

## Reactions of Alkyl Azides with Aryl Isothiocyanates

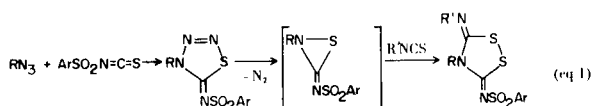
Gerrit L'abbé, Emiel Van Loock, Gabriël Verhelst and Suzanne Toppet

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, 3030 Heverlee, Belgium

Received March 18, 1975

Sir:

Recently (1), we reported that alkyl azides react smoothly with sulfonyl isothiocyanates at room temperature to give thiazirizoline derivatives. Upon thermolysis, these 1:1 adducts generate thiaziridinimines which are efficiently trapped by olefines, acetylenes, keto-stabilized phosphorus ylides and heterocumulenes such as isothiocyanates (eq. 1).



Parallel with this research, we are studying the title reactions which furnish 1:2 adducts after loss of nitrogen. A recent report by Revitt (2) prompts us now to communicate briefly on our findings. The 1:2 adducts are presumably formed by a mechanism analogous to eq. 1. However, in contrast to *N*-sulfonyliminothiaziridines, the *N*-aryliminothiaziridines have the potentiality to add to isothiocyanates in several ways. This was indeed observed as outlined below.

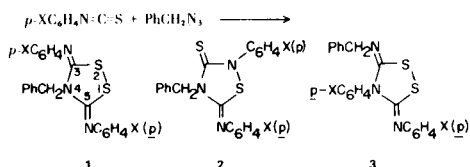


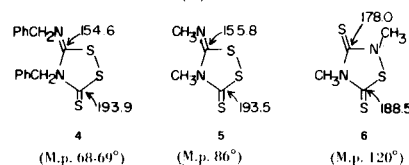
Table I

Reaction Products from Benzyl Azide and Aryl Isothiocyanates

X	Yields (%) and Melting Points		
	1 (a)	2	3
a. NO <sub>2</sub>	32 (223-225°)	4 (229-230°)	20 (168-169°)
b. Cl	19 (b) (178°)	8 (c) (150-152°)	
c. Me	22 (178-180°)		

(a) The yields of **1a** and **1b** were respectively 51 and 46% when the reactions were carried out at 100° (72 and 24 hours) without solvent. (b) 25% by nmr. (c) 14% by nmr.

When benzyl azide was allowed to react with 2 equivalents of aryl isothiocyanate in chloroform at 60-80° for ca. 30 days, three types of adducts (**1**, **2** and **3**) were isolated. The results are summarized in Table I. Structure elucidation was based on microanalysis, ir (C=N at 1610-1630 cm<sup>-1</sup>) and on comparison of the nmr data (deuteriochloroform) with those of model compounds **4**, **5** and **6** prepared by the method of Freund (3).



The structures **1b,c** were evident from their <sup>13</sup>C nmr spectra which showed C<sub>3</sub>-absorptions at δ 153-154 ppm comparable with those in model compounds **4** and **5** (the δ-values with respect to TMS are indicated on the structures). In addition, the <sup>1</sup>H and <sup>13</sup>C nmr spectra of **1** showed the presence of two identical *p*-substituted phenyl groups, pointing to a symmetric structure.

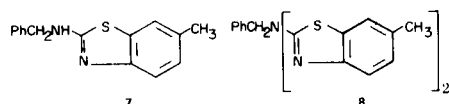
The synthesis of model compound **6**, for which an X-ray analysis has been determined recently (4), enabled structure elucidation of **2a,b**. Indeed, all these compounds exhibited a diagnostic C<sub>3</sub>-absorption at 178 ppm in their <sup>13</sup>C nmr spectra.

Finally, compound **3a** showed in the <sup>1</sup>H nmr spectrum two different *p*-nitrophenyl groups and a benzyl methylene absorption at δ 4.60. The latter was shifted upfield with respect to the methylene protons in **1a** (δ 5.44) and **2a** (δ 5.24) which is reasonable since the electron density on N<sub>4</sub> in **1** and **2** is strongly decreased by resonance. Note also that the same difference in shift value was found for the methylene protons in model compound **4** (at δ 4.47 and 5.01).

In our discussion, we have assumed that the structural isomers **1**, **2** and **3** result from different modes of addition of the intermediate *N*-aryliminothiaziridine and not from a Dimroth rearrangement (5) of the major product **1** during the reaction conditions. This is consistent with our obser-

vation that **1a** as well as **1b** did not isomerize at 60°, even not when heated at 100° for 1-3 days.

For the sake of completeness, we should also mention that the reaction of benzyl azide with *p*-tolyl isothiocyanate furnished, in addition to **1c**, small amounts of the benzthiazole **7** (3%, m.p. 176-178°) and the dibenzthiazole **8** (6%, m.p. 201-203°).



Acknowledgment.

The authors are indebted to the F. K. F. O. (Belgium) for financial support.

#### REFERENCES

- (1) E. Van Loock, J. M. Vandensavel, G. L'abbé, and G. Smets, *J. Org. Chem.*, **38**, 2916 (1973); G. L'abbé, E. Van Loock, R. Albert, S. Toppet, G. Verhelst, and G. Smets, *J. Am. Chem. Soc.*, **96**, 3973 (1974); G. L'abbé, *Bull. Soc. Chim. France*, in press.
- (2) D. M. Revitt, *J. Chem. Soc., Chem. Commun.*, **24** (1975).
- (3) M. Freund, *Ann. Chem.*, **285**, 154, 166 and 184 (1895); see also M. G. Paranjpe and R. K. Gosavi, *Indian J. Chem.*, **5**, 125 (1967).
- (4) C. L. Raston, A. H. White, A. C. Willis and J. N. Varghese, *J. Chem. Soc., Perkin II*, 1096 (1974).
- (5) M. Wahren, *Z. Chem.*, **9**, 241 (1969).