

One Step Synthesis of Octalones or Indanones by Friedel–Crafts Acylation

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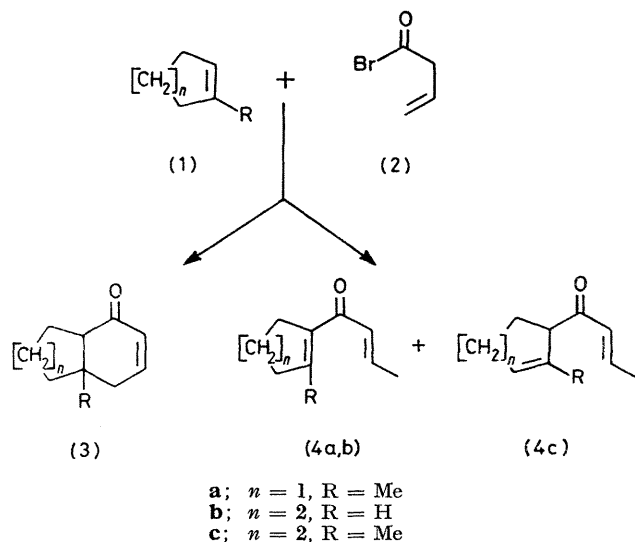
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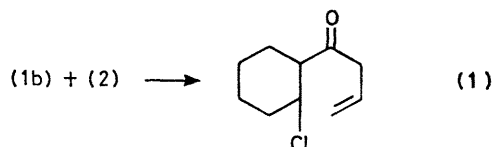
Summary Acylation of cyclohexene (or cyclopentene) by vinylacetyl bromide in the presence of AlCl_3 gave a mixture of the octalones (or indanones) (3) and the propenyl cyclohexenyl (or cyclopentenyl) ketones (4).

THE Robinson annulation reaction has long been employed as a convenient route to fused ring ketones.¹ We have found that bicyclodecenones and bicyclononenones can be prepared by a new and efficient one-step synthesis.

Treatment of the cycloalkenes (1) with but-3-enoyl bromide (2) in CH_2Cl_2 in the presence of AlCl_3 at low temperatures (-78 to 0°C) gave a mixture [70–80% overall yield from (2)] of the bicyclic ketones (3) and the dienones (4).



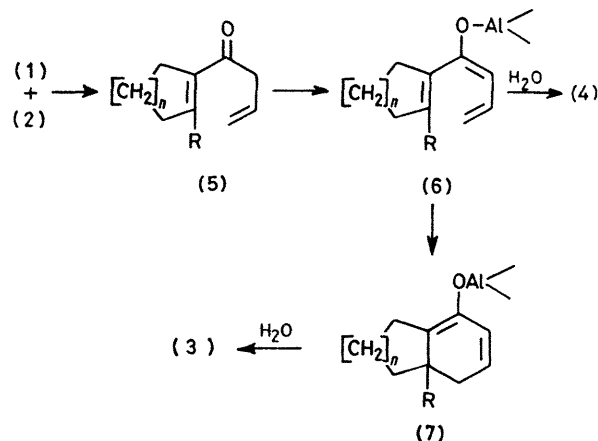
At low temperatures, chloro-ketone side-products were formed in <5% yield, but when experiments were performed at higher temperatures (ca. 0°C), the main products were β -chloro-ketones, see equation (1).



The formation of compounds (3) and (4) probably involves a Friedel–Crafts acylation of the cycloalkenes (1), followed by enolisation of the ketones (5), and a thermally allowed cyclisation of the enolates (6). Thermal cyclisation of (6) should be a disrotatory process,² but stereospecific non-concerted cyclisation has been observed.³

In a typical experiment anhydrous AlCl_3 (10 mmol) was stirred with CH_2Cl_2 (25 ml) and (2) (10 mmol) at room temperature until dissolution. The mixture was cooled to -78°C and cyclohexene (2 ml, ca. 20 mmol) was added. The mixture was kept at -78°C for 30 h and was then hydrolysed (basic work-up). With 1-methyl-cyclopentene and -cyclohexene the temperature was raised from -78 to 0°C over 24 h. Yields and ^1H n.m.r. data for compounds (3) and (4) were as follows: (3a) 55%, δ (CCl_4) 6.8 [1H, ddd (J 10.2, 4.4, and 3.8 Hz)], 5.92 [1H, d (J 10.2 Hz)], t (J 2 Hz)], 2.25 (2H, dd), and 1.13 (3H, s); (3b) 35%; (3c) 45%; *trans*-isomer 60%, δ (CDCl_3) 6.76 [1H, ddd (J 10, 5.0, and 2.75 Hz)], 5.94 [1H, ddd (J 10, 2.5, and 1.25 Hz)], 2.54 [2H, t (J 2.8 Hz)], and 1.0 (3H, s); *cis*-isomer 40%, δ (CDCl_3) 6.74, 5.92, 2.73 (2H, t), and 0.91 (3H, s); (4a) 45%; (4b) 65%;⁵ and (4c) 55%.

We observed that the acyl bromide (2) reacts rapidly at -78°C with the alkenes (1), but that several hours were required for the ketones (5) thus formed to be converted



into the cyclised enolates (7). This result may be related to the observed stereoselectivity in the Robinson annulation reaction when the solvent used is Me_2SO .⁶

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