Direct Observation of a Thermal Ring-walk Rearrangement in a Spironorcaradiene System

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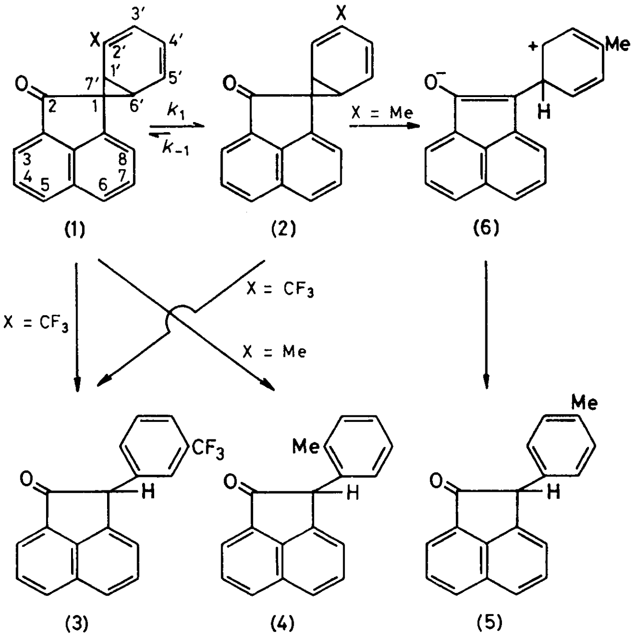
Summary At 100 °C in toluene, *cis*-2′-trifluoromethylspiro[acenaphthene-1,7′-norcaradiene]-2-one (**1**; X = CF_3) interconverts with its 3′-trifluoromethyl-substituted isomer (**2**; X = CF_3), this being the first directly observed example of a degenerate ring-walk rearrangement for a norcaradiene with a spiro-ring system attached at C-7.

WHEREAS the delicate balance of the norcaradiene–cycloheptatriene equilibrium continues to generate intense interest amongst theoretical[1] and experimental[2] investigators, comparatively little attention has been paid to the related degenerate ring-walk norcaradiene rearrangement discovered by Berson and Willcott,[3] apart from its stereochemical features.[4,5] We now report an unexpected thermal ring-walk of the norcaradiene system (**1**; X = CF_3) to (**2**; X = CF_3) which precedes the competing irreversible aromatisation[6] to the 2-arylacenaphthen-1-one (**3**). We believe this is the first directly observed example of this type of skeletal rearrangement involving a norcaradiene with a spiro-ring system attached at C-7.

Thus, irradiation of 2-diazoacenaphthen-1-one in ααα-trifluorotoluene through Pyrex with a medium pressure mercury lamp followed by removal of the bulk of the solvent and low-pressure chromatography (silica 90 mesh) with light petroleum–ether (9 : 1) as eluant gave the 3′-trifluoromethyl



spironorcaradiene (**2**; X = CF$_3$; 26%),† m.p. 155·5—156·5 °C, ν_{max} 1705 cm^{-1} (C=O); δ (CDCl$_3$) 7·98—7·28 (5H, complex m, 3—7-H), 6·72 (1H, d, *J* 7 Hz, 8-H), 6·65 (1 H, m, 2′-H), 6·56 (1H, d of d, *J* 9·5, 1·5 Hz, 4′-H), 6·34 (1H, m, 5′-H), and 3·22 (2H, m, 1′-, 6′-H); δ (^{19}F) −67·0 p.p.m. (t, *J* 1·5 Hz). Further elution yielded the isomeric 2′-trifluoromethyl derivative (**1**; X = CF$_3$; 35%), m.p. 97—101 °C, ν_{max} 1705 cm^{-1} (C=O), δ (CDCl$_3$) 8·03—7·27 (5H, complex m, 3—7-H), 6·89 (1H, m, 3′-H), 6·77 (1H, d, *J* 7 Hz, 8-H), 6·62—6·20 (2H, complex m, 4′-, 5′-H), and 3·28 (2H, m, 1′-, 6′-H), δ (^{19}F) −68·3 p.p.m. (d, *J* 1·3 Hz). No trace of the corresponding 1′-trifluoromethyl derivative was detected.

On heating in toluene at 100 °C the 2′-derivative (**1**; X = CF$_3$) underwent a walk rearrangement to the 3′-substituted isomer (**2**; X = CF$_3$) whilst at higher temperature in boiling xylene aromatisation occurred to give as the only product, 2-(3′-trifluoromethylphenyl)acenaphthen-1-one (**3**), m.p. 115—116 °C, ν_{max} 1720 cm^{-1} (C=O); δ (CDCl$_3$) 8·17—7·19 (10H, complex m, ArH) and 4·95 (1H, s, 2-H); δ (^{19}F) −62 p.p.m. ^{19}F N.m.r. spectroscopic monitoring of the rearrangement (**1**; X = CF$_3$) $\rightleftharpoons$ (**2**; X = CF$_3$) at intervals of 16·6 min over a period of several hours gave an equilibrium constant $K = 2{\cdot}2$, irrespective of whether the starting material was (**1**; X = CF$_3$) or (**2**; X = CF$_3$), and hence ΔG° (100 °C) = 2·4 kJ mol^{-1} in favour of (**2**; X = CF$_3$). The rate constants were determined to be $k_1 = (8{\cdot}2 \pm 0{\cdot}8) \times 10^{-5}\,\text{s}^{-1}$ and $k_{-1} = (3{\cdot}8 \pm 0{\cdot}3) \times 10^{-5}\,\text{s}^{-1}$ in keeping with values obtained for other degenerate norcaradiene rearrangements.[5]

Indirect evidence was also obtained for similar behaviour during the thermal aromatisation at 110 °C of a mixture of the corresponding 2′- and 3′-methyl norcaradiene derivatives (**1**; X = Me) and (**2**; X = Me) respectively, obtained in the ratio of 62:38 by photolysis in toluene as described above. This produced a mixture of the 2-arylacenaphthen-1-ones (**4**) and (**5**) in which the latter predominated in the ratio of 39:61, thereby demonstrating that the aromatisation is accompanied by the walk rearrangement (**1**; X = Me) $\rightleftharpoons$ (**2**; X = Me).

An explanation for the observed direction of ring-opening during aromatisation is provided by an ionic mechanism [*e.g.*, *via* (**6**)] which favours the formation of only the 2′-substituted isomer (**4**; X = Me) from (**1**; X = Me) and only the 4′-substituted isomer (**5**; X = Me) from (**2**; X = Me). Similarly, the trifluoromethyl-substituted analogue (**1**; X = CF$_3$), which is less prone to this carbocation process, gives only the 3′-substituted isomer (**3**) *via* the least destabilised ionic intermediate, the same product also arising from (**2**; X = CF$_3$).

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† New compounds had correct m.s. and analytical characteristics.

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