** to yield the elongated oligonitriles **4**.



Within the series of oxygen derivatives (**1-4**;  $X=O$ ) problems with the leaving group ability were observed. Not only the alkoxy group, but sometimes also the growing oligonitrile chain was split off, which may affect the overall yield of the chain elongated product considerably. We expected to avoid these problems by introducing a terminal group  $X$  different from oxygen, which allows a more facile alkylation and simultaneously delivers a better leaving group than ethoxy ( $R = \text{Et}$ ) thus enhancing the reactivity of the intermediates **2**.<sup>1,5</sup> 1-Thioacyl-oligonitriles (**1,4**;  $X = S$ ) are the obvious alternative, which are described in this communication.

The previously unknown 1-thioacyl-oligonitriles **7** and **8**, respectively, were prepared by nucleophilic ring opening reactions of the thiadiazinium salt **5**<sup>6</sup> with various secondary amines **6** (Table 1). Depending on the reaction temperature good yields of **7** (T = +40 °C) or **8** (T = -78 °C) were obtained.

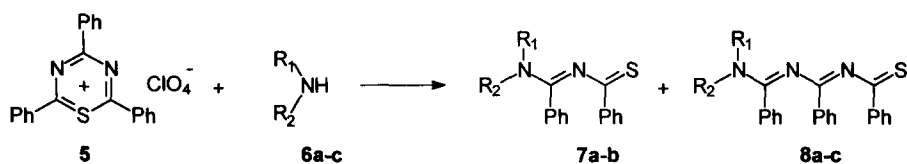


Table 1: Ring Opening Reactions of Thiadiazinium Salt **5** with Amines

<b>6</b>	Temperature [°C]	Product	Yield [%]
Piperidine ( <b>6a</b> )	+40	<b>7a</b>	67
Piperidine ( <b>6a</b> )	-78	<b>8a</b>	80
Morpholine ( <b>6b</b> )	+40	<b>7b</b>	95
Morpholine ( <b>6b</b> )	-78	<b>8b</b>	71
Diethylamine ( <b>6c</b> )	-78	<b>8c</b>	92

Similarly, treatment of **5** with the imine derivatives **9** gave the corresponding chain elongated products **10**, bearing an imine function in the ω-position (Table 2).

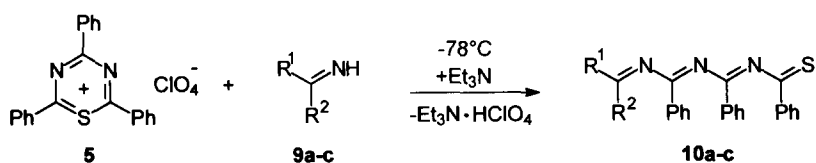
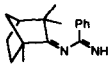
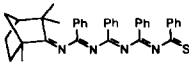
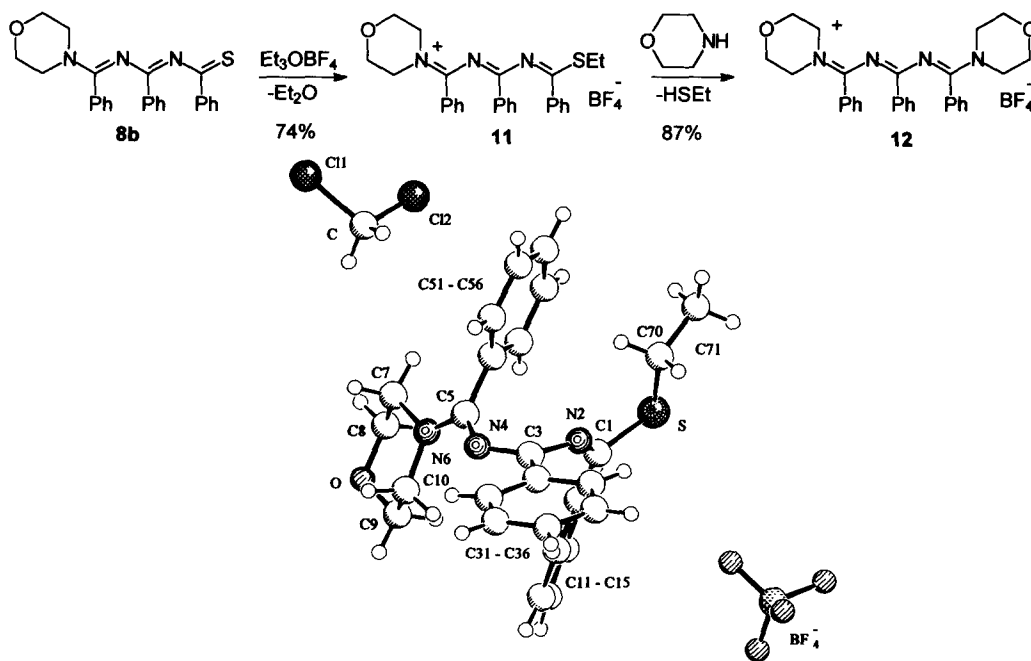


Table 2: Ring Opening Reactions of Thiadiazinium Salt **5** with Imines

<b>9a-c</b>	Product	Yield [%]
<b>9a</b> (R <sup>1</sup> =R <sup>2</sup> =Ph)	<b>10a</b> (R <sup>1</sup> =R <sup>2</sup> =Ph)	62
<b>9b</b> (R <sup>1</sup> =Ph, R <sup>2</sup> = <i>t</i> Bu)	<b>10b</b> (R <sup>1</sup> =Ph, R <sup>2</sup> = <i>t</i> Bu)	30
<b>9c</b> <sup>7</sup> 	<b>10c</b> <sup>12</sup> 	70

All these oligonitrile derivatives were subjected to alkylation using Meerwein's salt ( $\text{Et}_3\text{O}^+\text{BF}_4^-$ ) to form reactive cationic intermediates. For example, the yellow salt **11** was isolated in a yield of 74% from **8b**. Quite surprisingly, its X-ray analysis<sup>8</sup> (Fig. 1) revealed a three-dimensional structure of the cation with substantial deviations from planarity. The reaction of **11** with secondary amines offers a convenient access to the 1,5-diamino-2,4-diazapentadienylium salt **12**. The structure of **12** was also established by X-ray analysis.<sup>8,9</sup>

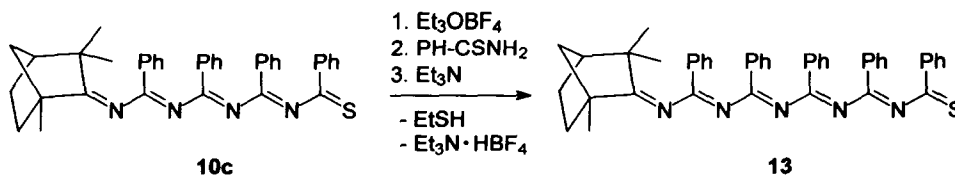


SCHAKAL

**Figure 1.** X-Ray Diffraction Analysis<sup>8</sup> of  $11 \times \text{CH}_2\text{Cl}_2$  (Selected Dihedral angles: C(70)-S-C(1)-N(2)  $-8(1)$ , S-C(1)-N(2)-C(3)  $164(1)$ , C(1)-N(2)-C(3)-N(4)  $-54(2)$ , N(2)-C(3)-N(4)-C(5)  $-12(2)$ , C(3)-N(4)-C(5)-N(6)  $139(1)$ , N(4)-C(5)-N(6)-C(7)  $156(1)$ )

To our knowledge, **12** is the first example of a triaryl substituted 1,5-diamino-2,4-diazapentamethinium salt (for chloro derivatives see ref. 10); such compounds have found theoretical interest in dyestuff chemistry.<sup>11</sup> In spite of similarities to the isoelectronic all-carbon pentamethinium salts (**12**, N = CH), **12** showed no absorption in the visible part of the UV spectra. This behavior is mainly a consequence of the three-dimensional, twisted structure of **12**,<sup>9</sup> whereas polymethine derivatives are colored due to their extended planar  $\pi$ -systems.<sup>11</sup>

Within the indicated repetitive synthetic strategy of activation and condensation, the  $12\pi$ -electron oligonitrile **13** was prepared using **10c**<sup>12</sup> as starting material after condensation of the cationic intermediate with thiobenzamide.



Because of experimental problems during the purification **13** was obtained in a low yield of 7%, although NMR spectra of the crude mixtures indicated about 36% condensation. The compound **13** is the longest oligonitrile derivative known so far. It is azavinylogous to **10c** and thus may serve as a suitable precursor for even longer oligonitrile derivatives.

### Acknowledgements

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG, Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme") and by the Fonds der Chemischen Industrie is gratefully acknowledged.

### REFERENCES

- Part 6: Aust, N.C.; Fröhlich, R.; Hecht, J.; Würthwein, E.-U. *Liebigs Ann./Recueil* **1997**, in press.
- Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J.C.S. Chem. Comm.* **1977**, 578-579.- Basescu, N.; Liu, Z.-X.; Moses, D.; Heeger, A. J.; Naarmann, H.; Theophilou, N. *Nature*, **1987**, 327, 403-405.- Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker, New York, **1986**; Vols. 1 and 2.
- Wöhrle, D. *Adv. Polym. Sci.* **1972**, 10, 35-70.- Wöhrle, D. *Makromol. Chem.* **1974**, 175, 1751-1760.
- Buhmann, M.; Möller, M. H.; Rodewald, U.; Würthwein, E.-U. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 2337-2339 and references therein.
- Schulte, N.; Fröhlich, R.; Hecht, J.; Würthwein, E.-U. *Liebigs Ann.* **1996**, 371-380.
- Shibuya, I. *Bull. Chem. Soc. Jpn.* **1980**, 53, 3369-3370.- Giordano, C.; Belli, A.; Bellotti, V. *Synthesis* **1975**, 266-268.
- Bondavalli, F.; Schenone, P.; Ranise, A. *Synthesis* **1979**, 830-832.- Bondavalli, F.; Bruno, O.; Schenone, P.; Filipelli, W.; Russo, S.; Marmo, E. *Farmaco* **1987**, 42, 941-946.
- The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.
- Dihedral angles of **12** along the C-N-C-N-C chain: 26.7(5)°, 54.0(4)°. Beckmann, A.; Kotila, S.; Wibbeling, B.; Würthwein, E.-U., University of Münster, to be published.
- Försterling, H.-D.; Huber, W.; Kuhn, H.; Martin, H. H.; Schweig, A.; Seelig, F. F.; Stratmann, W., "Neuere Verfahren zur Behandlung von  $\pi$ -Elektronensystemen" in *Optische Anregung organischer Systeme*, Ed. W. Foerst, Verlag Chemie, Weinheim, 1966.- Försterling, H.-D.; Kuhn, H. *Moleküle und Molekülanhäufungen*, Springer -Verlag, Berlin, Heidelberg, New York, **1984**, p. 91-102.
- Liebscher, J. *Synthesis* **1988**, 655-669.
- All new compounds were completely characterized by spectroscopic methods. For example: **10c**: red solid, m.p. 126 °C: <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.63 (s, br, 5H, CH<sub>3</sub>, fenchyl-H), 0.78 (s, 3H, CH<sub>3</sub>), 0.90-1.03 (m, 2H, fenchyl-CH), 1.18-1.54 (m, 4H, fenchyl-CH), 1.74 (br, 1H, fenchyl-CH), 7.12-7.18 (m, 2H, aromatic H), 7.27-7.48 (m, 12H, aromatic H), 7.87-7.90 (m, 2H, aromatic H), 8.23-8.26 (m, 2H, aromatic H), 8.33-8.37 (m, 2H, aromatic H).- <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  = 16.2, 23.1, 25.8 (CH<sub>3</sub>), 24.8, 32.9, 43.4, 53.8 (CH<sub>2</sub>, fenchyl), 46.0 (CH, fenchyl), 46.5 (C<sub>quart</sub>, fenchyl), 127.8, 128.0, 128.1, 128.2, 128.6, 129.2, 129.7, 130.6, 131.0, 131.2, 131.4, 131.9 (aromatic CH), 136.4, 137.1, 138.6, 140.0 (C<sub>q</sub>), 158.6, 160.2, 185.6 (C<sub>q</sub>).- UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}(\epsilon)$  = 276 (44700), 231 (46900).

(Received in Germany 30 April 1997; revised 17 June 1997; accepted 18 June 1997)