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

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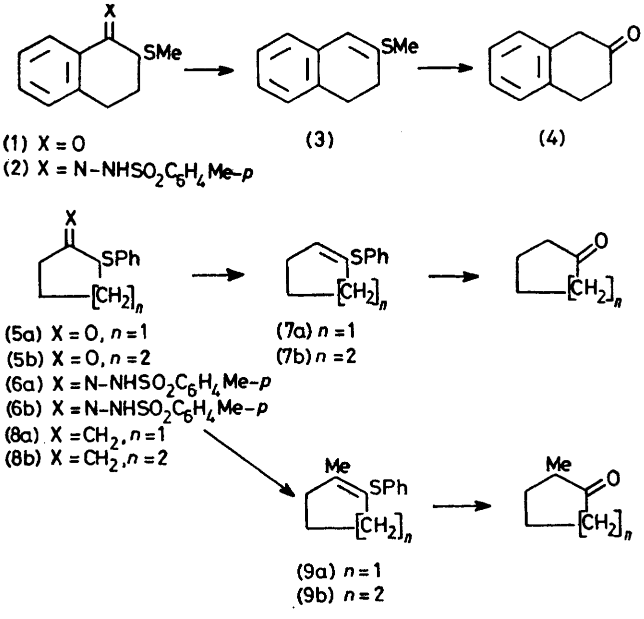
Summary A new method for the 1,2-transposition and alkylative 1,2-transposition of carbonyl groups using α-sulphenylated ketones as the starting material is described.

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 Bu^{n}Li (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**).



(1) X = O
(2) X = N-NHSO$_2$C$_6$H$_4$Me-*p*
(3)
(4)
(5a) X = O, *n* = 1
(5b) X = O, *n* = 2
(6a) X = N-NHSO$_2$C$_6$H$_4$Me-*p*
(6b) X = N-NHSO$_2$C$_6$H$_4$Me-*p*
(8a) X = CH$_2$, *n* = 1
(8b) X = CH$_2$, *n* = 2
(7a) *n* = 1
(7b) *n* = 2
(9a) *n* = 1
(9b) *n* = 2

The reaction of methyltriphenylphosphonium bromide with (**5a**) in Me_2SO in the presence of dimsylsodium[5] gave (**8a**) [δ 4·94 (2H, $=CH_2$)], in 87% yield. The *exo*-methylene double bond was selectively isomerized by treatment with Bu^nLi 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**). Hydrolysis 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.

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