

A NOVEL REACTION OF α -CHLOROSULFIDES.

A NEW SYNTHESIS OF DIARYLETHYLENES (STILBENES).

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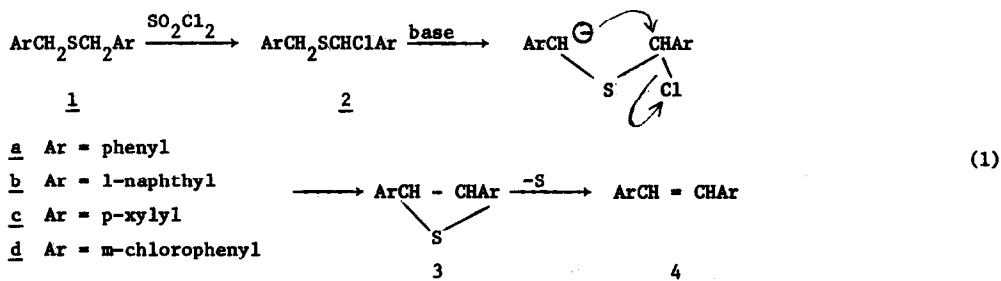
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There has been considerable recent interest in the development of new synthetic methods involving organosulfur intermediates.¹ In this respect, disubstituted sulfides make attractive intermediates, because they are easily prepared from readily accessible starting materials in good yields.² Moreover the synthesis is not limited to linear compounds, but can also be made to give good yields of cyclic compounds from difunctional precursors.³ If then the C-S-C linkage can be converted into a C-C single or double bond, a useful synthetic route develops. This conversion was first^{4a} achieved by Ramberg and Bäcklund in 1940, who reported that α -halosulfones, on treatment with aqueous alkali, are transformed into olefins.⁵ Since then the Ramberg-Bäcklund reaction has been studied in considerable detail, and is believed to proceed through an epi-sulfone intermediate.^{4b}

Although the reaction appears general^{9,10} for molecules containing the structural elements of a sulfonyl group, an α -halogen and at least one α' -hydrogen atom, surprisingly, there appears to be no report of a successful reaction attempted on a sulfide rather than the sulfone. I would now like to report the direct conversion of an α -chlorosulfide into an alkene, without proceeding through the sulfone.

Bearing in mind the acidity of benzylic protons, it was anticipated that the reaction shown in eq. 1 should be successful, provided that conditions could be found that would prevent both hydrolysis of the α -chlorosulfide, 2, and ring opening of the intermediate episulfide, 3, before extrusion of sulfur had taken place.



- a Ar = phenyl
b Ar = 1-naphthyl
c Ar = p-xylyl
d Ar = m-chlorophenyl

Episulfides can be desulfurised to olefins by trisubstituted phosphines,¹¹ of which triphenylphosphine appeared to be the most convenient since it is readily available and is stable under basic conditions. The choice of base however, was more restricted, since α -chlorosulfides are rapidly hydrolysed to thiols and aldehyde derivatives.¹² Further, intermolecular nucleophilic displacement of the halogen atom is quite possible,¹³ unlike the case of the corresponding sulfones.¹⁴ Potassium t-butoxide thus seemed a reasonable choice.

After considerable experimentation, the following reaction conditions gave repeatedly good yields of diarylethylenes: The diarylsulfides, 1a-d, were chlorinated in about 90% yields to the mono- α -chlorosulfides, 2a-d, by SO_2Cl_2 in CCl_4 .¹⁵ The α -chlorosulfide (5 mmole) was dissolved directly in THF (20 ml, dried over LAH) under a N_2 atmosphere. Triphenylphosphine (5 mmole) was added followed by potassium t-butoxide (5.5 mmole, freshly sublimed). The reaction mixture was brought to reflux over 15 minutes and heated under reflux for 24-36 hours.¹⁷ After acidification and chromatography on silica gel, the diarylethylenes, 4a-d, were isolated in good yields, (reaction, yield, trans/cis ratio: a, 82%, 10; b, 94%, >3; c, 90%, 9; d, 60%, 9). If the reaction were stopped in its early stages, a considerably greater percentage of cis-4 was present, however, the overall reaction yield was reduced.

The order of addition of triphenylphosphine and base is quite critical, since addition of the base first, resulted in a negligible yield of stilbene. It would thus seem that the mechanism of the reaction is more complicated than at first suspected. Possibly the phosphine complexes rapidly with the sulfur atom and prevents its loss as sulfide anion. That the phosphonium salt was not an intermediate was shown by prior reaction of 2a with P^\ominus in benzene when the salt 5 ($\text{OCH}_2\text{SCH}_2\text{P}^+\text{Cl}_3$) (mp 190-192°) separated in 64% yield.¹⁸ Subsequent treatment of 5 with KOBU^t gave a thermally stable bright orange ylide, which on addition of water returned sulfide 1a.

Despite the fact that the mechanism is not yet fully understood, the conversion of a dibenzylic sulfide to a diarylethylene by the new reaction is a facile process which occurs in good yield. The applicability of the reaction to aliphatic sulfides is currently under investigation.

Acknowledgement

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References and Footnotes

1. For a review see E. Block, J. Chem. Ed., **48**, 815 (1971).
2. Reaction of alkyl or aralkyl halides with sodium sulfide in DMSO, ethanol or benzene usually gives 70-95% yields of disubstituted sulfide. See for example, R. L. Shriner, J. Amer. Chem. Soc., **52**, 2066 (1930).
3. For a review containing a number of examples see F. Vögtle and P. Neumann, Synthesis, **85** (1973).
4. (a) L. Ramberg and B. Bäcklund, Arkiv. Kemi Mineral. Geol., **13A**, No. 27 (1940); Chem. Abstr., **34**, 4725 (1940).
(b) For recent reviews of the Ramberg-Bäcklund reaction, see F. G. Bordwell in "Organosulfur Chemistry". M. J. Janssen, Ed., John Wiley & Sons, Inc., New York, N.Y., 1968; L. A. Paquette, Accounts Chem. Res., **1**, 209 (1968).
5. More recently developed conversions are the high temperature pyrolysis of sulfones,^{6,7} the photolysis of sulfides in the presence of phosphines,⁷ and the Stevens rearrangement of sulfonium salts.⁸
6. E. C. Leonard, J. Org. Chem., **30**, 3258 (1965); M. P. Cava and J. A. Kuczkowski, J. Amer. Chem. Soc., **92**, 5800 (1970); F. Vögtle, Chem. Ber., **102**, 1449 (1969) and Angew. Chem. Int. Ed., **8**, 274 (1969).
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9. The Ramberg-Bäcklund reaction fails in those cases in which the carbanion is geometrically incapable of displacing the α -halogen atom.^{5b}
10. N. P. Neureiter, J. Amer. Chem. Soc., **88**, 558 (1966).
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12. A. Rieche, H. Gross and E. Höft, Chem. Ber., **93**, 88 (1960).
13. H. Gross and E. Höft, Angew. Chem. Int. Ed., **6**, 335 (1967).
14. F. G. Bordwell and G. D. Cooper, J. Amer. Chem. Soc., **73**, 5184, 5187 (1951).
15. In my hands the chlorination^{14,16} of sulfides yielded 50-60% (by n.m.r.) of monochloride and substantial amounts of dichloride. The yield of monochloride could be increased by running together dilute streams of sulfide in CCl_4 (1 mole/10 ml) and SO_2Cl_2 in CCl_4 (1 mmole/10 ml) such that initial reaction^{16b} was complete before bulk mixing took place.
16. (a) L. A. Paquette, J. Amer. Chem. Soc., **86**, 4085 (1964).
(b) L. A. Paquette, J. Amer. Chem. Soc., **86**, 4089 (1964).
17. Alternatively the solvent was evaporated in the N_2 stream over 2 hours reflux, and the resultant oily mass heated at 80-100°C for 10 hours.
18. The remainder forms an unidentified purple oil.