Novel Alumina-catalysed Reactions of Arylthioalkyl Halides

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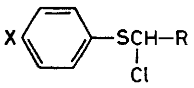
Summary ω-Chloroalkyl aryl sulphides rearrange to αω-bisaryl thioalkanes on treatment with alumina, and an alumina-catalysed equivalent of the Ullmann biphenyl synthesis is reported.

Reactions undergone by organic molecules when adsorbed on alumina are of considerable current interest and importance.[1] We have recently described[2] 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, α-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.[3]



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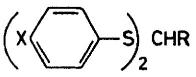

(2)

a; R = H, X = H, Me, Br
b; R = CO_2Et, X = H, Me, Br
c; R = Me, X = H, Me
d; R = Ph, X = H

$PhS[CH_2]_nCl$ (**3**)

$PhS[CH_2]_nSPh$ (**4**)

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

We now report that this new rearrangement is not restricted to α-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**)[4], (**4b**),[5] and (**4c**)[6] were obtained in near quantitative yields.†

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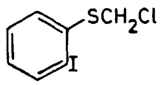
† Structures were confirmed by n.m.r. spectroscopy.

We have further observed that *o*-iodophenyl chloromethyl sulphide (**5**) was converted on gentle warming (50—55 °C)[2] with alumina into dithioacetal (**6**) (95%). On heating with alumina at 120 °C, either (**5**) or (**6**) eliminated iodine to yield (≥90%) the cyclised product (**7**).[7] 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.[8]



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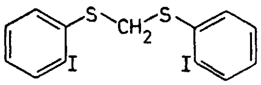

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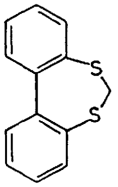

(7)

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