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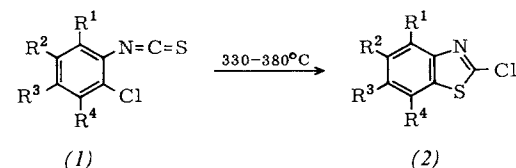
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Thermal Cyclization of *o*-Chloroaryl Isothiocyanates

By E. Degener, G. Beck, and H. Holtschmidt^[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

The observation that numerous polychloro amine derivatives undergo stabilization by ring closure when heated, induced us to study the thermal behavior of polychloroaryl isothio-



	R ¹	R ²	R ³	R ⁴	Yield (%)	M.p. (°C)
(a)	Cl	Cl	Cl	Cl	90	162–164
(b)	Cl	H	Cl	H	50	105–107
(c)	Cl	Cl	H	Cl	50	108–109
(d)	Cl	H	Cl	Cl	50	115–116
(e)	Cl	Cl	CN	Cl	50	185–189
(f)	–CCl=CCl–CCl=CCl–	Cl	Cl	Cl	90	260

cyanates. We found that *o*-chloroaryl isothiocyanates (1) cyclize to 2-chlorobenzothiazoles (2) in preparatively satisfactory yields at 330–380 °C, which are unusually high temperatures for organic reactions.

Ring closure is particularly smooth and uniform for the polychlorinated isothiocyanates (1a) and (1f); the less highly chlorinated isothiocyanates (1b)–(1d) give nitriles as well as (2).

This cyclization is related to the isomerization of cyano-*N*-(pentachlorophenyl)formimidoyl chloride to hexachloro-quinoxaline previously observed by us^[1]; this also occurs only at high temperatures (ca. 400 °C) and similarly involves migration of an *o*-chlorine atom.

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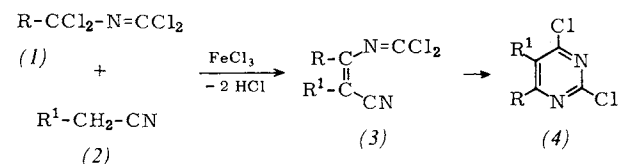
Direct Synthesis of Chlorinated Pyrimidines

By R. Braden, K. Findeisen, and H. Holtschmidt^[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

In recent years isocyanide dichlorides have become a readily accessible class of compounds^[1]; their high chemical reactivity has led to a wide variety of new compounds^[2]. On reaction with bifunctional nucleophiles, various kinds of ring closures can be accomplished^[2,3]. α -Chlorinated aliphatic isocyanide dichlorides, whose α -chlorine atoms generally react first on nucleophilic substitution^[4], occupy a special position. Compounds having mobile halogen atoms add readily to nitriles^[5,6].

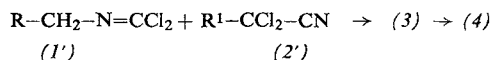
We have found that in the presence of Lewis acids at elevated temperatures α -dihalogenated isocyanide dichlorides (1) react with nitriles (2) bearing two hydrogen atoms in the α -position to give chlorinated pyrimidines (4). The reaction takes place in two stages, the rate-determining step being the elimination of hydrogen chloride. In a number of cases, however, it was possible to stop the reaction at the first stage and to detect the primary product (3).



R	(4) R ¹	Yield (%)	M.p. (°C)
Cl	H	88	89–93
Cl	Cl	94	68
Cl	CH ₃	61	68
Cl	ClCH ₂	74	112
Cl	C ₆ H ₅	57	159
Cl	<i>p</i> -O ₂ N–C ₆ H ₄	72	188
Cl	3,4-Cl ₂ C ₆ H ₃	75	141
Cl	2,3,4-Cl ₃ C ₆ H ₂	65	200
Cl	NC–CH ₂	14	125
Cl	2-(2,4,6-trichloro-5-pyrimidinyl)ethyl	32	200
CCl ₃	H	5	[a]
C ₆ H ₅	H	58	88

[a] B.p. 140–155 °C/0.5 torr.

If the α -chlorine atoms of the isocyanide dichloride are replaced by hydrogen and the α -hydrogen atoms of the nitrile by chlorine the reaction proceeds in an analogous fashion. Of particular interest is the reaction of trichloroacetonitrile (2'), $R^1 = Cl$, with trichloromethyl isocyanide dichloride (1), $R = Cl$; chlorine is evolved leaving a 30% yield of tetra-chloropyrimidine (m.p. 67°C).



R	R ¹	(4) yield (%)	m.p. (°C)	b.p. (°C/torr)
Cl	Cl	46	67	
ClCH ₂	Cl	5		130–145/0.5

The reaction is carried out in the following manner: The starting materials are mixed together, then mixed with about 0.1% of a Lewis acid (preferably iron(III) chloride) and heated to 200°C. The process may be performed in low-boiling polar solvents in an autoclave or in high-boiling solvents under normal pressure.

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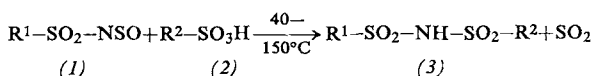
Synthesis of Disulfonimides, *N*-Sulfonyl Carboxamides, and α -Oxo *N*-Sulfonyl Carboxamides

By F. Bentz and G.-E. Nischk[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

Starting from *N*-sulfinyl sulfonamides (1) and sulfonic acids (2) we have prepared disulfonimides (3) in excellent yield^[1] (see Table for examples).

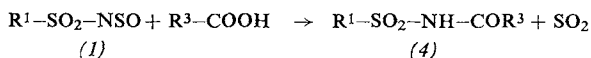
The *N*-sulfinyl sulfonamides (1) can usually be obtained by boiling the sulfonamides with an excess of thionyl chloride,



R ¹	R ²	(3) Yield (%)	M.p. (°C)
<i>m</i> -NO ₂ -C ₆ H ₄	<i>p</i> -CH ₃ -C ₆ H ₄	85	Isolated as K salt
C ₆ H ₅	<i>p</i> -CH ₃ -C ₆ H ₄	82	160
CH ₃	<i>p</i> -CH ₃ -C ₆ H ₄	92	116

usually without a solvent. Aliphatic or aromatic sulfonic acids may be used in the reaction, e.g., methane-, chloroethane-, or benzene-sulfonic acid or their substitution products such as toluene- or chlorobenzene-sulfonic acid.

The components (1) and (2) are usually allowed to react in the molar ratio 1 : 1 in a melt or in the presence of a solvent. Solvents used were inert organic solvents such as toluene, chlorobenzene, and dichlorobenzene. Aliphatic and aromatic *N*-sulfinyl sulfonamides (1) also react with aromatic or aliphatic monocarboxylic acids, giving *N*-sulfonyl carboxamides^[2].

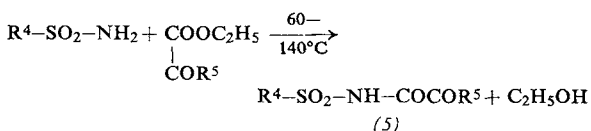


R ¹	R ³	(4) Yield (%)	M.p. (°C)
<i>m</i> -NO ₂ -C ₆ H ₄	C ₆ H ₅	73	173 (glacial acetic acid)
<i>m</i> -NO ₂ -C ₆ H ₄	C ₂ H ₅	84	115 (benzene)
C ₆ H ₅	ClCH ₂	67	104 (benzene)
<i>m</i> -NO ₂ -C ₆ H ₄	Cl ₂ CH	63	137 (benzene)
C ₆ H ₅	Cl ₃ C	61	92 (benzene)

The reactions, which are sometimes violent, are carried out in a melt or in an inert solvent (for examples see the Table).

N-Sulfinyl sulfonamides react with dicarboxylic acids, giving bis(substituted amides), e.g. *m*-nitrobenzene-*N*-sulfinylsulfonamide and adipic acid give an 82% yield of a product having m.p. 252°C.

With oxamic esters or oxalic esters, sulfonamides give α -oxo *N*-sulfonyl carboxamides (5) in very high yield^[3,4].



R ⁴	R ⁵	(5) Yield (%)	M.p. (°C)
<i>m</i> -NO ₂ -C ₆ H ₄	NHCH ₃	100	245
<i>m</i> -NO ₂ -C ₆ H ₄	OC ₂ H ₅	100	195
<i>p</i> -CH ₃ -C ₆ H ₄	NHCH ₃	100	156
<i>m</i> -NO ₂ -C ₆ H ₄	NH ₂	96	247
<i>m</i> -NO ₂ -C ₆ H ₄	N(CH ₃) ₂	100	230
CH ₃	CH ₂ =C-CONHCH ₂ NH	100	208 (water)
	CH ₃		
C ₆ H ₅	(CH ₂ =CHCH ₂) ₂ N	87	95
<i>m</i> -NO ₂ -C ₆ H ₄	CH ₂ =CHCH ₂ NH	100	178
C ₆ H ₅	CH ₂ =C-CONHCH ₂ NH	100	217
	CH ₃		

The sulfonamide is caused to react with an alkali hydroxide in an alcohol, preferably methanol, with addition of an aromatic hydrocarbon that boils higher than the alcohol. The alcohol and part of the aromatic hydrocarbon are distilled off at atmospheric pressure, then the oxamic ester or oxalic ester is added and the mixture is warmed (for examples see the Table).

The strongly acidic properties of these products (3), (4), and (5) give compounds of high molecular weight having very good dyeing properties towards basic dyestuffs.

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