

A Short Synthesis of (\pm)-Cuparene

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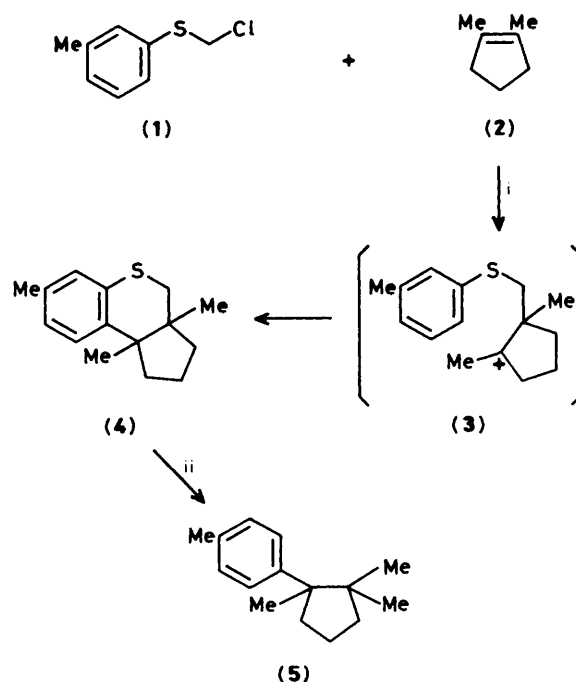
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Lewis-acid-promoted reaction of *m*-tolylthiomethyl chloride (1) with 1,2-dimethylcyclopentene (2) followed by desulphurisation of the resultant $[4^+ + 2]$ cycloadduct (4) gives (\pm)-cuparene (5).

The synthesis of cuparene and related compounds has presented an interesting problem in view of the steric congestion associated with two vicinal quaternary centres in a cyclopentane ring. The present communication offers our solution to this problem, exemplified by an extremely short synthesis of (\pm)-cuparene (5).¹

The key feature of our approach is based upon simultaneous 1,2-difunctionalisation of a tetrasubstituted alkene to give the vicinal quaternary carbon centres, by Lewis-acid-promoted $[4^+ + 2]$ polar cycloaddition with an arylthiomethyl chloride.²

Treatment of a mixture of *m*-tolylthiomethyl chloride (1) (2 mmol) and 1,2-dimethylcyclopentene (2) (2 mmol) with EtAlCl_2 (1 M solution in *n*-hexane) (2.2 mmol) in dry CH_2Cl_2 (5 ml) at 0°C for 10 min, then at room temperature for 1 h, gave the thiochroman derivative (4)[†] in 60% yield as an oily single stereoisomer. A mechanistic rationalisation of the formation of (4) is based on the assumption that the chloro sulphide (1), with the aid of EtAlCl_2 , attacks the double bond of (2) to form the new carbenium ion (3). This is followed by intramolecular Friedel-Crafts-type cyclisation to give the $[4^+ + 2]$ cycloadduct (4). EtAlCl_2 is the best of several Lewis



Scheme 1. Reagents and conditions: i, EtAlCl_2 , CH_2Cl_2 , 0°C to room temp.; ii, Raney nickel (W-2), EtOH, reflux.

[†] Satisfactory elemental analytical and spectroscopic data were obtained: δ (CDCl_3 ; 300 MHz) 1.14 (3H, s), 1.25 (3H, s), 1.5–1.95 (5H, m), 2.0–2.15 (1H, m), 2.23 (3H, s), 2.58 (1H, d, J 13.1 Hz), 2.88 (1H, d, J 13.1 Hz), 6.84 (1H, br. dd, J 8.2 and 2.0 Hz), 6.90 (1H, br. s), and 7.24 (1H, d, J 8.2 Hz). At present it is not clear which stereoisomer of (4) is obtained.

acids we have examined for this reaction [AlCl_3 (27%), Et_2AlCl (37%), SnCl_4 (33%), TiCl_4 (36%)].

Treatment of compound (**4**) with Raney nickel (W-2) in refluxing ethanol afforded (\pm)-cuparene (**5**), in 77% yield; i.r. and ^1H n.m.r. spectroscopic data were identical with those reported elsewhere.³

The starting chloride (**1**) (b.p. 73 °C at 2 mmHg) was readily prepared (56%) from *m*-thiocresol by reaction with an excess of bromochloromethane in the presence of 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) in MeCN at room temperature.

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References

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