Ethanonoradamatanes by Rearrangement and by Synthesis. Evaluation of Empirical Force Field Calculations

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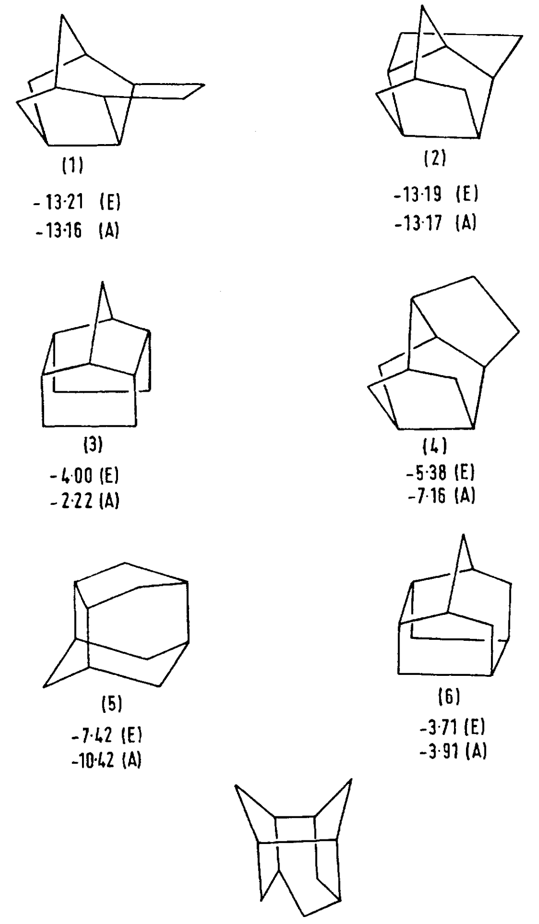
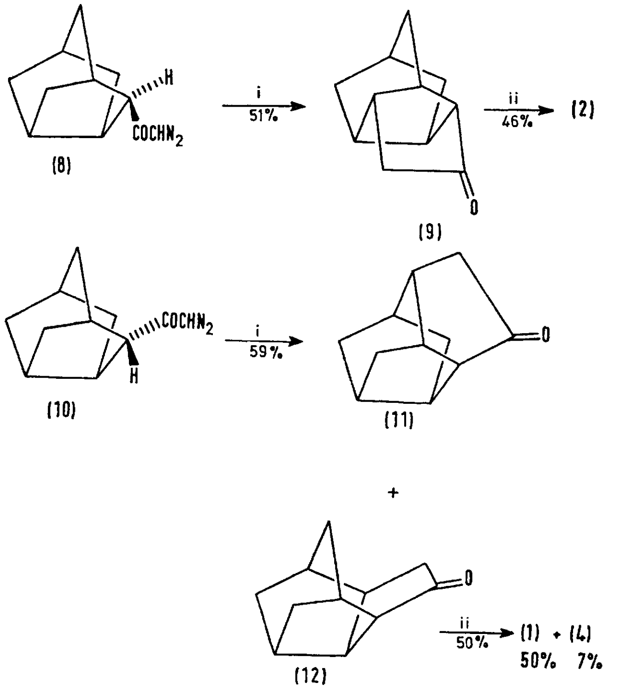
Summary Empirical force field calculations predict that 2,4-ethanonoradamantane (**1**) and 2,8-ethanonoradamantane (**2**) should be the most stable tetracyclic $C_{11}H_{16}$ isomers and both should have comparable stability; experimentally, $AlBr_3$ isomerisation yielded only (**1**) and (**2**) (also synthesised independently) but in a ratio of 97 : 3.

Among the C_{11} polycyclic hydrocarbons, 1-methyladamantane[1] is known to be the most stable tricyclic compound while D_3-trishomocubane[2] is the most stable pentacyclic isomer. We now report the identification of the thermodynamically most stable tetracyclic compound, 2,4-ethanonoradamantane (tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecane) (**1**).

Theoretically, a total of 2486 tetracycloundecanes are possible, but most of these are highly strained. Empirical force field calculations[3] on the most likely candidates, (**1**)—(**7**), predict (**1**) and (**2**) to be the most stable isomers. Both force fields employed also predict comparable stability of (**1**) and (**2**), $\Delta\Delta H^\circ = \pm$ 0·02 kcal mol^{-1}($\Delta\Delta S^\circ$ is expected to be near 0).


(1) -13·21 (E) -13·16 (A)
(2) -13·19 (E) -13·17 (A)
(3) -4·00 (E) -2·22 (A)
(4) -5·38 (E) -7·16 (A)
(5) -7·42 (E) -10·42 (A)
(6) -3·71 (E) -3·91 (A)
(7) 14·23 (E) 8·13 (A)

Calculated ΔH_f°s (kcal mol^{-1}) for representative tetracycloundecanes: E, Engler force field; and A, Allinger 1971 force field.[4] A strain-free tetracycloundecane, $[CH_2]_5[CH]_6$, should have ΔH_f° −38·61 (E) and −38·88 (A) kcal mol^{-1}. Strain energies for the molecules shown can be calculated as differences from these values.



(i) PhMe, Cu, reflux; (ii) N_2H_4, Na, diethylene glycol.

In general, $AlBr_3$ rearrangement of polycyclic hydrocarbons leads to the thermodynamically most stable isomer.[4] Such isomerisation (CS_2 solvent; wt. of $AlBr_3$ 1—2 times the weight of hydrocarbon) of tetracyclo[6.3.0.0^{2,6}.0^{5,9}]undecane (**3**), obtained from the synthesis of D_3-trishomocubane,[2] under thermodynamically controlled conditions gave in 84% yield a mixture of two *m/e* 148 isomers in a ratio of 97 $\pm$ 1 : 3 $\pm$ 1. Small amounts (<10%) of the disproportionation products, adamantane and 1-methyladamantane, also were obtained. The major component with *m/e* 148 [obtained analytically pure by preparative g.l.c., m.p. 167—168 °C, δ ($CDCl_3$) 2·6—1·2 (16H, complex), *m/e* 148 (M^+), 130, 119, 92, 91, 80, and 79] displays a ^{13}C n.m.r. spectrum of six resonances [one possible coincidence at δ 51·0 (d), also 43·3 (d), 40·9 (d), 38·4 (d), 30·2 (t), and 27·5

(t) p.p.m.]. The isomeric ethanonoradamantanes (**1**) and (**2**) both have 7 carbon atoms by symmetry and either would be consistent with the ^{13}C n.m.r. spectrum. The identity of the rearrangement products was determined by independent syntheses.

The stereochemical control imposed on the C–H insertions of the carbenes generated from the isomeric diazoketones (**8**) and (**10**) under high dilution conditions[5] formed the basis for the synthesis of (**1**) and of (**2**).[6] The *exo*-diazoketone (**8**) gave the ketone (**9**) while *endo*-(**10**) yielded a mixture of ketones (**11**) and (**12**).† Wolff-Kishner[7] reduction of (**9**) gave a product identical (g.l.c., m.s.) with the minor isomer (3%) obtained by rearrangement of (**2**). 2,8-Ethanoadamantane (**2**) is a clear oil, δ ($CDCl_3$) 2·17—0·83 (16H, br m), ^{13}C n.m.r. spectrum ($CDCl_3$) δ 48·5 (d), 44·9 (d), 43·0 (d), 40·4 (t), 34·2 (d), 32·0 (t), and 28·8 (t) p.p.m., *m/e* 148 (M^+), 119, 79, and 66.

Reduction of a mixture of the ketones (**11**) and (**12**) gave, in a 93 : 7 ratio, the ethanonoradamantanes assigned structures (**1**) and (**4**). The major isomer was identical with (**1**) obtained by rearrangement (g.l.c., and ^1H n.m.r., i.r., and mass spectra); 2,9-ethanonoradamantane (**4**) was assumed to be the minor (7%) reduction product. The ^{13}C n.m.r. spectrum excludes (**4**) as the structure of the major $AlBr_3$ rearrangement product. In addition, rearrangement of the 93 : 7 mixture of (**1**) and (**4**) gave a 96 ± 1 : 4 ± 1 ratio of (**1**) and (**2**); the g.l.c. peak corresponding to (**4**) disappeared completely. Similarly, $AlBr_3$ isomerization of (**2**) gave a 98 ± 1 : 2 ± 1 ratio of (**1**) and (**2**). These equilibria indicate a *ca.* 2 kcal mol^{-1} free energy difference between (**1**) and (**2**) in contrast to the 0 kcal mol^{-1} difference predicted by both force fields.

The preparation of noriceane (**5**) was reported recently.[8] A sample of this material was not identical in retention time with (**1**), (**2**), or (**4**) or any other g.l.c. peak seen in the isomerisation experiments. In agreement with the force field calculations, (**5**) in preliminary studies rearranged with $AlBr_3$ completely to the usual mixture of (**1**) and (**2**).

These results demonstrate the predictive power of force field calculations, but indicate the limitation in the quantitative accuracy of the methods in their present state of development.[9]

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† *Exo*-2-noradamantyl carboxylic acid was obtained epimerically pure (>98%, stereochemistry determined by ^{13}C n.m.r. spectroscopy) by carboxylation of the 2-noradamantyl-lithium. The lithium derivative was prepared from 2-noradamantyl iodide which was obtained by the reaction of aqueous HI with 2-noradamantanol (A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Letters*, 1967, 2851). The *endo*-acid (95% epimerically pure) was obtained by oxidation of the product of hydroboration–oxidation of 2-methylenenoradamantane.

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