

# Multistage Cycloadducts from the Condensation of *N,N'*-Dipyrrolylmethane with Acetylenic Dienophiles: Synthesis of the 10,12-Diazapentacyclo[7.3.1.0<sup>4</sup>.12.0<sup>5</sup>.13.0<sup>6</sup>.10]trideca-2,7-diene Ring System

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*N,N'*-Dipyrrolylmethane (1) forms domino and pincer-type pericyclic adducts with dimethyl acetylenedicarboxylate and hexafluorobut-2-yne by reactions showing kinetic and thermodynamic control and which lead to novel bisethenodiazanoradamantanes.

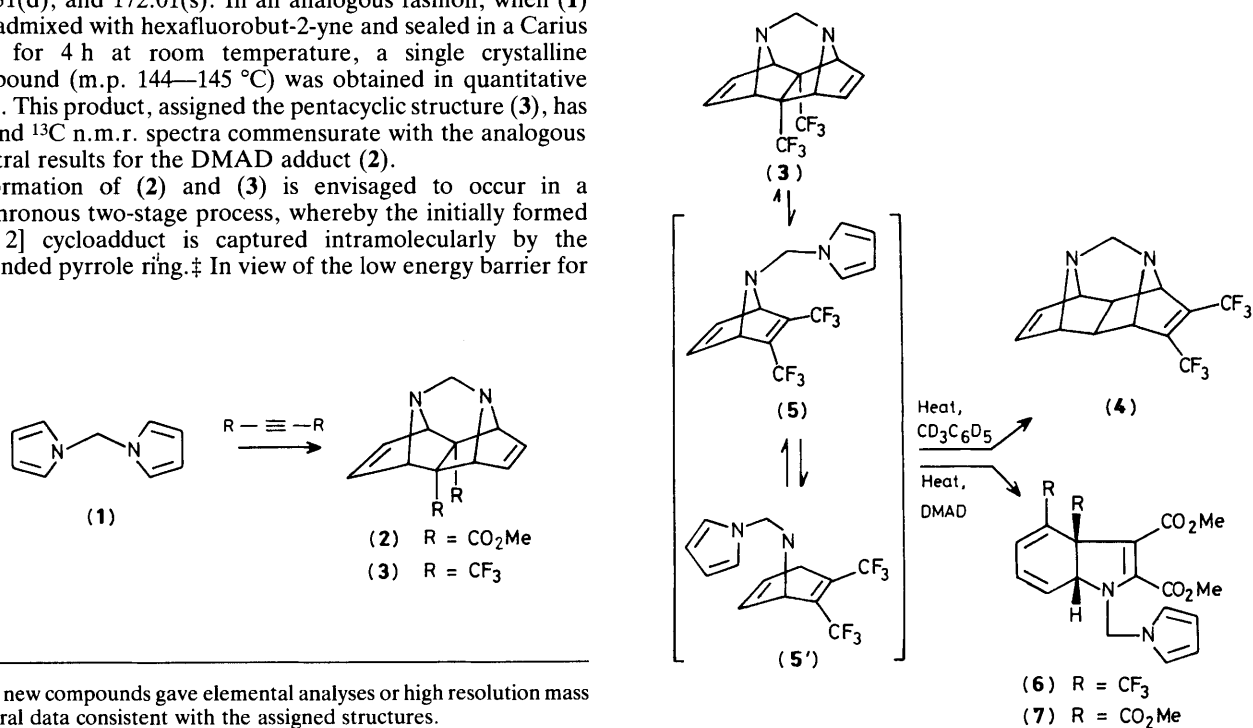
The condensation of pyrroles with dimethyl acetylenedicarboxylate (DMAD) and perfluorobut-2-yne generally affords dihydroindoles as well as 1 : 1 Michael-type addition products, whereas the corresponding [4 + 2] cycloadducts are often not isolated owing to their penchant for further rearrangement.<sup>1</sup> In this report we describe the novel tandem cycloaddition reaction of *N,N'*-dipyrrolylmethane (1)<sup>2</sup> with the aforementioned acetylenic dienophiles which accomplishes the rapid construction of the heretofore unknown bisethenodiazanoradamantane (10,12-diazapentacyclo[7.3.1.0<sup>4</sup>.12.0<sup>5</sup>.13.0<sup>6</sup>.10]trideca-2,7-diene) ring system. In addition the thermal conversion of the pincer<sup>3</sup> type adduct (3) to the domino<sup>3</sup> Diels-Alder adduct (4) provides an exemplary and as yet unique case of thermodynamic vs. kinetic control in a multistage inter-,intra-molecular [4 + 2] cycloaddition reaction.

Treatment of (1) with DMAD in benzene at 40 °C afforded the crystalline adduct (2)<sup>†</sup> (m.p. 133–135 °C), albeit in moderate yield (38%). The <sup>1</sup>H n.m.r. spectrum of (2) (C<sub>6</sub>D<sub>6</sub>) shows a methoxy singlet at δ 3.24 (6H), as well as absorptions at 3.65 (t, *J* 1.6 Hz, 4H), 3.84 (s, 2H), and 6.58 (t, *J* 1.6 Hz, 4H) consistent with C<sub>2v</sub> symmetry for the cycloadduct. The <sup>13</sup>C n.m.r. spectrum (CDCl<sub>3</sub>) at 25.5 MHz exhibits six resonances at δ 51.78(q), 66.82(t), 76.70(s), 70.39(d), 138.31(d), and 172.01(s). In an analogous fashion, when (1) was admixed with hexafluorobut-2-yne and sealed in a Carius tube for 4 h at room temperature, a single crystalline compound (m.p. 144–145 °C) was obtained in quantitative yield. This product, assigned the pentacyclic structure (3), has <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra commensurate with the analogous spectral results for the DMAD adduct (2).

Formation of (2) and (3) is envisaged to occur in a synchronous two-stage process, whereby the initially formed [4 + 2] cycloadduct is captured intramolecularly by the appended pyrrole ring.<sup>‡</sup> In view of the low energy barrier for

inversion at nitrogen, one might have expected addition of the second pyrrole ring to either of the two non-equivalent π-centres of the azanorbornadiene. Exclusive isolation of adduct (3) however, suggested that Diels-Alder addition to the unactivated dienophilic centre of (5) was kinetically an unfavourable process. This conjecture was confirmed when upon thermolysis in [2H<sub>6</sub>]toluene, the pincer-type adduct (3) was quantitatively converted (*t*<sub>1/2</sub> 90 h at 60 °C) into the domino Diels-Alder adduct (4) (m.p. 86–87 °C) (Scheme 1). The <sup>1</sup>H n.m.r. spectrum of (4) (C<sub>6</sub>D<sub>6</sub>; 100 MHz) features olefinic protons at δ 5.97 (t, *J* 1.5 Hz, 2H), a methylene resonance at δ 3.65 (s, 2H), two sets of bridgehead protons at δ 3.48 (s, 2H) and 2.98 (t, *J* 1.5 Hz, 2H), and a high-field resonance at δ 1.71 (s, 2H), for the methine hydrogens.

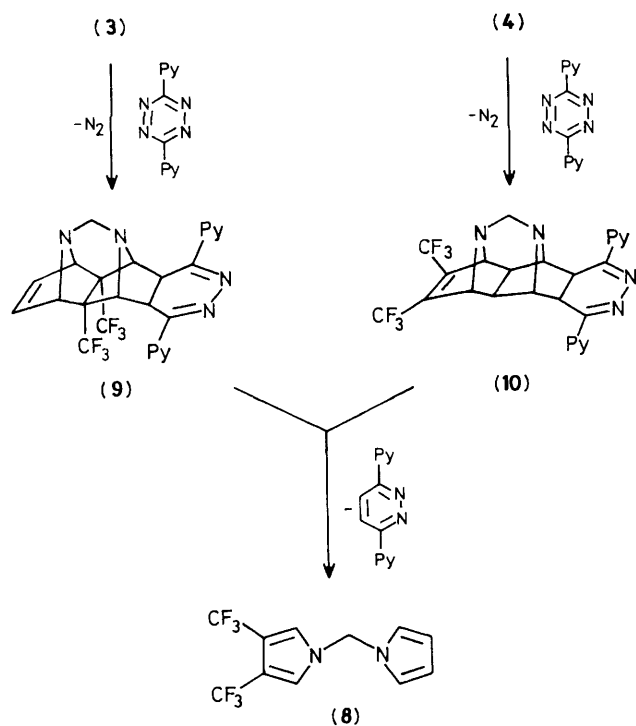
Although the conversion of (3) into (4) was monitored by <sup>1</sup>H n.m.r. spectroscopy, the azanorbornadienes (5) and (5') were never observed. Interception of this intermediate was inferred,<sup>5</sup> however, in the conversion into the dihydroindole (6), by refluxing (3) in toluene with excess of DMAD. Likewise the thermolysis of (1) in benzene with 4 equiv. of DMAD gave the dihydroindole (7). Thus for the hexafluorobut-2-yne addition formation of the C<sub>2v</sub> isomer (3) is kinetic in



<sup>†</sup> All new compounds gave elemental analyses or high resolution mass spectral data consistent with the assigned structures.

<sup>‡</sup> The first published case of an intramolecular cycloaddition to a pyrrole ring appeared (ref. 4) while this work was in progress.

Scheme 1



Scheme 2. Py = 2-pyridyl.

origin, whereas the isomer of reduced ( $C_s$ ) symmetry (4) is thermodynamically favoured.

Finally, it is interesting to note that treatment of (3) or (4) with the electron-deficient diene 3,6-di-2-pyridyl-1,2,4,5-tetrazine afforded the *N,N'*-dipyrrolylmethane (8)<sup>6</sup> together with 3,6-dipyridylpyridazine (Scheme 2). Presumably, addition of the tetrazine is accompanied by loss of  $N_2$  to give the dihydropyridazines (9) and (10) as short-lived intermediates. Subsequent cycloreversion of (9) and (10) would lead to the observed products.

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