Convenient Synthesis of Allenyl Sulphides; Application to the Synthesis of αβ-Unsaturated Ketones†

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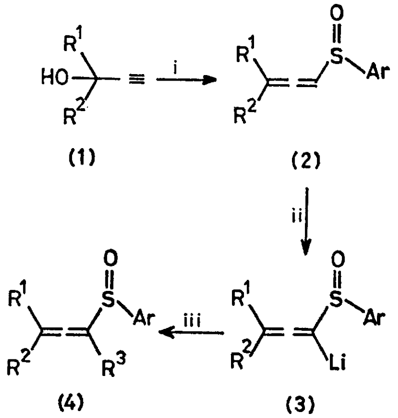
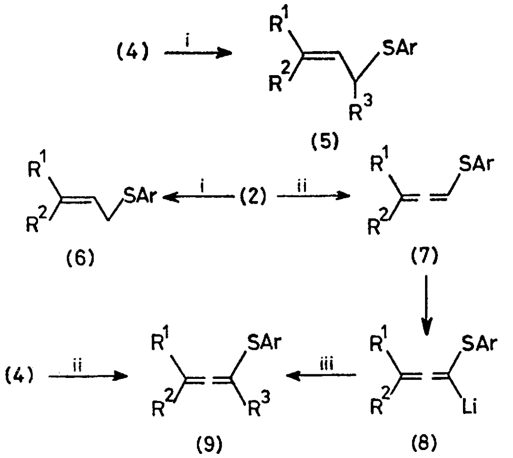
Summary P_2S_5 in methylene chloride containing pyridine reduces allenyl phenyl sulphoxides to sulphides; the difficult hydrolysis of the latter is eased by the introduction of a methoxy group into the benzene ring and this method then becomes a practicable synthesis of αβ-unsaturated ketones.

ALLENYL SULPHOXIDES (**2**) are easily made from propynyl alcohols and benzenesulphenyl chloride.[1] We find that the sulphoxides (**2**) are readily metallated with n-butyl-lithium in ether, and are then alkylated with a variety of electrophiles (Scheme 1). However, reaction of the lithium derivative (**3**) with epoxides is sluggish, and to make the organolithium reagents more nucleophilic, the oxygen atom was removed. Lithium aluminium hydride in ether reduced the allenyl sulphoxides (**2**) and (**4**) to the allyl sulphides (**6**) and (**5**) in almost quantitative yield (hence an equivalent of exclusively α-alkylation in allyl systems). P_2S_5 in dry methylene chloride containing pyridine[2]‡ at room temperature or below gave in good yield the corresponding synthetically useful[3] allenyl sulphides (**7**) from (**2**) (Scheme 2 and Table), which were converted into their lithium derivatives[4] (**8**) with n-butyl-lithium in tetrahydrofuran (THF) at −80 °C. These reacted readily with a variety of electrophiles, including now epoxides.

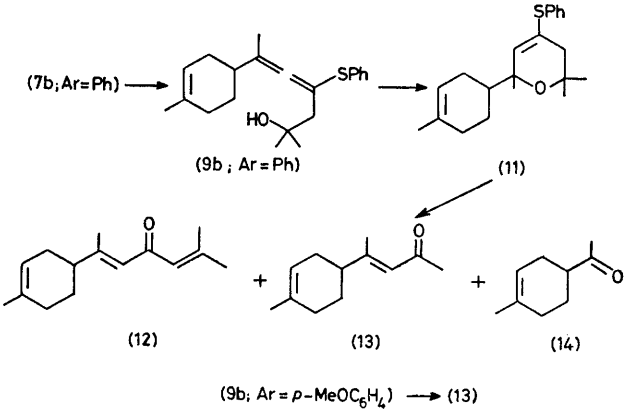


SCHEME 1. i, PhSCl or *p*-$MeOC_6H_4SCl$, Et_3N, Et_2O, −20 to −30 °C; ii, Bu^nLi, Et_2O, −78 °C; iii, electrophile, *e.g.*, MeI, RCHO, R_2CO.



SCHEME 2. i, $LiAlH_4$, Et_2O; ii, P_2S_5, C_5H_5N, CH_2Cl_2, 20 °C; iii, electrophile, *e.g.*, MeI, RCHO, R_2CO, $R\overline{CHCH_2O}$ $R_2\overline{CCH_2O}$.

For example, the allenyl phenyl sulphide (**7b**; Ar = Ph) after treatment with n-butyl-lithium in THF opened isobutylene oxide to give the alcohol (**9b**; Ar = Ph) (Scheme 3). Toluene-*p*-sulphonic acid in THF cyclised (**9b**; Ar = Ph) to (**11**) which was converted into atlantone[5] (**12**) (10:1, *trans*:*cis*) with mercuric chloride in wet acetonitrile.[6] However, the yield in the last step was only 35% [accompanied by the diene (**13**) and 4-acetyl-1-methylcyclohexene (**14**) from reversed aldol condensations], and several other syntheses were thwarted by the difficulty in hydrolysis of phenylthio-olefins,[7] and -allenes. Of several alternatives to the phenylthio group the *o*- and *p*-methoxyphenylthio§ were more successful.



SCHEME 3

Thus treatment of the allenyl sulphide (**7b**; Ar = *p*-$MeOC_6H_4$) in THF with n-butyl-lithium at −80 °C followed by addition of methyl iodide gave the sulphide (**9b**; Ar = *p*-

TABLE

Compd.	Sulphoxide (**2**) R¹	R²	% Yield of sulphide (**7**) Ar=Ph	Ar=*p*-$MeOC_6H_4$
a	Me	Me	91	82
b	Me	4-Methylcyclohex-3-enyl	69	65
c	$-[CH_2]_5-$		88	—
d	H	H	58	—
e	$Me_2C{=}CHCH_2CH$	Me	58	61
	Me	H	84	—

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‡ P_2S_5 reduction without pyridine (necessary here) has been applied to rather more stable systems (R. D. Baechler, S. K. Daley, B. Daly, and K. McGlynn, *Tetrahedron Letters*, 1978, 101).

§ The required *o*- and *p*-methoxybenzenesulphenyl chlorides were made by reaction of the methoxyphenyl Grignard reagent with sulphur and treatment of the resulting disulphide with chlorine.

$MeOC_6H_4$). Reaction of this compound with 1 equiv. of mercuric chloride in wet acetonitrile at room temperature gave *cis*- and *trans*-(**13**) in 68% yield, compared with 8% from the corresponding phenylthioallene (**9b**; Ar = Ph).

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