

## Novel Alumina-catalysed Reactions of Arylthioalkyl Halides

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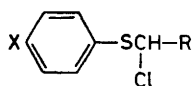
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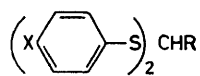
**Summary**  $\omega$ -Chloroalkyl aryl sulphides rearrange to  $\alpha\omega$ -bisaryl thioalkanes on treatment with alumina, and an alumina-catalysed equivalent of the Ullmann biphenyl synthesis is reported.

REACTIONS undergone by organic molecules when adsorbed on alumina are of considerable current interest and importance.<sup>1</sup> We have recently described<sup>2</sup> a novel reaction in which chloromethyl aryl sulphides of type (1a) or (1b) are readily transformed into bisarylthiomethanes (2a, b) on

treatment with alumina. More recent studies further indicate the generality of this process,  $\alpha$ -chloroalkyl aryl sulphides (1c) and (1d) being also transformed in high yield (>80%) into dithioacetals (2c,d). This method therefore offers a convenient and direct route into this class of useful synthons.<sup>3</sup>

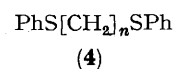
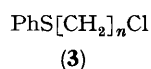


(1)



(2)

- a; R = H, X = H, Me, Br  
 b; R = CO<sub>2</sub>Et, X = H, Me, Br  
 c; R = Me, X = H, Me  
 d; R = Ph, X = H

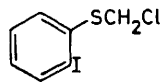


- a; n = 2  
 b; n = 3  
 c; n = 4

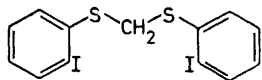
We now report that this new rearrangement is not restricted to  $\alpha$ -chlorosulphides, but may be extended to systems in which the halogen and sulphur are separated by more than one methylene unit. Thus, when chloroalkyl aryl sulphides (3a-c) were heated (120 °C) over neutral alumina, the bisarylthio-products (4a)<sup>4</sup>, (4b)<sup>5</sup> and (4c)<sup>6</sup> were obtained in near quantitative yields.†

† Structures were confirmed by n.m.r. spectroscopy.

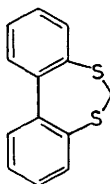
We have further observed that *o*-iodophenyl chloromethyl sulphide (5) was converted on gentle warming



(5)



(6)



(7)

(50—55 °C)<sup>2</sup> with alumina into dithioacetal (6) (95%). On heating with alumina at 120 °C, either (5) or (6) eliminated iodine to yield ( $\geq 90\%$ ) the cyclised product (7).<sup>7</sup> This reaction, which did not occur in absence of alumina, represents, to our knowledge, a unique alumina-catalysed aryl coupling which compares interestingly with the conventional Ullmann procedure.<sup>8</sup>

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<sup>1</sup> For a review see G. H. Posner, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 487.

<sup>2</sup> M. M. Campbell, V. B. Jigajinni, K. A. MacLean, and R. H. Wightman, *Tetrahedron Lett.*, 1980, **21**, 3305.

<sup>3</sup> E.g. T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, 1972, **94**, 8641; P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074; T. Shono, Y. Matsumura, and S. Kashimura, *Tetrahedron Lett.*, 1980, **21**, 1545.

<sup>4</sup> R. F. Brookes, J. E. Cranham, W. A. Cummings, D. Greenwood, B. S. Jackson, and H. A. Stevenson, *J. Sci. Food Agric.*, 1957, **8**, 31.

<sup>5</sup> F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1949.

<sup>6</sup> C. S. Marvel and R. R. Chambers, *J. Am. Chem. Soc.*, 1948, **70**, 993.

<sup>7</sup> D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. C*, 1971, 3454.

<sup>8</sup> For a review see P. E. Fanta, *Synthesis*, 1974, 9.