A New 1,2-Rearrangement of Carbon from Sulphur to Carbon in 2,2-Diaryl-1,3-dithianes

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2,2-Diaryl-1,3-dithianes undergo with lithium di-isopropylamide in tetrahydrofuran a Wittig-type rearrangement to form the anions of the 2,2-diaryltetrahydrothiophene-3-thiols which are further converted into bis(2,2-diaryltetrahydrothiophen-3-yl) disulphides by treatment with aqueous ammonium chloride and after subsequent autoxidation.

In most cases, carbanions adjacent to sulphur in sulphides are stable and do not rearrange.[1,2] Only a few examples of Wittig-type rearrangements of sulphides involving migration of carbon from sulphur to an α-carbanion are found in the literature.[1,3] We now report a new example of a Wittig-type rearrangement which occurs upon metallation of several 2,2-diaryl-1,3-dithianes (1) with lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) and after subsequent quenching with an aqueous solution of ammonium chloride. The compounds (1) were readily metallated with an excess of LDA in THF at low temperature. Treatment of the reaction mixture with aqueous ammonium chloride also at low temperature affords the bis(2,2-diaryltetrahydrothiophen-3-yl) disulphides (5) in good to nearly quantitative yields (Scheme 1, Table 1). The structures of compounds (5) were confirmed on the basis of their ^{1}H and ^{13}C n.m.r. and mass spectra.†

Quenching of the reaction mixture with an alkyl halide

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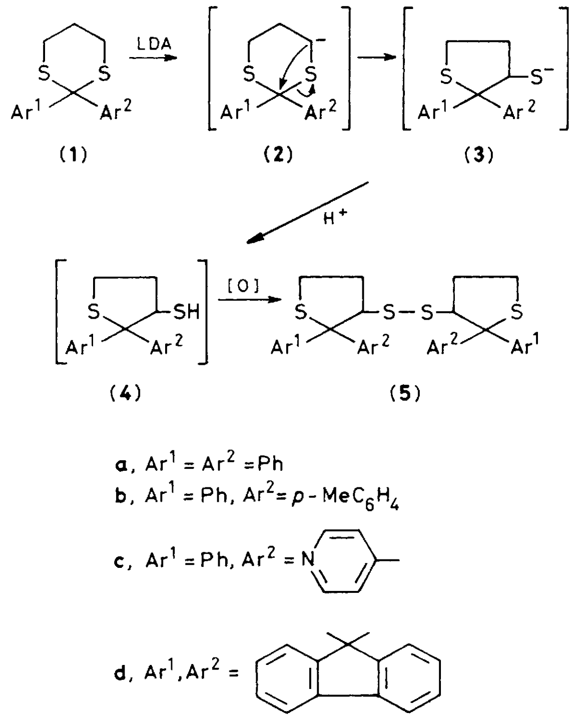
† N.m.r. spectroscopic data for (**5a**): ^{1}H, δ ($CDCl_3$) 0.9—1.4 (m, 2H), 1.7—2.7 (m, 4H), 2.8—3.1 (m, 2H), 3.9—4.3 (m, 2H), 6.8—7.5 (m, 20H); ^{13}C, δ ($CDCl_3$) 28.61 (t), 38.49 (t), 48.21 (d), 68.80 (s), 126.60 (d), 126.83 (d), 127.07 (d), 128.06 (d), 130.29 (d), 142.40 (s), 145.03 p.p.m. (s). The data for (**5b**–**d**) are analogous.



Scheme 1

Table 1. The formation of bis(2,2-diaryltetrahydrothiophen-3-yl) disulphides (**5**) from 2,2-diaryl-1,3-dithianes (**1**).

Starting substrate (**1**)	Product (**5**)[a]	Yield (%)	M.p. (°C) or b.p. (°C/Torr)
a[b]	**a**	97	155/3
b[b]	**b**	95	156/2.5
c	**c**	88	67—73[c] (Hexane)
d	**d**	97	138—139 (Hexane)

[a] All the products showed correct combustion analysis (±0.3%). [b] One equivalent of *N,N,N′,N′*-tetramethylethylenediamine based on LDA was used as the additive. [c] The correct melting point could not be determined because it is an amorphous solid.

instead of aqueous ammonium chloride, gave the corresponding 2,2-diaryl-3-alkylthiotetrahydrothiophene,[4] which suggested the anionic species (**3**) as an intermediate in the reaction. The initial metallation of the methylene group attached to sulphur in (**1**) to give (**2**) is probable by analogy with other known reactions.[5–8] Presumably, (**2**) undergoes a Wittig-type rearrangement involving migration of the carbon atom bearing the two aryl substituents from the sulphur to the carbanion to give (**3**). This mechanism may be supported by experiment which shows that one of the requirements for this reaction is the presence of two electron-withdrawing substituents at the 2-position of (**1**). Treatment of (**3**) with aqueous ammonium chloride gave the corresponding thiols (**4**). However, all attempts to isolate (**4**) in a pure state failed. The compounds (**4**) were extremely susceptible to air oxidation to (**5**). The easy conversion of (**4**) to (**5**) is probably due to the electron-withdrawing aryl groups in (**4**).

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