# Regiospecific and Convergent Synthesis of α-Phenylthio-ketones

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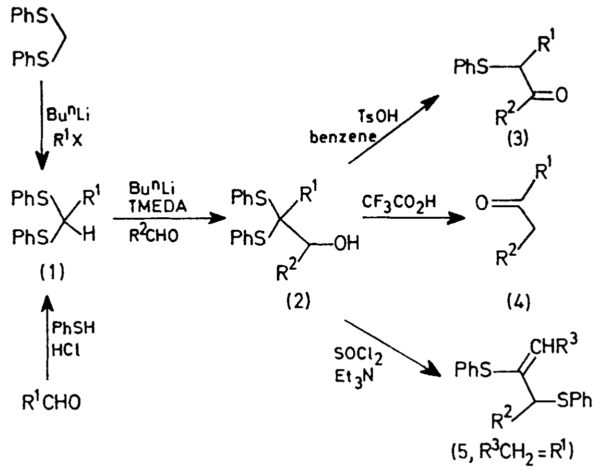
*Summary* Adducts of bis(phenylthio) carbanions and aldehydes give unrearranged α-phenylthio-ketones on treatment with toluene-*p*-sulphonic acid.

α-PHENYLTHIO-KETONES (*e.g.* **3**), being ketones activated on one side of the carbonyl group by an easily removable functional group (PhS), are useful synthetic intermediates[1] able to act as specific enol equivalents, or as precursors for

$\alpha\beta$-unsaturated ketones.[2] They are usually made by direct sulphenylation of the parent ketone,[1,2] a route which gives good yields if the ketone is symmetrical or blocked on one side, but which is not otherwise regiospecific. We report a new synthesis of $\alpha$-phenylthio-ketones which is regiospecific and convergent[3] since the bond between the carbonyl carbon and the carbon atom bearing the phenylthio group is made in the first step.



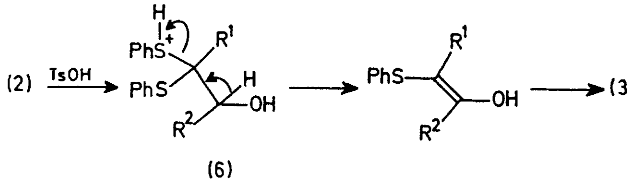
SCHEME. TMEDA = *NNN′N′*-tetramethylethylenediamine.

The adducts (**2**, Scheme) formed from bis(phenylthio) carbanions (from **1**) and aldehydes[4] react rapidly with toluene-*p*-sulphonic acid (TsOH) in benzene under reflux (2—3 min) to give $\alpha$-phenylthio-ketones (**3**) isolated in reasonable yield by washing with aqueous base and chromatography. No rearrangement occurs during this reaction, the original carbonyl group of the aldehyde being regenerated. We suppose that the mechanism involves a simple elimination of benzenethiol (**6**) or a hydride shift similar to the alkyl shifts observed in adducts of (**1**) and ketones.[5]

TABLE

| $R^1$ | $R^2$ | Yields of reaction products/% |  |
|---|---|---|---|
|  |  | Aldehyde adducts (**2**) | $\alpha$-Phenylthio-ketones (**3**) |
| Me | Me | 52 | 82 |
| Et | Me | 66 | 45 |
| Et | Et | 44 | 52 |
| Et | $[CH_2]_6Me$ | 59 | 58 |
| Bu^n | Me | 62 | 78 |
| Me | Ph | 57 | 64 |

The route appears to be general† (Table) making available unsymmetrical ketones sulphenylated on only one $CH_2$ group. Though the yields are only moderate (45—82%), separation from the other regioisomer is avoided since it cannot be formed. All the compounds (**2**) listed in the Table also give the ketones (**4**) and the specific enol equivalents (**5**) under the right conditions (Scheme),[4] emphasising their remarkable versatility.



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† $R^1$ may not be aryl since the carbanion from (**1**; $R^1$ = Ph) does not react with aldehydes. However, compounds of the type (**3**; $R^1$ = Ar) may be made by the regioselective sulphenylation of the parent ketone (see ref. 1).

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[3] I. Fleming, 'Selected Organic Syntheses,' Wiley, London, 1973, p.100.
[4] P. Blatcher, J. I. Grayson, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 547.
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