Formation of Furans Involving Cyclisation of γ-Sulphenyl-βγ-unsaturated Ketones with $TiCl_4$

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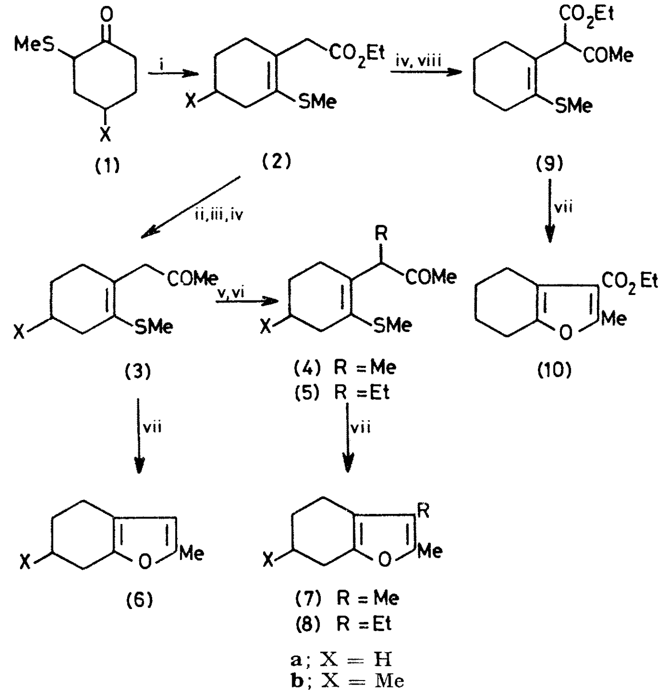
Summary Cyclisation of γ-methylthio-βγ-unsaturated ketones, which can be considered to be masked 1,4-diketones, with $TiCl_4$ afforded furan derivatives in moderate yield.



Scheme. i, (EtO)$_2$P(:O)CH$_2$CO$_2$Et, NaCH$_2$SOMe–Me$_2$SO; ii, KOH–EtOH; iii, 2 equiv. lithium di-isopropylamide (LDA)–tetrahydrofuran (THF), −78 °C; iv, MeCOCl; v, NaH–THF; vi, RI; vii, TiCl$_4$; viii, LDA–THF, −78 °C, 10 min.

During an investigation on the synthetic utility of γ-sulphenyl-$\beta\gamma$-unsaturated ketones, which can be considered to be masked 1,4-diketones, we found that they were smoothly converted into furan derivatives by the action of TiCl$_4$, and now report our results.

1-Acetonyl-2-methylthiocyclohexene (**3a**) was prepared from α-methylthiocyclohexanone (**1a**)[1] by the usual route *via* (**2a**) (Scheme) in 75% yield, and was treated with 2·2 equiv. of TiCl$_4$ in acetonitrile at room temperature under anhydrous conditions for 1 h to give 4,5,6,7-tetrahydro-2-methylbenzo[*b*]furan (**6a**)[2,3] [δ (CDCl$_3$) 2·17 (2-Me) and 5·63 (3-H); *m/e* 136 (M^+)] in 75% yield. Compounds (**6b**) (60%), (**7a**) (76%), (**7b**) (75%), (**8a**) (72%), and (**8b**) (77%) were obtained similarly by cyclisation of the corresponding 1-acetonyl-2-methylthiocyclohexenes (**3b**), (**4a,b**), and (**5a,b**) with TiCl$_4$. Compounds (**4a,b**) and (**5a,b**) were prepared by alkylation of (**3a,b**) with alkyl iodide. Furthermore, the reaction of compound (**9**), obtained from (**2a**), with TiCl$_4$ in acetonitrile gave compound (**10**) in 20% yield.

Since these cyclisations were carried out under anhydrous conditions, without using a procedure involving hydrolysis of a vinyl sulphide,[4] it is most probable that the cyclisations proceed without formation of 1,4-diketone intermediates, the sulphenyl group behaving as a good leaving group under the action of TiCl$_4$.[†]

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[†] The reaction mechanism, scope, applications, and limitations are under active investigation.

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