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THE REACTION OF THIOBENZOYL ISOCYANATES WITH N,N'-DIPHENYLSULFUR DIIMIDE[1]

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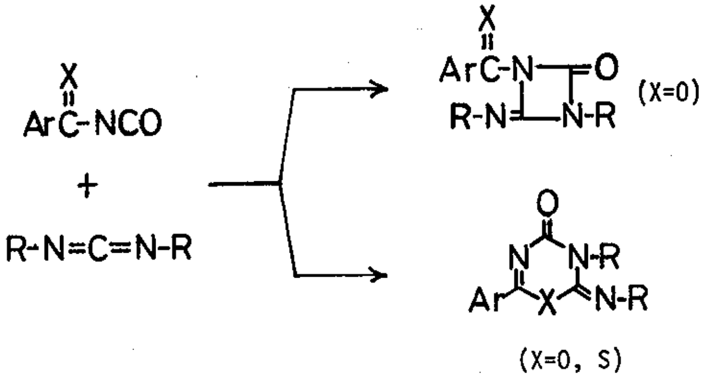
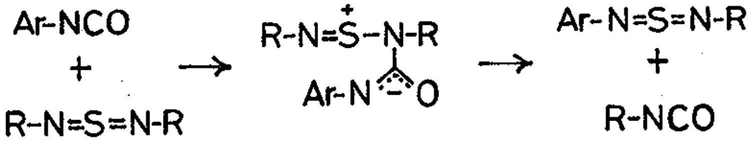
Thiobenzoyl isocyanates (1) reacted with N,N'-diphenylsulfur diimide (2) affording phenyl isocyanate (3), 2,5-diaryl-1,3,2,4-dithiadiazoline (4), 5-aryl-1,2,4-dithiazolin-3-one (5), and N-phenyl-N'-thiobenzoylurea (7), along with traces of 2,5-diaryl-1,2,4-thiadiazolin-3-one (6).

It is known that an isocyanate (RNCO) and a carbodiimide (R'-N=C=N-R') combine to give an unstable [2+2] cycloadduct, which is readily decomposed to a new isocyanate (R'NCO) and a mixed carbodiimide (R-N=C=N-R').[2] Previously, we reported that benzoyl and thiobenzoyl isocyanates added to carbodiimides across the cumulative C=N double bond in the fashion of 1,2- and/or 1,4-cycloaddition depending on the nature of isocyanates, carbodiimides, and reaction conditions.[3] However, little attention has been paid to the reaction of isocyanates with sulfur diimides which are S-analogues of carbodiimides. The only one example appeared in the literature; aryl isocyanate reacted with N,N'-di-tert-butylsulfur diimide yielding tert-butyl isocyanate and N-aryl-N'-tert-butylsulfur diimide.[4]





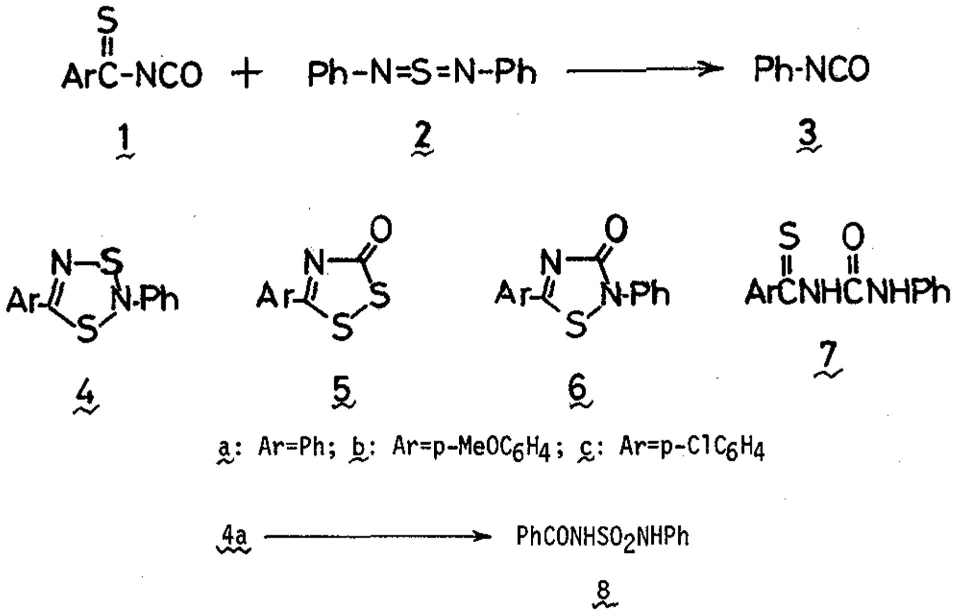
R=tert-butyl

Our interest in the reaction of benzoyl and thiobenzoyl isocyanates with heterocumulenes prompted us to investigate the behavior of the isocyanates toward a sulfur diimide. We wish to report here on the reaction of thiobenzoyl isocyanates (1) with N,N'-diphenylsulfur diimide (2).[5]

When thiobenzoyl isocyanate (1a)[6], generated in situ by the thermolysis of 2-phenylthiazoline-4,5-dione in xylene, was allowed to react with an equimolar amount of the sulfur diimide 2 in benzene at room temperature for 6 hr, phenyl isocyanate (3), 2,5-diphenyl-1,3,2,4-dithiadiazoline (4a), 5-phenyl-1,2,4-dithiazolin-3-one (5a), 2,5-diphenyl-1,2,4-thiadiazolin-3-one (6a), and N-phenyl-N'-thiobenzoylurea (7a) were obtained; the yields are shown in Table 1.

The structure of 4a was deduced on the basis of its spectral data and chemical conversion. Although the molecular formula of 4a agreed with that of N-phenyl-N'-thiobenzoylsulfur diimide (Ph-N=S=N-CSPh), no characteristic bands for -N=S=N- group were observed around and above 420 nm in the uv spectrum

[λ_{max}^{EtOH} nm (log ε) 234 (3.4), 280 (3.3), 359 (2.6)]. The mass spectrum (Table 2) supported the assigned structure; no peak did appear at m/e 121 ([PhCS]$^+$). On treatment with 35% hydrogen peroxide in a solution of benzene-acetic acid, 4a afforded a 25% yield of N-benzoyl-N'-phenylsulfamide (8), mp 165° dec, as pale yellow prisms [ir 3280, 3240 (NH), 1660 (CO), 1360, 1180 cm^{-1} (SO_2); m/e 276 (M^+)].



a: Ar=Ph; b: Ar=p-$MeOC_6H_4$; c: Ar=p-ClC_6H_4

$$4a \longrightarrow PhCONHSO_2NHPh$$

The structures of 5a and 6a were assigned on the basis of their spectral data and comparison of the melting points with reported ones (Table 2), and 7a was identical with the authentic sample prepared from 1a and aniline.

Similarly, p-methoxythiobenzoyl (1b)[6] and p-chlorothiobenzoyl isocyanate (1c)[6], generated in situ from the corresponding 2-arylthiazoline-4,5-dione, reacted with the sulfur diimide 2 affording 3, the 1,3,2,4-dithiadiazolines (4b, 4c), 1,2,4-dithiazolin-3-ones (5b, 5c), 1,2,4-thiadiazolin-3-ones (6b, 6c), and ureas 7b, 7c. The yields, and physical and spectral data are given in Tables 1 and 2, respectively.

Table 1. Yields of Products 3-7

	Ar	Yield, %				
		3[a)]	4	5	6	7
a	Ph	20	43	13	+[b)]	20
b	p-$MeOC_6H_4$	33	33	15	2	15
c	p-ClC_6H_4	17	48	11	+[b)]	23

a) The yield of 3 was determined as N,N'-diphenylurea.

b) A plus sign, +, means traces.

Table 2. Physical and Spectral Data[a)]

	Mp., °C	Ir, cm^{-1}	MS, m/e (rel. intensity %)
4a	73-74	1590(C=N)	258(M^+, 43), 155(M^+- PhCN, 61), 154(+, 100), 103($[PhCN]^+$, 52)
4b	78-79	1590(C=N)	288(M^+, 45), 155(M^+- ArCN, 69), 154(100), 133 ($[ArCN]^+$, 53)
4c	77-78	1590(C=N)	294, 292(M^+, 13, 34), 155(M^+- ArCN, 51), 154 (100), 139, 137($[ArCN]^+$, 13, 37)
5a	89 (lit.[b)] 86)	1590(C=N) 1680(C=O)	
5b	116.5-117.5	1595(C=N) 1670(C=O)	225(M^+, 30), 197(M^+- CO, 4), 193(M^+- S, 9), 133($[ArCN]^+$, 100)
5c	147.5-148.5	1590(C=N) 1670(C=O)	231, 229(M^+, 13, 35), 203, 201(M^+- CO, 16, 39), 199, 197(M^+- S, 2, 6), 139, 137($[ArCN]^+$, 16, 47)
6a	135-136 (lit.[c)] 142)	1600(C=N)	254(M^+, 12), 135(M^+- PhNCO, 100), 123($[PhNS]^+$, 41), 103($[PhCN]^+$, 33)
6b	188-189	1600(C=N) 1680(C=O)	284(M^+, 96), 165(M^+- PhNCO, 100), 133($[ArCN]^+$, 31), 123($[PhNS]^+$, 82)

Table 2. *Continued*

6c	237-238	1595(C=N) 1660(C=O)	290, 288(M$^+$, 19, 49), 171, 169(M$^+$ - PhNCO, 31, 86), 139, 137([ArCN]$^+$, 5, 17), 123([PhNS]$^+$, 100)

7a: Mp 200° dec, 1705 cm^{-1} (C=O). 7b: Mp 200° dec, 1700 cm^{-1}(C=O). 7c: Mp 213-214° dec, 1700 cm^{-1}(C=O).

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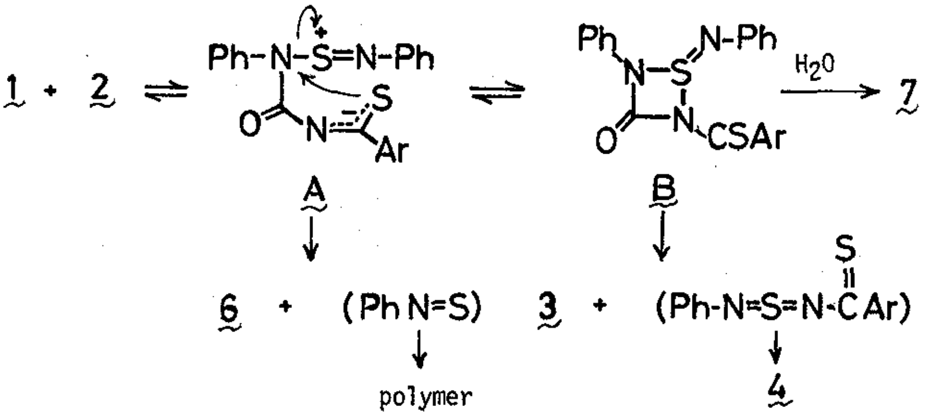
a) Satisfactory microanalyses were obtained for all compounds.

b) J. Goerdeler and R. Weiß, Chem. Ber., 1967, 100, 1627.

c) J. Goerdeler and R. Schimpf, ibid., 1973, 106, 1496.

The formation of major products 3, 4, and 7 can be rationalized as follows. An initial attack of 1 on the nitrogen atom of 2 might form the betaine A, followed by cyclization into the four-membered cyclic 1,2,4-thiadiazetidine B. Subsequent hydrolysis[7] or dissociation of B leads to 7 or 3 and N-phenyl-N'-thiobenzoylsulfur diimide, which then cyclizes to 4. The formation of the minor



product 6 is tentatively viewed to be due to a nucleophilic attack of the sulfur atom of thiocarbonyl group on the nitrogen atom in the betaine A with the concurrent loss of thionitrosobenzene, as shown in the above scheme. Although it has been reported that the reaction of 1 with sulfur gave 5, the pathway for the formation of 5 in the present reaction is not clear.

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4 D. H. Clemens, A. J. Bell, and J. L. O'Brien, Tetrahedron Lett., 1965, 1491.

5 Benzoyl isocyanate did not react with the sulfur diimide 2.

6 J. Goerdeler and H. Schenk, Chem. Ber., 1965, 98, 2954.

7 This hydrolysis would probably occur on workup of the reaction mixture.

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