E2-53: A convenient synthesis of arylsulfides from diazonium tetrafluoborates using phenyltrimethylsilane

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The synthesis of arylsulfides has attracted continued interest since the discovery of the Ziegler reaction. Many methods have been employed profitably in the synthesis of arylsulfides of which (i) metal catalysis with arenes or aryliodides, (ii) photo and electrochemical induction with aryliodides and (iii) dediazotization reactions in the presence of various thiols and thiolates, are significant. This paper presents a new, convenient Ziegler type method for the synthesis of unsymmetrical thioethers such as diaryl and alkyl arylthioethers from diazoniumtetrafluoborate and the corresponding thiotrimethylsilanes. The yields are variable. The main by-products are the protodediozatized products or diphenyldisulfide which are easy to remove.

The Ziegler reaction is characterized by the ready availability of the starting materials and its simplicity. However accumulation of the diazoester, which is a heat labile intermediate has caused rare explosions, and modifications of the method are now used.

Aryldiazoniumtetrafluoborates too are attractive starting materials because of their stability and ease of preparation. They can be easily dediozotized. This paper explores the use of an activated thiolate namely phenylthiotrimethylsilane with aryldiazoniumtetrafluoborates, to prepare arylsulfides safely.

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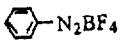
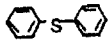
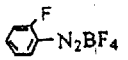
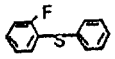
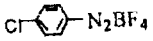
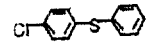
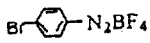
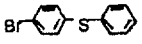
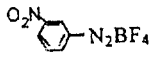
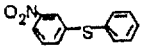
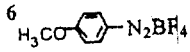
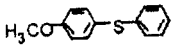
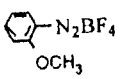
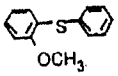
The general procedure for the synthesis of arylphenylsulfide: A solution of phenylthiotrimethylsilane (2.0g, 1.1 mmol.) in 5 ml spectroscopic grade dimethylformamide, is added dropwise over 20 min to a solution of the corresponding diazoniumtetrafluoborate salt (1.0 g) maintained at -10°C (by an ice-salt mixture). The solution was allowed to attain room temperature. The solution was stirred with 10 ml 20% aqueous sodium sulfide solution for 12 h and extracted with 3x20 ml portions of methylenechloride. The organic layer was washed with 2x30 ml portions of 20% aqueous sodium hydroxide and 30 ml water, and 30 ml brine. The solvent was removed under reduced pressure, under nitrogen, and the product isolated on a silica column with hexane:methylene chloride, preparative layer chromatography, or vacuum distillation. The products were characterized by GC-MS, high resolution mass spectroscopy and NMR.

This modification of the Ziegler reaction gave arylsulfides at room temperature without any hazard. The yields vary (see Table), ortho substituted salts giving comparatively lower yields.

Table 1: The synthesis of phenylarylsulfides from aryldiazoniumtetrafluoborate and phenylthiotrimethylsilane.

	Diazonium salt	Product	Yield(%, GC-MS)@	Isolated yields(%)
1			00	98
2			52	36
3			52 (90@)	74
4			72	64
5			46	
6			70	52
7			0	

@ Values indicate yields with cupric sulfide