

## Novel Cationic Rearrangements in a [4.3.3]Propellanic System

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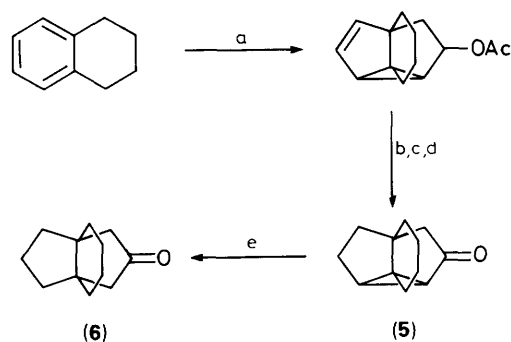
The cationic rearrangements of tetracyclo[4.3.3.0<sup>1.6</sup>.0<sup>7.12</sup>]dodecan-8-one (**5**) leads to novel and synthetically exploitable tricyclic ketones (**7**) and (**8**).

Not very long ago, we described the novel cationic rearrangement of the tetracycle (**1**) to the tricyclic enones (**3**) (quadrane) and (**4**) (angular triquinane) *via* the intermediacy of the [3.3.3]propellanone cation (**2**).<sup>1</sup> In view of the fact that propellane rearrangements display marked sensitivity to ring size, it was of interest to study the rearrangements of (**5**), the next higher homologue of (**1**). In this communication, we document the first observation of a cationic rearrangement in a [4.3.3]propellanic system (**5**), which represents an unexpected and interesting deviation from the corresponding [3.3.3]propellanic system.

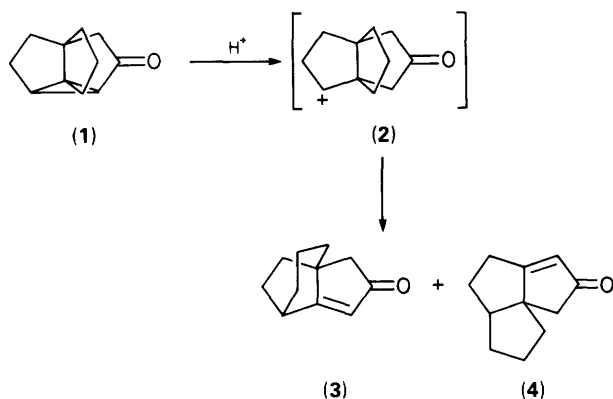
Tetracyclo[4.3.3.0<sup>1.6</sup>.0<sup>7.12</sup>]dodecan-8-one (**5**) was synthesised from tetralin and vinyl acetate employing arene-alkene photocyclisation strategy<sup>2</sup> as shown in Scheme 1. The structure of (**5**)<sup>†</sup> was confirmed by its characteristic <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra and further conversion to [4.3.3]propellan-8-one (**6**)<sup>†</sup> (7 line <sup>13</sup>C n.m.r.) on Li-liq. NH<sub>3</sub> reduction. Exposure of (**5**) to BF<sub>3</sub>-Et<sub>2</sub>O furnished a ~1:1 mixture of tricyclic ketones (**7**) and (**8**) in 66% yield.<sup>3</sup> The structures of (**7**) and (**8**)<sup>†</sup> follow from spectral data (<sup>1</sup>H and <sup>13</sup>C n.m.r.) and transformation of (**7**) to the known<sup>4</sup> tricyclic hydrocarbon (**9**) on Wolff-Kishner reduction. It is important to recall that, unlike (**1**), (**5**) does not furnish any enone products. When (**5**) was treated with 85% HCO<sub>2</sub>H, the tricyclic formate (**10**) and enones (**7**) and (**8**) (2:2:1) were formed in 60% yield. Base-hydrolysis of (**10**) to (**11**) and its exposure to toluene-*p*-sulphonic acid led to (**7**) and (**8**) (1:1; 60%). This was a useful

observation and it delineated the involvement of cation (**13**) in the rearrangement process.

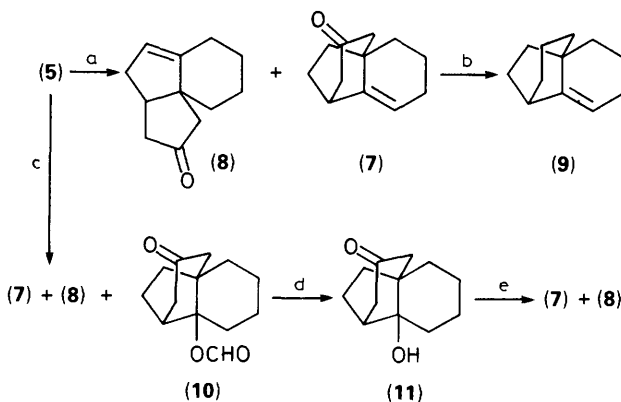
The likely mechanism of formation of (**7**) and (**8**) is shown in Scheme 3. The key carbonium ion (**13**) leading to products (**7**) and (**8**) can be formed from (**5**) through either path 'a' or 'b', Scheme 3. Both pathways 'a' and 'b' are unusual in the sense that, while the former involves migration of a carbon atom  $\alpha$  to a ketone, (**12**)  $\rightarrow$  (**13**), in preference to the carbon of the cyclohexane, (**12**)  $\rightarrow$  (**14**), the latter leads to an unexpected regioselective C(6)-C(7) bond cleavage [*cf.* (**1**)  $\rightarrow$  (**2**)].



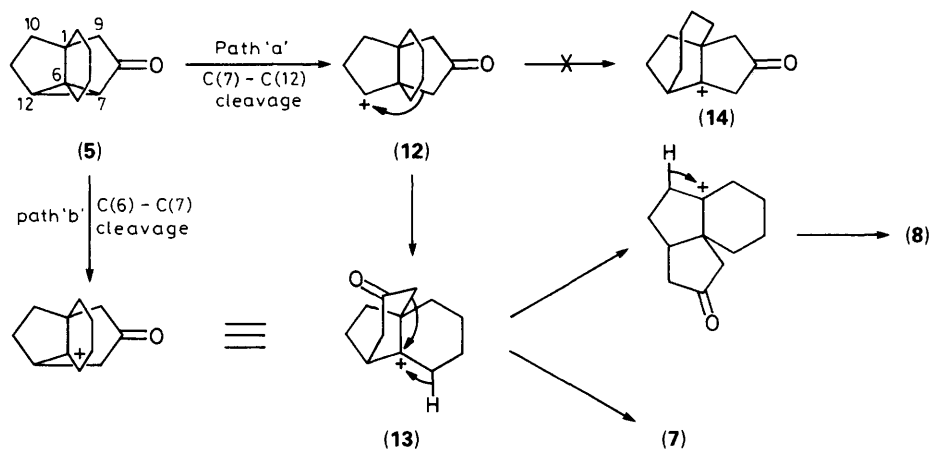
**Scheme 1.** Reagents and conditions: (a) vinyl acetate, *h* $\nu$ , Vycor, cyclohexane, 60 h, 12% (unoptimised and based on recovered starting material); (b) KOH-MeOH, room temp., 2 h; (c) 15 equiv. BaMnO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp., 8 h, 56%; (d) 10% Pd/C, H<sub>2</sub>, EtOAc, 0.5 h, 90%; (e) Li-liq. NH<sub>3</sub>, tetrahydrofuran (THF); pyridinium chlorochromate, CH<sub>2</sub>Cl<sub>2</sub>, 4 Å molecular sieves, 85%.



<sup>†</sup> Compound (**5**):  $\nu_{\max}$  (neat) 3040, 1720 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 100 MHz),  $\delta$  2.4–1.3 (m, 16H); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz),  $\delta$  213.5 (s), 52.3 (t), 46.2 (s), 45.9 [t, s (superimposed signals), 2C], 45.0 (d), 35.9 (d), 30.9 (t), 24.1 (t, 2C), 20.2 (t), and 17.9 (t). (**6**):  $\nu_{\max}$  (neat) 1740 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  2.2 (s, 4H), 1.9–1.2 (m, 14H); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  219.7, 49.7, 48.0, 36.2, 31.7, 21.7, 20.6. (**7**):  $\nu_{\max}$  (neat) 3020, 1715 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  5.58 (t, *J* 4 Hz, 1H), 2.8–1.2 (m, 15H); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  212.5, 147.1, 115.3, 56.0, 51.8, 40.9, 40.3, 36.9, 34.3, 28.7, 25.0, 20.0. (**8**):  $\nu_{\max}$  (neat) 3020, 1740 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  5.19 (s, 1H), 2.8–1.2 (m, 15H); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz)  $\delta$  219.7, 147.9, 119.2, 54.9, 47.5, 45.5, 45.0, 40.3, 39.0, 27.7, 27.5, 23.6.



**Scheme 2.** Reagents and conditions: (a) BF<sub>3</sub>-Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, 80 °C, 5 h, 66%; (b) K<sub>2</sub>CO<sub>3</sub>, diethylene glycol, NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O, 210 °C, 4 h, 45%; (c) 85% HCO<sub>2</sub>H, 80 °C, 2 h, 60%; (d) KOH-MeOH, room temp., 1 h, 65%; (e) toluene-*p*-sulphonic acid, C<sub>6</sub>H<sub>6</sub>, 80 °C, 2 h, 60%.



Scheme 3

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### References

- 1 G. Mehta, K. Pramod, and D. Subrahmanyam, *J. Chem. Soc., Chem. Commun.*, 1986, 247; G. Mehta and D. Subrahmanyam, *Tetrahedron Lett.*, 1989, 2709.
- 2 C. S. Angadiyavar, J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *Tetrahedron Lett.*, 1973, 4407; P. A. Wender and G. B. Dreyer, *J. Am. Chem. Soc.*, 1982, **104**, 5805.
- 3 The carbocyclic ring systems (7) and (8) are present in many natural products. In particular, (8) forms the carbocyclic portion of novel lycopodium alkaloids magellanine and magellaninone: M. Castillo, L. A. Loyola, G. Morales, I. Singh, C. Calvo, H. L. Holland, and D. B. Maclean, *Can. J. Chem.*, 1976, **54**, 2893; L. A. Loyola, G. Morales, and M. Castillo, *Phytochemistry*, 1979, **18**, 1721. These alkaloids have not yielded to total synthesis. For recent approaches to the carbocyclic portion, see: G. Mehta and K. S. Rao, *J. Chem. Soc., Chem. Commun.*, 1987, 1578; G. C. Hirst, P. N. Howard, and L. E. Overman, *J. Am. Chem. Soc.*, 1989, **111**, 1514.
- 4 K. Kakiuchi, K. Itoga, T. Tsugara, Y. Hato, Y. Tobe, and Y. Odaira, *J. Org. Chem.*, 1984, **49**, 659. We thank Prof. Kakiuchi for kindly providing the comparison spectra of (9).