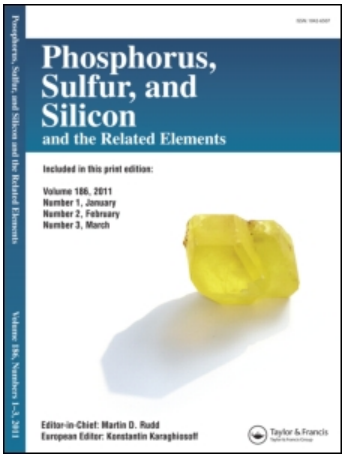

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DITHIOCARBOXYLATION REACTIONS OF N-CONTAINING C-NUCLEOPHILES

WOLFGANG DÖLLING,[a] VERA BIRKNER,[a] HELMUT HARTUNG,[b] AND MATTHIAS BIEDERMANN[b]

Martin Luther University Halle-Wittenberg, [a]Institute of Organic Chemistry, Kurt-Mothes-Straße 2, D-06120 Halle (Saale), [b]Institute of Physical Chemistry, Mühlpforte 1, D-06108 Halle (Saale), Federal Republic of Germany

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

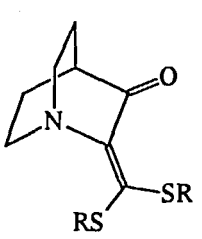
In the course of our systematic investigations concerning reactions of α-heteroatom substituted carbanionic species with sulfur-containing heterocumulenes we have studied the dithiocarboxylation of α-aza-carbanions. The reactions of carbon disulfide with carbon nucleophiles have been reviewed.[1]

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]



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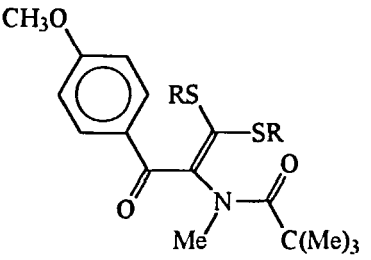

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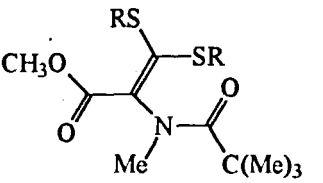

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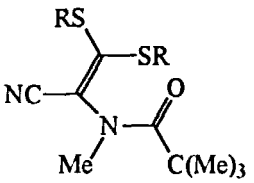

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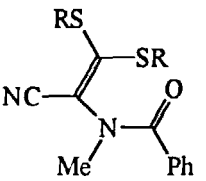

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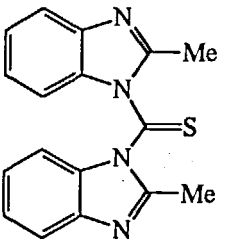


6

Scheme I

2-Methyl-benzimidazole leads to the product of N-attack, but using 1,2-dibromo-ethane 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-carboximido-thioic acid methyl ester **7** (see Fig. I). 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]

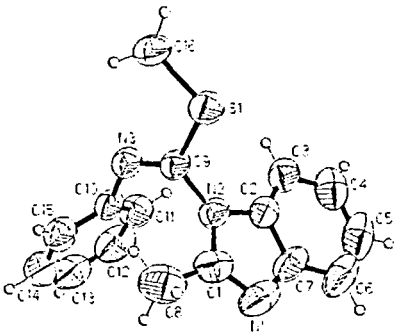
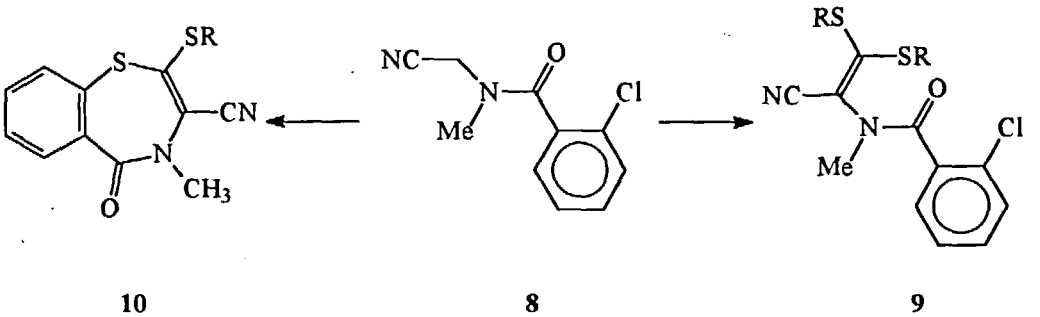


Fig. 1 ORTEP-drawing of the molecular structure of **7** with displacement ellipsoids at the 50% probability level; selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses: S1-C9 1.746(3), S1-C16 1.790(3), N1-C1 1.307(4), N1-C7 1.380(4), N2-C1 1.386(4), N2-C2 1.390(4), N2-C9 1.433(4),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



10 **8** **9**

Scheme II

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

ACKNOWLEDGEMENT

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