

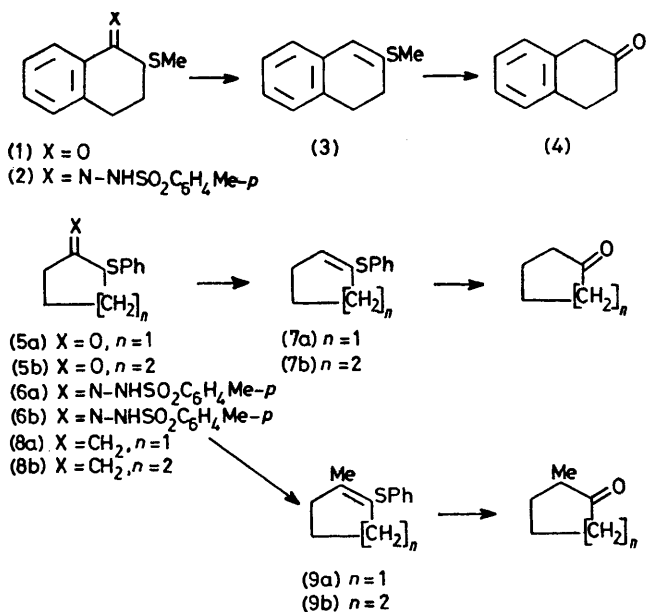
New 1,2-Transpositions and Alkylative 1,2-Transpositions of a Carbonyl Group

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Summary A new method for the 1,2-transposition and alkylative 1,2-transposition of carbonyl groups using α -sulphenylated ketones as the starting material is described.

RECENTLY, α -sulphenylated ketones have been proposed as key intermediates for the 1,2-transposition of carbonyl groups.¹ We have investigated the conversion of α -sulphenylated ketones into vinyl sulphide type compounds as a new method for the 1,2-transposition and alkylative 1,2-transposition of ketone groups.

The toluene-*p*-sulphonylhydrazone (2), prepared from (1), was treated with MeLi (6 mol. equiv.)² in ether at room temperature and afforded (3) [δ 2.23 (3H, SMe), 5.19 (1H, 1-H)]. Hydrolysis of (3) with mercuric chloride in acetonitrile-water gave (4)^{3,4} in 85% yield from (2). The toluene-*p*-sulphonylhydrazone (6a) was treated with BuⁿLi (2 mol. equiv.) in the presence of diazabicyclo[2.2.2]octane (3.2 mol. equiv.) in tetrahydrofuran (THF) at -78 °C. The mixture was kept at -78 °C for 15 min, and then kept at room temperature for 6 h to give (7a) [δ 5.53 (1H, 2-H)], in 90% yield; hydrolysis of (7a) with mercuric chloride gave cyclopentanone in 88% yield. Similarly the toluene-*p*-sulphonylhydrazone (6b) was converted into cyclohexanone via (7b) [δ 5.93 (1H, 2-H)], in 82% yield from (6b).



The reaction of methyltriphenylphosphonium bromide with (5a) in Me₂SO in the presence of dimethylsodium⁵ gave (8a) [δ 4.94 (2H, =CH₂)], in 87% yield. The *exo*-methylene double bond was selectively isomerized by treatment with BuⁿLi in THF at room temperature to yield (9a) [δ 1.83 (3H, 1-Me)]. Similarly, (5b) was converted into (9b) [b.p. 124—126 °C (1 mmHg), δ 1.91 (3H, 1-Me)] via (8b). Hydro-

lysis of (9a) and (9b) with mercuric chloride afforded 2-methylcyclopentanone and 2-methylcyclohexanone in 85 and 90% yield, respectively. This sequence of reactions should prove to be widely applicable to alkylative 1,2-transpositions of carbonyl groups.

(Received, 30th December 1977; Com. 1323.)

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