

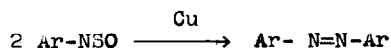
THE CHEMISTRY OF CUMULATED DOUBLE BOND COMPOUNDS V  
THE SYNTHESIS OF AZO COMPOUNDS FROM N-SULFINYLAMINES

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In a previous paper (1), we reported new routes to sulfurdiimides from arylthionylamines through the use of anionic catalysts. In this paper, the synthesis of azo compounds from N-sulfinylamines is described. When a mixture of the arylthionylamine and finely divided copper was simply heated at temperatures in the range of 110° to 140°, the formation of azo compounds was observed (method A) (2).



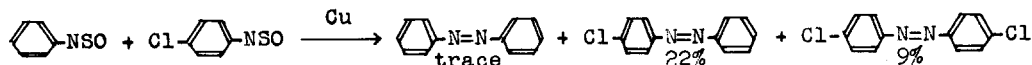
In the presence of aromatic hydrocarbons, copper powder catalyzed similarly the decomposition of arylthionylamines to azo compounds (method B).

Based on a limited number of observations, we propose that electron attracting substituents increase the reactivity of arylthionylamines in the formation reaction of azo compounds. Examples are (substituents and yields are given): 4-chloro-, 39.4%; 2-chloro-, 31.9%; 4-methyl, 2.9%.

Further examples are found in Table 1.

Unsymmetrical azo compounds were prepared in a similar manner as above.

For example, thionylaniline reacted with 4-chlorothionylaniline to give a following yield of 4-chloroazobenzene (Table 2).



However, it is needed to investigate further regarding the optimum conditions for preparation of symmetrical and unsymmetrical azo compounds.

The copper-catalyzed reaction mechanism is not apparent at present.

TABLE 1

## THE SYNTHESIS OF SYMMETRICAL AZO COMPOUNDS FROM ARYLTHIONYLAMINES

Run.	Reactants R-NSO	Conditions		Method	Products (Yields <sup>d</sup> %) R-N=N-R
		temp. (°c)	time (hr.)		
1	C <sub>6</sub> H <sub>5</sub> -	130	4	A <sup>a</sup>	30.0
2	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	130	7	A	52.8
3	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	140	8	A	8.3
4	o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	130	8	A	trace
5	C <sub>6</sub> H <sub>5</sub> -	110	8	B <sub>1</sub> <sup>b</sup>	3.3
6	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	110	8	B <sub>1</sub>	2.9
7	p-ClC <sub>6</sub> H <sub>4</sub> -	110	8	B <sub>1</sub>	39.4
8	o-ClC <sub>6</sub> H <sub>4</sub> -	110	8	B <sub>1</sub>	31.9
9	o-ClC <sub>6</sub> H <sub>4</sub> -	140	5	B <sub>2</sub> <sup>c</sup>	39.8
10	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	140	8	B <sub>2</sub>	11.6

a. 0.1 mole of R-NSO/0.1 mole of copper.

b. 0.1 mole of R-NSO/0.1 mole of copper in 30 ml. toluene.

c. 0.1 mole of R-NSO/0.1 mole of copper in 30 ml. xylene.

d. Yields based on the starting N-sulfinylamines.

TABLE 2

## THE SYNTHESIS OF UNSYMMETRICAL AZO COMPOUNDS FROM ARYLTHIONYLAMINES

Reactants <sup>a</sup>		Conditions		Products (Yields <sup>b</sup> %)		
R-NSO	R'-NSO	temp. (°c)	time (hr.)	R-N=N-R	R-N=N-R'	R'-N=N-R'
C <sub>6</sub> H <sub>5</sub> -	p-ClC <sub>6</sub> H <sub>4</sub> -	130	8	trace	22	9

a. 0.1 mole of R-NSO/0.1 mole of R'-NSO/0.2 mole of copper.

b. Yields are based on products isolated by column chromatography.

## REFERENCES

- (1) T. Minami, T. Agawa, et al., Tetrahedron Letters in press.
- (2) T. Minami and T. Agawa, Abstracts of 20th Annual Meeting of Chemical Society of Japan, Tokyo, in April 1967, Vol. III P.446.