New Synthesis of 8a-Hydroxy-2-thiadecalins and Spirocyclopropanes from Dimethyl(vinyl)sulphonium Salts and Cyclic Ketones

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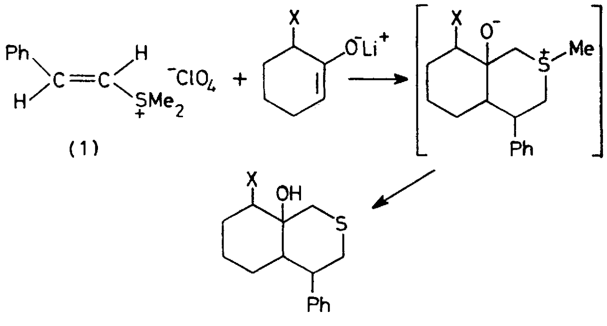
Summary Reactions of dimethyl(styryl)sulphonium perchlorate with cyclohexanone and 2-methylcyclohexanone lead to 8a-hydroxy-2-thiadecalin derivatives in the presence of lithium di-isopropylamide; similar reactions of α-tetralone and cyclopentanone give the spirocyclopropane derivatives (**6**) and (**7**), respectively.

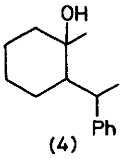
Many reactions of vinylsulphonium salts with ketone enolate anions are known to give cyclopropanes[1] and oxirans[2] but it has not been reported so far that these reactions also may yield cyclic sulphides and spirocyclopropanes. The spirocyclopropane derivatives 4-oxospiro[2,4]pentanes have been synthesized by the reaction of dimethylsulphonium methylide with α-chloro[3] and α-methylenecyclopentanones.[4] We now report a new method of synthesis of 8a-hydroxy-2-thiadecalins and spirocyclopropanes from dimethyl(styryl)sulphonium perchlorate (**1**) and cyclic ketones.

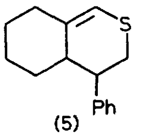


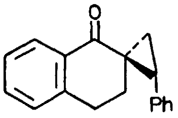
(1)

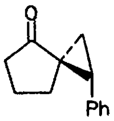
(2) X = H
(3) X = Me

When a mixture of lithium cyclohexanone enolate, generated from cyclohexanone and lithium di-isopropylamide, and the vinylsulphonium salt (**1**) in tetrahydrofuran–dimethylformamide was heated at 50 °C for 10 h, the thiadecalin (**2**)† (54%), m.p. 128—129 °C, was obtained. The yield was increased to 95% by addition of sodium phenoxide.[5] Treatment of (**2**) with Raney Ni gave the cyclohexane (**4**) (73%), b.p. 57—60 °C at 1 mmHg, and treatment with toluene-*p*-sulphonic acid led to the $\Delta^{1(8a)}$ compound (**5**), b.p. 87—90 °C at 1 mmHg, quantitatively. Similar treatment of the vinylsulphonium salt (**1**) with 2-methylcyclohexanone gave the 8-methyl-compound (**3**)‡ (62%), m.p. 127—129 °C.


(4)


(5)


(6)


(7)

Reactions of the vinylsulphonium salt (**1**) with the enolate anions of α-tetralone and cyclopentanone afforded the spiro-compounds (**6**) (98%), b.p. 130—132 °C at 1 mmHg, and (**7**) (62%), b.p. 92—94 °C at 1 mmHg, respectively.

The ring size of the cyclic ketones and the electrophilicity of the carbonyl groups seem to be important factors in determining the path the reaction takes.

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† All compounds had the expected elemental analyses and spectral data.

‡ The products (**2**), (**3**), and (**4**) exist as one stereoisomer but the absolute configuration has not yet been determined.

[1] See for example, J. Gosselck, H. Ahlbrecht, F. Dost, and G. Schmidt, *Tetrahedron Letters*, 1968, **995**; K. Kondo, Y. Liu, and D. Tunemoto, *J.C.S. Perkin I*, 1974, 1279.

[2] K. Takaki and T. Agawa, *J. Org. Chem.*, in the press.

[3] P. Bravo, G. Gaudina, C. Ticozzi, and A. Umani-Ronchi, *Tetrahedron Letters*, 1968, **4481**.

[4] O. Tsuge and I. Shinkai, *Bull. Chem. Soc. Japan*, 1970, **43**, 3514.

[5] T. Minami, I. Niki, and T. Agawa, *Phosphorus and Sulfur*, 1977, **3**, 55.