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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Dölling, Wolfgang , Birkner, Vera , Hartung, Helmut and Biedermann, Matthias(1997) 'Dithiocarboxylation Reactions of N-Containing C-Nucleophiles', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 467 — 469

To link to this Article: DOI: 10.1080/10426509708545601

URL: <http://dx.doi.org/10.1080/10426509708545601>

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DITHIOCARBOXYLATION REACTIONS OF N-CONTAINING C-NUCLEOPHILES

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Abstract 3-Quinuclidinone reacts with carbon disulfide, strong base and an alkylating agent in dipolar aprotic solvents giving 2-dialkylthiomethylene compounds **1**. N-acceptor methyl substituted 2,2,N-trimethyl-propionamides afford in this procedure compounds **2-4** and the N-cyanomethyl-N-methyl-benzamide forms compounds **5**. 2-Methyl-benzimidazole leads to the product of N-attack, whereas using 1,2-dibromoethane 1,1'-carbonothioyl-bis(2-methyl-benzimidazole) **6** is formed. 2-Chloro-N-cyanomethyl-N-methyl-benzamide **8** gives on treatment with 2 equivalents of a suitable base, carbon disulfide, and an alkylating agent at lower temperatures the expected substituted ketene dithioacetals **9**. At higher temperature the 2-alkylthio-4-methyl-5-oxo-4,5-dihydrobenzo[f]-1,4-thiazepine-3-carbonitriles **10** are formed. Reaction products have been identified and structurally characterized by X-ray analysis.

INTRODUCTION

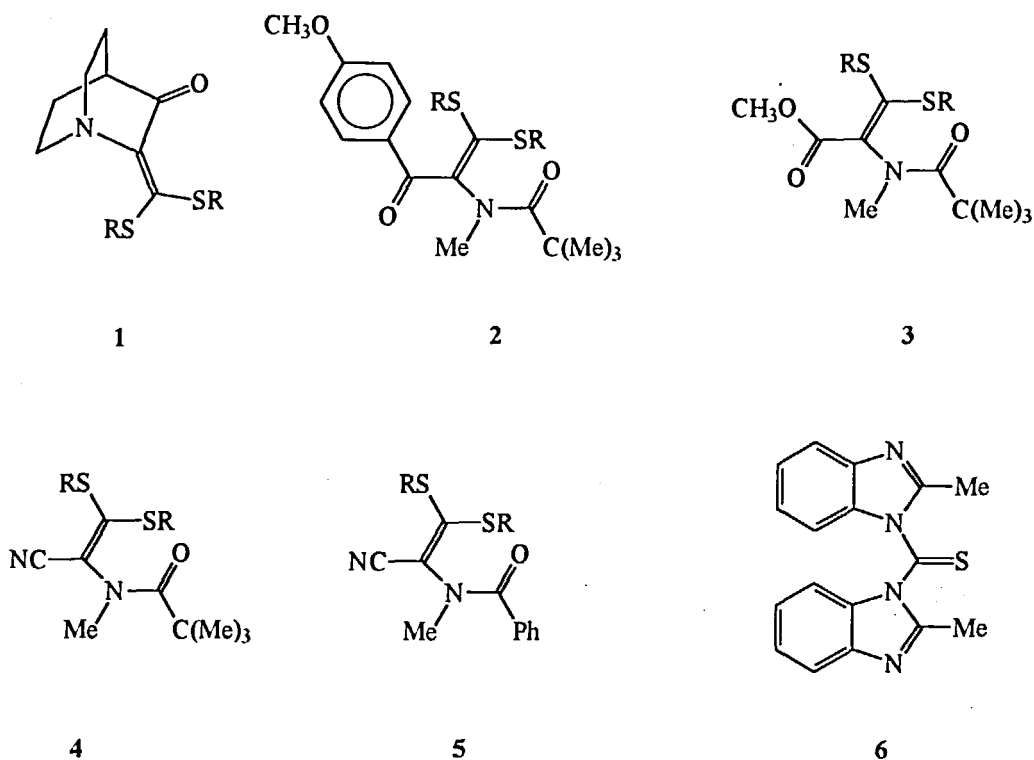
In the course of our systematic investigations concerning reactions of α -heteroatom substituted carbanionic species with sulfur-containing heterocumulenes we have studied the dithiocarboxylation of α -aza-carbanions. The reactions of carbon disulfide with carbon nucleophiles have been reviewed.¹

RESULTS

3-Quinuclidinone reacts with carbon disulfide, strong base and an alkylating agent in dipolar aprotic solvents giving 2-dialkylthiomethylene compounds **1**.² NMR-studies confirm in these cases the resulting compounds.

N-acceptor methyl-substituted 2,2,N-trimethyl-propionamides and N-cyanomethyl-N-methyl-benzamide as potential α -heteroatom substituted C-nucleophiles have been prepared for the first time and the reaction products proved by means of NMR investigations to be mixtures of E/Z-isomers. These amides give on treatment with two

equivalents of sodium hydride and carbon disulfide in dry DMF the ene dithiolate which can be alkylated to compounds 2-4 or compounds 5, respectively (Scheme I, $R = CH_3$; $R-R = -(CH_2)_2$ -, $-(CH_2)_3$ -).³



Scheme I

2-Methyl-benzimidazole leads to the product of N-attack, but using 1,2-dibromoethane 1,1'-carbonothioyl-bis(2-methyl-benzimidazole) 6 is formed.⁴ We have found a thiophosgene-free synthesis of this compound. N-attack of the electrophile phenyl isothiocyanat was also found giving 2-methyl-N-phenyl-1H-benzimidazole-1-carboximidothioic acid methyl ester 7 (see Fig. 1). Both reaction products 6 and 7 have been identified and structurally characterized by X-ray analysis.

2-Chloro-N-cyanomethyl-N-methyl-benzamide 8 gives on treatment with 2 equivalents of a suitable base, carbon disulfide, and an alkylating agent at lower temperatures the expected substituted ketene dithioacetals 9 (Scheme II, $R = CH_3$). At higher temperature the 2-alkylthio-4-methyl-5-oxo-4,5-dihydrobenzo[f]-1,4-thiazepine-3-carbonitriles 10 ($R = CH_3$, C_2H_5) are formed by nucleophilic aromatic substitution.⁵

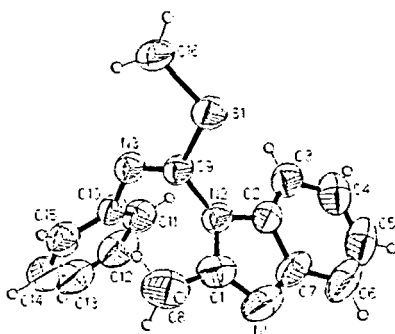
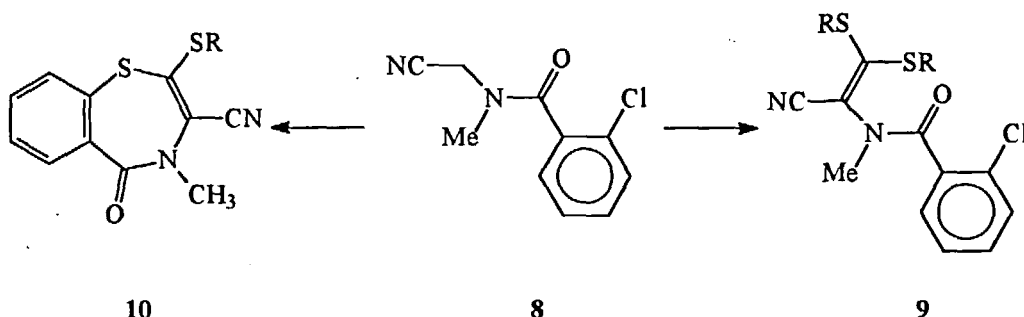


Fig. 1 ORTEP-drawing of the molecular structure of **7** with displacement ellipsoids at the 50% probability level; selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses: S1-C9 1.746(3), S1-C16 1.790(3), N1-C1 1.307(4), N1-C7 1.380(4), N2-C1 1.386(4), N2-C2 1.390(4), N2-C9 1.433(4), N3-C9 1.254(4), C1-C8 1.478(5), C2-C7 1.387(4); N1-C1-N2 112.7(3), N1-C1-C8 125.9(4), N2-C1-C8 121.4(4), S1-C9-N2 110.4(2), S1-C9-N3 124.4(3), N2-C9-N3 125.1(3).



Scheme II

Further studies are in progress in order to can better define scope and limitations of the described processes and reactions.

ACKNOWLEDGEMENT

The support by the Fonds der Chemischen Industrie is gratefully acknowledged.

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