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THE CHEMISTRY OF CUMULATED DOUBLE BOND COMPOUNDS III.

THE REACTION OF N-SULFINYL AMINES WITH ISOTHIOCYANATES

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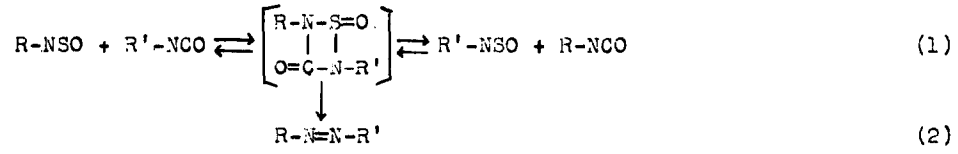
In a previous paper(1), we reported the reaction of N-sulfinylamines with isocyanates. It was found that an exchange reaction of N-sulfinylamines and isocyanates and a formation reaction of azo compounds took place at the same time.



$$R\text{-}NSO + R'\text{-}NCO \rightleftharpoons \left[\begin{array}{l} R\text{-}N\text{-}S{=}O \\ \quad | \quad | \\ O{=}C\text{-}N\text{-}R' \end{array}\right] \rightleftharpoons R'\text{-}NSO + R\text{-}NCO \qquad (1)$$

$$\left[\begin{array}{l} R\text{-}N\text{-}S{=}O \\ \quad | \quad | \\ O{=}C\text{-}N\text{-}R' \end{array}\right] \downarrow$$

$$R\text{-}N{=}N\text{-}R' \qquad (2)$$

In this paper, we report the reaction of N-sulfinylamines with isothiocyanates. When N-sulfinylamines and isothiocyanates were simply heated together at temperatures in the range of 180° to 200° in an atmosphere of nitrogen, the formation of carbodiimides and the elimination of sulfur were observed with an exchange reaction at the same time. These results are presented in Table 1.

In the reaction of thionylaniline with benzoylisothiocyanate, benzonitrile and phenylisothiocyanate were obtained in low yields (Table 2).

The formation of benzonitrile suggests that N-sulfinylbenzamide, expected to be prepared in an exchange reaction, decomposed to benzonitrile under these conditions(2). However, neither acetyl-nor benzoyl-isothiocyanate gave any carbodiimide, unidentified polymeric products being obtained in fairly large quantities. When N-sulfinylamines were treated in a sealed tube with excess carbon disulfide instead of isothiocyanates, corresponding isothiocyanates and sulfur were obtained quantitatively (Table 3).

TABLE 1.

THE REACTION OF N-SULFINYLAMINES WITH AROMATIC ISOTHIOCYANATES

$$R\text{-}NSO + R'\text{-}NCS \longrightarrow R'NSO + RNCS + R(\text{or } R')\text{-}N{=}C{=}N\text{-}R'(\text{or } R) + S$$

Run.	Reactants[a]		Conditions		Products[b] (Yields %)[c]		
	R-NSO	R'-NCS	temp.(°c)	time(hr.)	R'-NSO	R-NCS	R(orR')-N=C=N-R'(orR)
1	C_6H_5-	C_6H_5-	180~185	9.0	---	---	11.0
2	o-$CH_3C_6H_4$-	C_6H_5-	180~200	9.0	22.6	24.6	25.8
3	p-$CH_3C_6H_4$-	C_6H_5-	180~200	9.0	22.3	36.8	21.4
4	p-$CH_3OC_6H_4$-	C_6H_5-	185~200	9.0	11.1	11.1	18.5
5	o-ClC_6H_4-	C_6H_5-	185~190	9.0	13.7	30.6	15.8
6	o-$CH_3C_6H_4$-	o-$CH_3C_6H_4$	190~200	9.0	---	---	35.7
7	p-$CH_3C_6H_4SO_2$-	C_6H_5-	170	8.0	8.2	---	0.0

a The reaction was carried out by using equimolar amounts of N-sulfinylamines and isothiocyantates.

b N-sulfinylamines and isothiocyantates formed were identified by comparison to g.l.p.c.and i.r. spectrum of authentic samples prepared independently. Carbodiimides, which were formed in each reactions, were distilled as a mixture of three components and confirmed by i.r. spectrum and by leading to guanidine- and urea-derivatives, respectively. In run 1 and 6, diphenyl-and o-tolyl-carbodiimide were sole product.

c Yields based on starting isothiocyanates in all cases. Yields of N-sulfinyl-amines and isothiocyanates were obtained from g.l.p.c., (silicone column at 180°, folw rate 26.1 ml. H_2/min.). Yields of carbodiimides were calculated by estimating as diphenylcarbodiimide except run 6.

From the results of reaction between N-sulfinylamines and isothiocyanates or carbondisulfide, the following scheme could be proposed.

$$R\text{-}NSO + R'\text{-}NCS \rightleftharpoons \left[\begin{array}{l} R\text{-}N\text{-}S{=}O \\ \quad\ \ | \ \ | \\ S{=}C\text{-}N\text{-}R' \end{array}\right] \rightleftharpoons R\text{-}NCS + R'NSO \qquad (3)$$

$$\left[\begin{array}{l} R\text{-}N\text{-}S{=}O \\ \quad\ \ | \ \ | \\ R'\text{-}N{=}C\text{-}S \end{array}\right] \longrightarrow R\text{-}N{=}C{=}N\text{-}R' + S + [SO] \qquad (4)$$

$$R\text{-}NSO + CS_2 \rightleftharpoons \left[\begin{array}{l} R\text{-}N\text{-}S{=}O \\ \quad\ |\ \ | \\ S{=}C\text{-}S \end{array}\right] \rightleftharpoons R\text{-}N{=}C{=}S + S + [SO] \qquad (5)$$

TABLE 2.

THE REACTION OF THIONYLANILINE WITH ACYLISOTHIOCYANATES

$$C_6H_5NSO + RCONCS \longrightarrow C_6H_5NCS + RCN + S + SO_2$$

Run.	Reactants[a]	Conditions		Products (Yields %)[b]		
	R-CONCS	temp.(°c)	time(hr.)	C_6H_5NCS	R-CN	S
1	C_6H_5-	170	8.5	8.2	18.5	75.8
2	CH_3-	145	5.0	trace	trace	50.0

a Equimolar amounts of isothiocyanates and thionylaniline were used.

b Yields based on starting isothiocyanates. Yields of phenylisothiocyanate and nitrile were obtained from g.l.p.c., (silicone column at 180°, flow rate 26.1 ml. H_2/min.). Yields of sulfur were obtained by column chromatography on activated alumina.

TABLE 3.

THE REACTION OF N-SULFINYLAMINES WITH CARBON DISULFIDE

Run.	Reactants[a]	Conditions		Products (Yields %)[b]
	R-NSO	temp.(°c)	time(hr.)	R-NCS
1	C_6H_5-	200	10.5	100
2	o-$CH_3C_6H_4$-	200	13.0	100
3	m-$CH_3C_6H_4$-	200	15.5	100
4	o-ClC_6H_4-	200	13.0	100

a A mixture of carbon disulfide (0.15mole) and N-sulfinylamines (0.03mole) was heated together in a sealed tube.

b Yields based on starting N-sulfinylamines.

REFERENCES

(1) T.Minami, H. Miki and T. Agawa, Kogyo Kagaku Zasshi 70, 1831 (1967).

(2) A. Michaelis and H. Siebert, Liebigs Ann. Chem. 274, 312 (1893).