A New Approach to Spirosesquiterpenes of the Acorane Family

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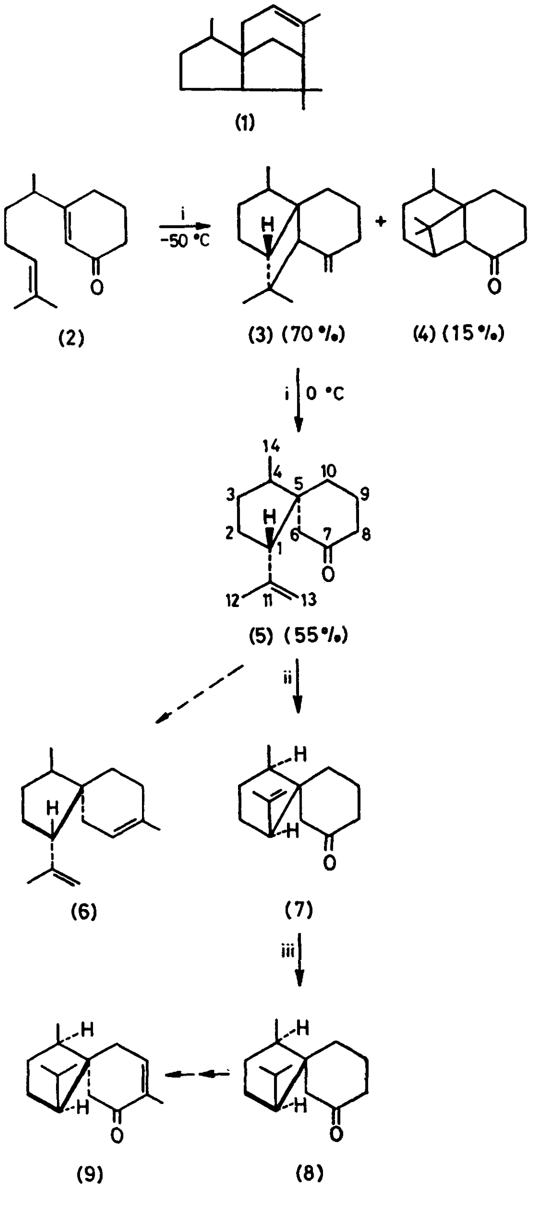
Summary Intramolecular [2 + 2] photocycloaddition of 3-(1,5-dimethylhex-4-enyl)cyclohex-2-enone leads to a major intermediate which can be converted into the noracorenone system (**5**), via a Norrish type II fission;

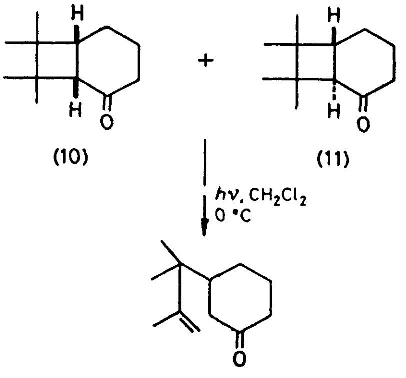
Lewis acid (Ag^+) treatment of the isopropenyl group transformed (**5**) into the isomeric spiro[4.5]decane system (**7**).

DURING recent work on the total synthesis of cedrene (**1**), it was shown that a tricyclic intermediate (**3**)[1] could be formed by a stereoselective intramolecular [2 + 2] photocycloaddition of the dienone (**2**) (Scheme). The interesting feature is that the major cyclization compound (**3**) has precisely the stereochemistry required for conversion into the noracorenone system (**5**).



SCHEME. *Reagents*, i, *hν*, CH_2Cl_2, ii, $AgNO_3$/MeOH–H_2O, iii, H_2, $(PPh_3)_3RhCl$, C_6H_6.

Selective cyclobutane fragmentations have come to play an important part in synthesis.[2] Our motivation in initiating a study of cyclobutane cleavage, formed by the fission pathway usually encountered in Norrish type II reactions,[3] was the proximity of one methyl group and a carbonyl function in a suitably substituted ketone (**3**). It was discovered that bicyclic [4.2.0] carbonyl compounds (**10**) and (**11**) are photoreactive in Norrish type II fragmentation, producing only the cyclobutane fission ketone (**12**)† (85%).[4]



This preliminary experiment suggested that the same photochemical reaction could be applied to the ketone (**3**), the expected product being the spiroketone (**5**). The dienone (**3**),[1,5] when irradiated (Hanau, TQ 150 lamp, 6 h, Pyrex filter, methylene chloride solution, −50 °C) yielded three products (80%) (**3**), (**4**), and (**5**) in the ratio 7:1·5:0·3, which were separated by reversed-phase chromatography (Lichrosorb RP-18 with water–acetonitrile 6:4). On further irradiation (36 h) at 0 → 5 °C, the mixture of photocyclization products gave the ketone (**5**) [400 MHz ^{1}H n.m.r.: δ 0·91 (3H, d, *J* 7 Hz), 1·78 (3H, s), 2·23 (2H, s), 2·26 (1H, m), 2·33 (2H, m), 4·7 (1H, s), and 4·9 (1H, s)] which was isolated (55%) by liquid chromatography, with a normal phase system (Lichrosorb Si-60, hexane–ether 9:1). Its ^{13}C n.m.r. spectrum is in agreement with the proposed structure (**5**) (Table), a novel intermediate in (±)-α-acoradiene (**6**) synthesis.[4] Lewis acid ($AgNO_3$/MeOH–H_2O) treatment of (**5**) produced an isomeric ketone (**7**) [400 MHz ^{1}H n.m.r.: δ 0·89 (3H, d, *J* 7 Hz), 1·76 (3H, s), 2·15 (2H, m),

TABLE. ^{13}C N.m.r. data (25·2 MHz) [δ($CDCl_3$)/p.p.m.].

	(5)	(7)
C-1	55·2	52·5
C-2	27·4	27·1
C-3	32·3	30·1
C-4	31·5	39·3
C-5	51·9	52·3
C-6	48·1	48·1
C-7	212·1	212·7
C-8	41·0	41·3
C-9	22·2	22·6
C-10	31·5	30·1
C-11	145·3	145·2
C-12	22·7	23·9
C-13	114·1	113·8
C-14	17·2	16·3

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† I.r., ^{1}H n.m.r., and ^{13}C n.m.r. spectra of (**12**) were in full agreement with the assigned structure.

2·30 (2H, m), 2·52 (1H, t), 4·75 (1H, s), and 5·00 (1H, s); see Table for ^{13}C n.m.r. data].

Homogenous catalytic hydrogenation [$(PPh_3)_3RhCl$ in benzene] of (**7**) yielded the ketone (**8**) [400 MHz ^{1}H n.m.r.: δ 0·85 (3H, d, *J* 7 Hz), 0·88 (3H, d, *J* 7 Hz), 1·00 (3H, d, *J* 7 Hz), 1·27 (3H, br. s), 2·17 (2H, m), and 2·37 (2H, m)], a precursor of ($\pm$)-acorenone B (**9**).[4,5]

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