

Novel Rearrangement of $\alpha\alpha$ -Dichlorodibenzyl Sulphides. A New Synthesis of Acetylenes

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Summary $\alpha\alpha$ -Dichlorodibenzyl sulphides are converted directly into diarylacetylenes by reaction with triphenylphosphine and potassium *t*-butoxide in anhydrous tetrahydrofuran.

THE Ramberg-Bäcklund rearrangement¹ of $\alpha\alpha$ -dichlorodibenzyl sulphones with aqueous sodium hydroxide gives complex mixtures consisting of 1-chloro-*cis*- and -*trans*-1,2-diphenylethylenes, diphenylacetylenes, and vinylsulphonic acid salts.² A recent³ improvement uses triethylenediamine in dimethyl sulphoxide to effect the rearrangement to the 2,3-diphenylthiiren 1,1-dioxide which can then subsequently be thermally decomposed to form the diphenylacetylenes in good yields.

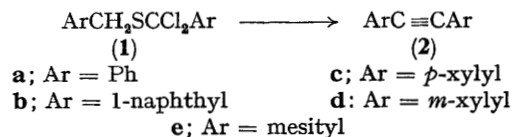
I have found that $\alpha\alpha$ -dichlorodibenzyl sulphides can be treated with triphenylphosphine followed by potassium *t*-butoxide in anhydrous tetrahydrofuran to give good yields of diarylacetylenes directly, without the necessity of proceeding through the sulphone.

As with the related rearrangement⁴ of α -chlorodibenzyl sulphides to give diarylethylenes, the order of addition of the reagents is critical, and as such the mechanism of the reaction probably is not analogous to that of the Ramberg-Bäcklund rearrangement.¹

Despite the fact that the mechanism is at present unknown, the synthesis of acetylenes in this manner from readily accessible starting materials (initially the benzyl halides) is simple, inexpensive, and fast, particularly bearing in mind that there are relatively few methods available⁵ for the synthesis of acetylenes from species derived by cleavage of the triple bond.

The following conditions gave repeatedly good yields of products. To a solution of the $\alpha\alpha$ -dichlorosulphide² (**1a—e**) (5 mmol) in tetrahydrofuran (20 ml, dried over LiAlH₄) under N₂, PPh₃ (5 mmol) was added followed by KOBu^t (11 mmol, freshly sublimed) at 0–20 °C. The mixture was brought to reflux over 15 min and heated under reflux for 24–36 h. After acidification and filtration through silica gel, the diarylacetylenes (**2a—e**) were isolated in the following yields: (**2a**), 92; (**2b**) 93; (**2c**), 70; (**2d**), 72; (**2e**), 62%. Satisfactory spectra, and elemental analyses where appropriate, were obtained for all compounds.

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¹ F. G. Bordwell, 'Organosulfur Chemistry,' ed. M. S. Janssen, Interscience, New York, 1967, ch. 16; L. A. Paquette, *Accounts Chem. Res.*, 1968, **1**, 209.

² L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, 1967, **89**, 4483.

³ J. C. Philips, J. V. Swisher, D. Haidukewych, and O. Morales, *Chem. Comm.*, 1971, 22.

⁴ R. H. Mitchell, *Tetrahedron Letters*, 1973, 4395.

⁵ See for example: C. A. Buehler and D. E. Pearson, 'Survey of Organic Syntheses,' Wiley-Interscience, New York, 1970, ch 3.