

## Generation of Eight-pi Non-Kekulé Polyenes from the $2\pi + 4\pi$ , Diethyl Azodicarboxylate + Tropone Cycloadduct<sup>1</sup>

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In this paper it is shown that the  $2\pi + 4\pi$ , diethyl azodicarboxylate + tropone cycloadduct can be used to make precursors to eight-pi non-Kekulé polyenes. These are the first eight-pi non-Kekulé polyenes that have been observed spectroscopically (triplet ESR spectra) and the first non-Kekulé polyenes for which distinct spectra can be associated with particular *cis/trans* isomers. The enone moiety of diethyl 4-oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate was elaborated into a triene by reaction with hexynyllithium, a Meyer-Schuster rearrangement using water-acetic acid-sulfuric acid, and a Peterson methylenation [(i) trimethylsilylmethylmagnesium chloride, (ii) thionyl dichloride, (iii) aq. ammonium chloride]. The carbamate groups were hydrolysed with potassium hydroxide-methanol and the resultant -NHNH- system was oxidised with mercury(II) oxide. The resultant *Z* and *E* isomers of 4-(2'-butylallylidene)-6,7-diazabicyclo[3.2.2]nona-2,6-diene were separated by column chromatography. UV irradiation of the *Z* isomer in an EPA glass at 77 K gave a triplet ESR spectrum  $|D/hc|$  0.0223,  $|E/hc|$  0.0022  $\text{cm}^{-1}$ . Similar irradiation of the *E* isomer gave  $|D/hc|$  0.0133,  $|E/hc|$  0.0044  $\text{cm}^{-1}$ . A study of the temperature dependence of the intensities of the  $\Delta m = 2$  transitions confirmed that both spectra are associated with biradicals with a triplet ground state.

As part of a programme of work aimed at developing synthetic routes to the non-Kekulé polyenes shown in Fig. 1<sup>1-3</sup> we have recently shown that the  $2\pi + 4\pi$  diethyl azodicarboxylate + tropone adduct **11** can be converted into compound **12** which acts as a precursor to the vinyl-TMM (vinyltrimethylene-methane) biradical **13**<sup>3</sup>. In principle, the route could be modified to make any non-Kekulé polyene with 1,5-biradical character (*i.e.*, derivatives of any of the biradicals 4-8 in Fig. 1). In this paper we demonstrate that this is possible and that the adduct **11** can be converted into a precursor of the biradical **14** which is a derivative of the biradical **4**. It was the first eight-pi non-Kekulé polyene to be observed spectroscopically and the first for which distinct spectra have been obtained for both *cis* and *trans* isomers.\*

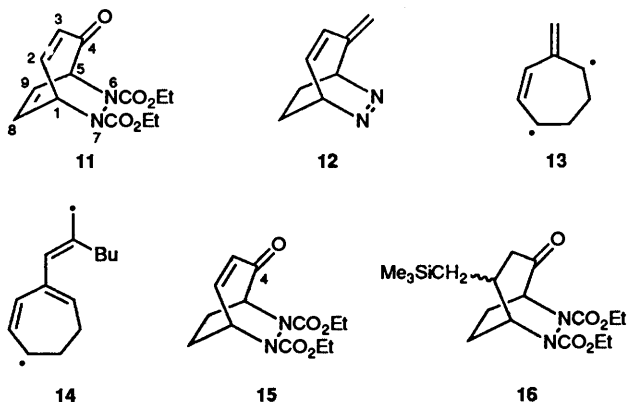
In converting the  $2\pi + 4\pi$ , diethyl azodicarboxylate + tropone cycloadduct **11** into the vinyl-TMM precursor **12** it was necessary selectively to reduce the 8,9 double bond to give the intermediate **15** and then to convert the 4-keto group into a methylene. To make a precursor to the biradical **14**, after forming the same intermediate **15**, it is necessary to convert the keto group into an *allylidene* group. Reactions at this position were, however, surprisingly difficult. Methylenation could be achieved either through a Wittig reaction (20% yield) or by reaction with methylolithium followed by dehydration (50% overall yield) but an attempted Peterson methylenation led to the 1,4-addition product **16**. Attempts to generate trisubstituted olefins by Wittig, alkylolithium, or Peterson routes were even less successful. Substituted Wittig reagents gave very low yields (<5%)<sup>5</sup> whereas most organometallic reagents showed a preference for 1,4- rather than 1,2-addition (Table 1). Many factors can affect the balance between 1,2- and 1,4-addition, and the reactions shown in Table 1 follow a variety of mechanisms, but it is hard to escape the conclusion that the overriding factor in this system is a steric effect. Table 1 shows that only sterically undemanding nucleophiles add in a 1,2-fashion. Models suggest that in at least some conformations attack at C-4 from the side *anti* to the carbamate bridge and at the Burgi-Dunitz angle<sup>6</sup>

Table 1 Ratios of 1,2- to 1,4-addition in the reactions of the enone **15**

Reagent/conditions	1,4-Addition (%)	1,2-Addition (%)	Ref.
HC(OEt) <sub>3</sub> , TsOH	91 <sup>a,b</sup>	0 <sup>a</sup>	3
Me <sub>3</sub> SiCH <sub>2</sub> MgCl, Et <sub>2</sub> O/25 °C	86 <sup>a</sup>	0 <sup>a</sup>	f
Me[CH <sub>2</sub> ] <sub>4</sub> MgBr, Et <sub>2</sub> O/25 °C	47 <sup>a</sup>	(35) <sup>a,c</sup>	f
Me[CH <sub>2</sub> ] <sub>3</sub> Li, Et <sub>2</sub> O/-15 °C	30 <sup>d</sup>	34 <sup>d</sup>	f
MeLi, Et <sub>2</sub> O/-15 °C	7 <sup>a</sup>	52 <sup>a</sup>	3
CH <sub>2</sub> =CHCH <sub>2</sub> MgBr, Et <sub>2</sub> O/25 °C	0 <sup>a</sup>	36 <sup>a,b</sup>	f
Me[CH <sub>2</sub> ] <sub>3</sub> C=CLi, Et <sub>2</sub> O/25 °C	0 <sup>a</sup>	80 <sup>a,e</sup>	f
HC≡CLi, THF/-78 to 25 °C	0 <sup>a</sup>	90-95 <sup>a,e</sup>	f
NaBH <sub>4</sub> , CeCl <sub>3</sub> , MeOH/25 °C	0 <sup>a</sup>	100 <sup>a</sup>	f

<sup>a</sup> Isolated yield. <sup>b</sup> Addition product *anti* to the carbamate bridge. <sup>c</sup> 1,2-Reduction product. <sup>d</sup> Identified and product ratio only on the basis of the <sup>1</sup>H NMR analysis of a mixed fraction. <sup>e</sup> ~ 1:1 *syn:anti*. <sup>f</sup> This work.

suffers steric hindrance from the methylene at C-8 (**17**) whereas attack at C-2 is unhindered. Whether or not this is the crucial factor the practical outcome is that the only 1,2-additions which allowed the desired elaboration of the C-4 position to occur were those of acetylenide anions; ions of high nucleophilic character but modest steric demands. The acetylenide adducts could be converted into the desired allylidene derivatives



\* Examples in which diastereoisomers of a pi biradical give different, distinctive triplet ESR spectra have recently been reported.<sup>4</sup>

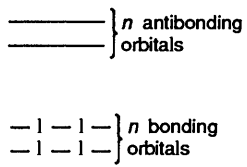
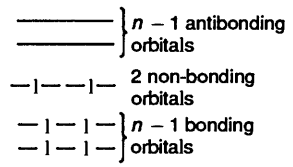

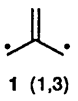
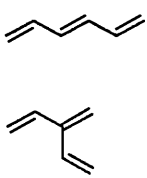
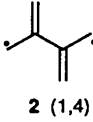
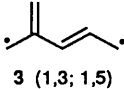
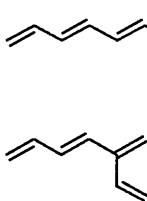
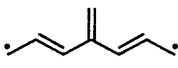
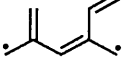
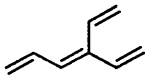
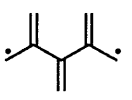

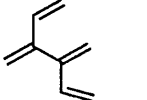
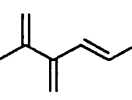
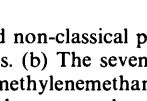
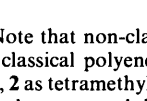
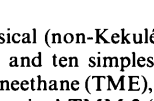
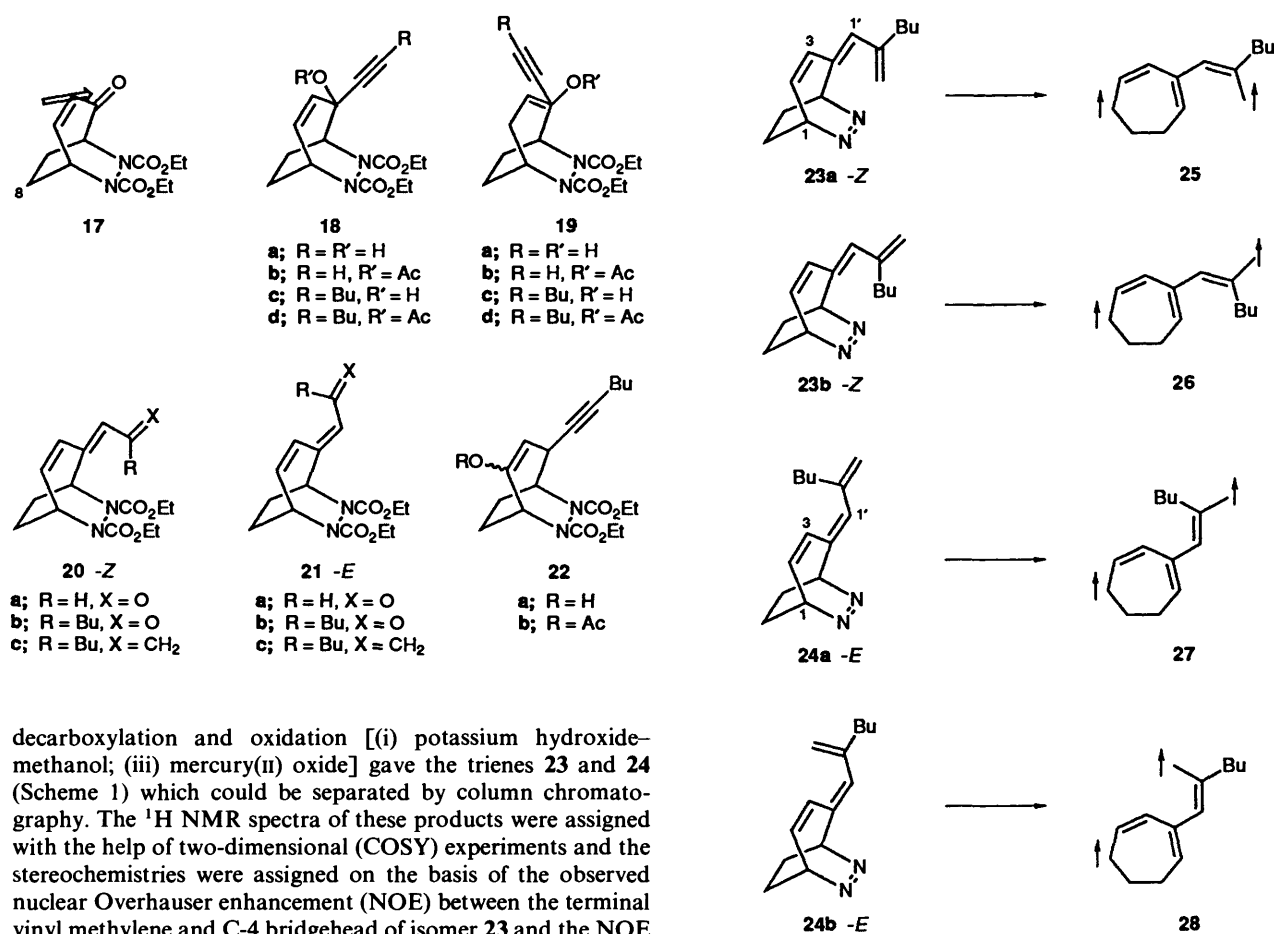
Formula	Number of pi electrons	Classical or Kekule	Non-classical or non-Kekule
(a)			
$C_{2n}H_{2n+2}$	$2n$		
(b)			
$C_4H_6$	4		 1 (1,3)
$C_6H_8$	6		 2 (1,4)  3 (1,3; 1,5)
$C_8H_{10}$	8		 4 (1,3; 1,5; 1,7)  5 (1,3; 1,5)
			 6 (1,3; 1,5)  7 (1,3; 1,5; 1,7)
			 8 (1,5)
			 9 (1,4; 1,6)  10 (1,6)

Fig. 1 (a) A comparison of HMO pi orbital energies for classical and non-classical polyenes. Note that non-classical (non-Kekulé) polyenes are characterised by a degenerate pair of non-bonding molecular orbitals. (b) The seven simplest classical polyenes and ten simplest non-classical polyenes. The non-classical polyene 1 is known by the trival name of trimethylenemethane (TMM), 2 as tetramethyleneethane (TME), and 3 as vinyl-TMM. Note that TMM 1 (for example) is isomeric with butadiene and has an equal number of pi electrons, and that vinyl-TMM 3 (for example) is isomeric with hexatriene and also has six pi electrons. Note also that whereas TMM 1 is simply a 1,3-biradical and TME is simply a 1,4-biradical, vinyl-TMM can be written as either a 1,3- or a 1,5-biradical. For other non-classical polyenes the 1,*n*-biradical character is indicated in brackets.

through a Meyer-Schuster rearrangement and methylenation of the resultant dienone.

Reaction of the ketone 15 with lithium acetylide in tetrahydrofuran (THF) at  $-78^\circ\text{C}$ <sup>7</sup> gave a good yield of a 1:1 mixture of the alcohols 18a and 19a. These could be separated by column chromatography and were separately converted into the acetates 18b and 19b. An attempted Meyer-Schuster rearrangement using sulfuric acid in 80% acetic acid<sup>8</sup> was unsuccessful but the method of Pelletier and Mody (silver-catalysed rearrangement of the propargylic acetates either separately or as a mixture)<sup>9</sup> gave the aldehydes 20a and 21a in good yield. Subsequent reactions in this series, however, gave poorer yields than equivalent reactions based on the hexyne

adducts 18c and 19c. These adducts underwent the Meyer-Schuster rearrangement simply upon treatment with a catalytic amount of sulfuric acid in 80% aq. acetic acid and gave a mixture of the ketones 20b and 21b.<sup>8</sup> When the reaction was monitored by TLC two 'intermediates' could be detected. The first of these was an acetate (probably 22b and second was the alcohol 22a. Formation of this rearranged alcohol has numerous precedents in Meyer-Schuster rearrangements of ethynyl vinyl carbinols.<sup>10</sup> Although the mixture of ketones 20b and 21b could not be separated by chromatography, Peterson olefination [(i) trimethylsilylmethylmagnesium chloride; (ii) thionyl dichloride; (ii) aq. ammonium chloride]<sup>11</sup> gave a reasonable yield of the mixed trienes 20c and 21c. Hydrolysis,

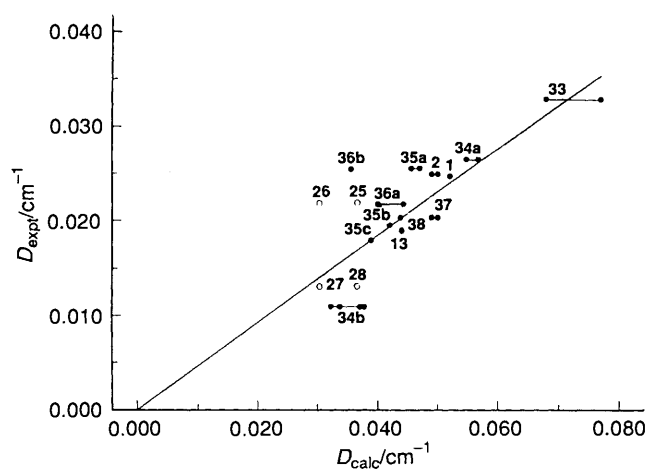


decarboxylation and oxidation [(i) potassium hydroxide-methanol; (iii) mercury(II) oxide] gave the trienes **23** and **24** (Scheme 1) which could be separated by column chromatography. The <sup>1</sup>H NMR spectra of these products were assigned with the help of two-dimensional (COSY) experiments and the stereochemistries were assigned on the basis of the observed nuclear Overhauser enhancement (NOE) between the terminal vinyl methylene and C-4 bridgehead of isomer **23** and the NOE between the C-4 and C-1' protons in isomer **24**.<sup>1</sup> Alternatively the assignment can be based on the <sup>1</sup>H NMR chemical shifts of the protons at C-4 and C-3. By using extensive chemical-shift data collected for cartenoids of known stereochemistry the predicted differences in chemical shift for the two isomers  $\delta_{\text{H}}(\mathbf{24}) - \delta_{\text{H}}(\mathbf{23})$  at positions C-4 and C-3 are  $-0.50$  and  $+0.52$  ppm, respectively, and the measured differences are  $-0.78$  and  $+0.54$  ppm, respectively.<sup>12</sup> UV irradiation of the diazine **23** in a glassy matrix at 77 K gave the triplet ESR spectrum  $|D/hc|$  0.0223 cm<sup>-1</sup>,  $|E/hc|$  0.0022 cm<sup>-1</sup>. Diazine **24** gave the triplet ESR- $|D/hc|$  0.0133 cm<sup>-1</sup>,  $|E/hc|$  0.0044 cm<sup>-1</sup>. Whereas most of the properties of eight-pi non-Kekulé polyenes are expected to be simple extensions of those of trimethylenemethane (TMM) and tetramethyleneethane (TME) the difference between the two ESR spectra underlines one new property associated with the 'higher' members of the series; the potential that exists for forming distinct *cis/trans* isomers. In the case of the biradical **4** there are ten such isomers but for the bridged analogues **14** there are only four (**25–28**) (Scheme 1). It is not clear which biradical or mixture of biradicals arises from which precursor. The Scheme is based on the assumption that elimination of nitrogen occurs on a least-motions basis. Hence for isomer **23** the rotamer **23a** would give biradical **25** and rotamer **23b** biradical **26**, and for isomer **24** rotamer **24a** would give biradical **27** and rotamer **24b** biradical **28**. The situation can be clarified to some extent by calculating the value of the zero-field splitting  $|D/hc|$ <sup>13</sup> using the point charge approximation of McWeeny.<sup>14</sup> A results of such calculations for most known planar pi-biradicals are shown graphically in Fig. 2. These suggest that the diazine **23** exists mainly as rotamer **23a** and gives the biradical **25**. A significant population of this rotamer is consistent with the observed NOE interaction between the terminal methylene and the bridgehead C-4 hydrogen of species **23**.<sup>1</sup> It also suggests that the diazine **24** exists mainly as rotamer **24a** and gives the

**Scheme 1** 'Least motions' products from the photolysis of the diazenes **23** and **24**

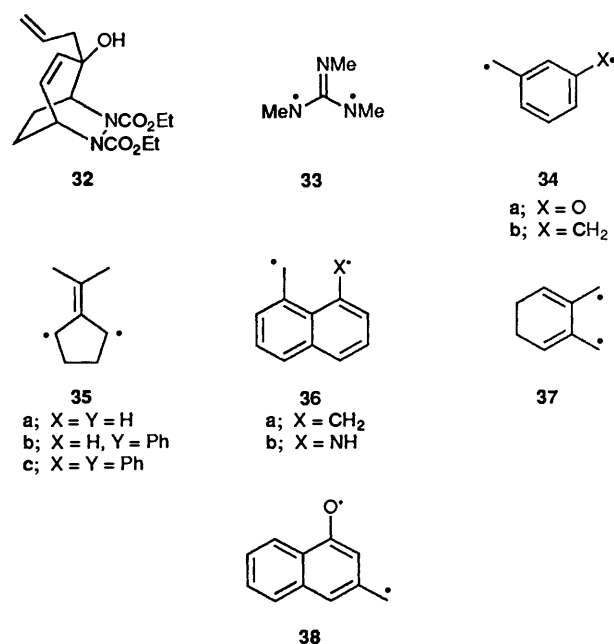
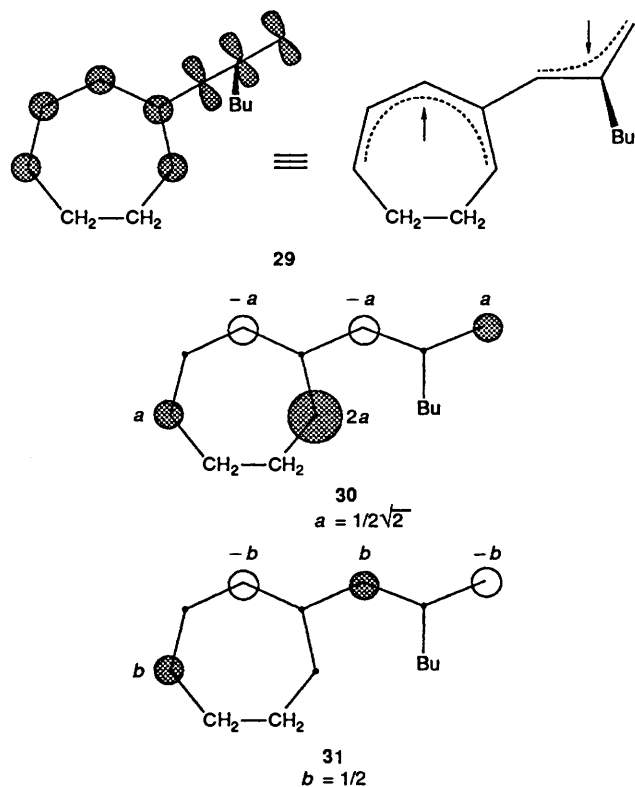
biradical **27**. This is consistent with absence of a significant NOE interaction between the terminal methylene and the C-3 vinyl hydrogen of species **24**.<sup>1</sup> Whilst these results are internally consistent two problems exist. First, in these systems, the calculated zero-field splittings are strongly dependent on what is assumed to be the internal C–C–C angle in the seven-membered ring.<sup>3</sup> All of the values in Fig. 2 were based on assumed C–C–C angles of 120°. A calculation based on an internal C–C–C angle of 130° for the seven-membered ring reduces the calculated  $|D/hc|$  by  $\sim 0.006$  cm<sup>-1</sup> for biradical **13** and by  $\sim 0.003$  cm<sup>-1</sup> for biradicals **25–28**. Secondly, whereas the triplet states of these biradicals are planar and fully pi delocalised, the singlet state of biradical **14** is essentially a pentadienyl radical plus an allyl radical and will either be orthogonal about the connecting bond as shown in formula **29** or, at least, the barrier to rotation about this exocyclic carbon–carbon bond will be very low. Hence, if the photolyses of diazines **23** and **24** pass, as expected, through the singlet biradical **29** on the way to the triplet biradicals **25–28** or, if the triplet biradicals are in equilibrium with the singlet states, the least motions argument outlined above can only be supported on the assumption that, within a frozen glassy matrix, such rotations are suppressed. Analogous 'matrix' effects are, however, known in related systems.<sup>16</sup>

The triplet ESR spectra could, in principle, arise from either a triplet ground state or a situation in which the triplet lies just above the singlet state and is thermally populated. However, a study of the temperature dependence of the intensity of the  $\Delta m = 2$  transition for each biradical between 8 and 36 K showed the Curie Law dependence expected for a triplet ground state.<sup>1</sup> Indeed, it is expected that for these systems where the



**Fig. 2** A comparison of calculated and experimentally measured values of the zero-field splitting  $|D/hc|$  for planar (or probably planar) pi biradicals. Most of the values are based on an HMO description of the SOMOs and are taken from refs. 3 and 13 and from ref. 15(a) but include the corrected value for TME (ref. 15b). For biradicals 13 and 25–28 a carbon-carbon bond length of 1.427 Å was assumed, also that all carbon atoms were  $sp^2$ -hybridised (carbon-carbon-carbon bond angles of  $120^\circ$ ), and finally that each  $p$ -orbital is represented by a pair of points 0.68 Å above and below the plane of the molecule (ref. 14). The correlation line shown is a 'least squares' fit but is close to the suggested correlation  $D_{\text{calc}} = 2D_{\text{expt}}$  (ref. 13). The numbers refer to the biradical formulae in the text.

The open circles show all of the possible assignments for the spectra and are based on the assumption of a least-motions result, *i.e.* precursor 23,  $D_{\text{expt}}$  0.022  $\text{cm}^{-1}$ , gives biradicals 25,  $D_{\text{calc}}$  0.0370  $\text{cm}^{-1}$  or 26,  $D_{\text{calc}}$  0.0305  $\text{cm}^{-1}$ , and precursor 24,  $D_{\text{expt}}$  0.0133  $\text{cm}^{-1}$ , gives biradicals 27,  $D_{\text{calc}}$  0.0305  $\text{cm}^{-1}$  or 28,  $D_{\text{calc}}$  0.0370  $\text{cm}^{-1}$ . The best fit to the correlation line is obtained if it is assumed that diazene 23 gives biradical 25 and diazene 24 gives biradical 27 but the reversed assignments (23 gives 26, and 24 gives 28) are possible and within experimental error.



singly occupied molecular orbitals (SOMOs) are non-disjoint (formulae 30 and 31) that there will be a strong exchange interaction and a triplet ground state.<sup>17</sup>

### Experimental

Instrumentation and General Procedures were described in detail in the last full paper of this series.<sup>3</sup> All reactions were carried out under a slight positive pressure of dry nitrogen and unless otherwise specified preparative chromatography was performed on Merck Kieselgel 'G' Type 60 (0.04–0.063 mm) and  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  solution;  $J$ -values are given in Hz. Compounds and mixtures characterised only by an accurate mass were homogeneous by TLC and pure by  $^1\text{H}$  NMR spectroscopy. In the case of the carbamates, there was some evidence of temperature and field dependence arising from hindered rotation, and in some cases broadening of the spectra and loss of spin-coupling information or splitting of the resonances was a problem.

**Reaction of Trimethylsilylmethylmagnesium Chloride with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of the Grignard reagent was prepared by reaction of chloromethyl(trimethyl)silane (1.6  $\text{cm}^3$ ) with magnesium (260 mg) in diethyl ether (10  $\text{cm}^3$ ). A portion (1  $\text{cm}^3$ ) of this solution was added to a solution of the enone 15<sup>3</sup> (382 mg) in diethyl ether (7  $\text{cm}^3$ ). The resultant gelatinous mixture was heated under reflux for 3 h, cooled to  $0^\circ\text{C}$ , stirred with thionyl dichloride (0.1  $\text{cm}^3$ ) and treated with saturated aq. ammonium chloride. The mixture was filtered and the aqueous phase was extracted with diethyl ether ( $2 \times 15 \text{ cm}^3$ ). The extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed on flash silica [(3:1) diethyl ether–light petroleum] to give *diethyl 2-oxo-4-trimethylsilylmethyl-6,7-diazabicyclo[3.2.2]nonane-6,7-dicarboxylate 16* as a pale yellow oil (442 mg, 88%) (Found:  $M^+$ , 370.1915.  $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_5\text{Si}$  requires  $M$ , 370.1923);  $\nu_{\text{max}}$ (Nujol)/ $\text{cm}^{-1}$  1690–1740 (CO);  $\delta_{\text{H}}$  4.8–4.0 (6 H, m, including two overlapping quartets,  $J$  7, bridgeheads and  $\text{OCH}_2\text{Me}$ ), 2.7–1.7 (7 H, m, bicyclononane  $\text{CH}_2$  and CH), 1.3 and 1.31 (6 H,  $2 \times t$ ,  $J$  7,  $\text{OCH}_2\text{Me}$ ), 1.0 and 1.01 (2 H,  $2 \times d$ ,  $J$  7,  $\text{CH}_2\text{Si}$ ) and 0.1 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  360 ( $M^+$ , 4%), 225 (6), 83 ( $\text{C}_5\text{H}_7\text{O}^+$ , 18) and 73 ( $\text{Me}_3\text{Si}^+$ , 100).

**Reaction of Pentylmagnesium Bromide with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of the Grignard reagent was prepared by reaction of 1-bromopentane (0.75 cm<sup>3</sup>) with magnesium (340 mg) in diethyl ether (4 cm<sup>3</sup>). A portion (2 cm<sup>3</sup>) of this solution was added to a solution of the enone **15**<sup>3</sup> (500 mg) in diethyl ether (2 cm<sup>3</sup>). The mixture was hydrolysed with saturated aq. ammonium chloride, then filtered, the ether layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 cm<sup>3</sup>). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–light petroleum] to give *diethyl 2-oxo-4-pentyl-6,7-diazabicyclo[3.2.2]nonane-6,7-dicarboxylate* (497 mg, 47%), m.p. 62–66 °C (Found: C, 61.1; H, 8.5; N, 7.9%; M<sup>+</sup>, 354.2153. C<sub>18</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub> requires C, 61.0; H, 8.5; N, 7.9%; M, 354.2154;  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  1690–1750 (C=O);  $\delta_{\text{H}}$  4.6 (1 H, m, 1-H), 4.3 (1 H, m, 5-H), 4.2 (4 H, 2 × q, J 7, OCH<sub>2</sub>Me), 2.7 (1 H, dd, J 15 and 9, 3-H), 2.2 (1 H, dd, J 15 and 7, 3-H) and 2.8–1.3 (22 H, m); *m/z* 354 (M<sup>+</sup>, 5%), 254 (26), 209 (43), 181 (19), 111 (26), 105 (8), 83 (63) and 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 100). Chromatography also yielded *diethyl 4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate* as an oil (172 mg, 35%) (Found: M<sup>+</sup>, 284.1368. C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub> requires M, 284.1372);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3450 (OH) and 1740–1700 (C=O);  $\delta_{\text{H}}$  6.3–5.5 (2 H, m, vinyl H), 5.0–4.4 (3 H, m, bridgeheads and CHOH), 4.2 (4 H, 2 q, J 7, OCH<sub>2</sub>Me), 2.5–1.6 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>) and 1.3 (6 H, 2 t, J 7, OCH<sub>2</sub>Me); *m/z* 284 (M<sup>+</sup>, 33%), 212 (9), 211 (18), 158 (29), 130 (100), 83 (64) and 68 (34).

**Reaction of Butyllithium with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of butyllithium (1.5 mol dm<sup>-3</sup>; 0.5 cm<sup>3</sup>, 0.75 mmol) was added to a solution of the enone **15**<sup>3</sup> (200 mg, 0.71 mmol) in diethyl ether (2 cm<sup>3</sup>) at –15 °C. Water (15 cm<sup>3</sup>) was added and the mixture was allowed to warm up to room temperature. The layers were separated and the aqueous phase was extracted with diethyl ether (3 × 10 cm<sup>3</sup>). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(3:1) light petroleum–diethyl ether] to give *diethyl 4-butyl-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate* as an oil (8 mg, 4%) (Found: M<sup>+</sup>, 340.1992. C<sub>17</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub> requires M, 340.1998);  $\delta_{\text{H}}$  6.0 (1 H, dd, J 11 and 7, 2-H), 5.6 (1 H, dd, J 11 and 1, 3-H), 4.6 (2 H, m, bridgeheads), 4.2 (4 H, 2 q, J 7, OCH<sub>2</sub>Me) and 2.0–0.8 (19 H); *m/z* 340 (M<sup>+</sup>, 15%), 240 (M<sup>+</sup> – CO – C<sub>4</sub>H<sub>8</sub>, 20), 239 (13), 195 (M<sup>+</sup> – C<sub>2</sub>O<sub>4</sub> – C<sub>4</sub>H<sub>9</sub>, 31), 167 (16), 83 (45) and 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 100).

Chromatography also yielded an oil (147 mg, 60%), which was identified on the basis of <sup>1</sup>H NMR spectroscopy as a 1:1 mixture of the 1,2-adduct and the 1,4-adduct diethyl 4-butyl-2-oxo-6,7-diazabicyclo[3.2.2]nonane-6,7-dicarboxylate. The characteristic peaks for this second product were  $\delta_{\text{H}}$  2.5 (1 H, dd, J 16 and 8, 3-H) and 2.4 (1 H, dd, J 16 and 6, 3-H).

**Reaction of Allylmagnesium Bromide with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of the Grignard reagent was prepared by reaction of allyl bromide (0.3 cm<sup>3</sup>) with magnesium (170 mg) in diethyl ether (4 cm<sup>3</sup>). A solution of the enone **15**<sup>3</sup> (500 mg) in diethyl ether (4 cm<sup>3</sup>) was added to the stirred Grignard reagent at 0 °C. After 2 h at 0 °C the solution was allowed to warm up to room temperature and was then treated with saturated aq. ammonium chloride. After separation of the layers the aqueous phase was extracted with diethyl ether (2 × 10 cm<sup>3</sup>). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–light petroleum] to give *diethyl 4-allyl-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-*

*dicarboxylate 32* as a solid (208 mg, 36%), m.p. 71–74 °C (Found: C, 59.2; H, 7.4; N, 8.5%; M<sup>+</sup>, 324.1686. C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub> requires C, 59.3; H, 7.4; N, 8.6%; M, 324.1685);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  3500 (OH), 1740–1690 (C=O) and 995 and 905 (C=CH);  $\delta_{\text{H}}$  6.0 (3 H, m, 2- and 3-H, and CH=CH<sub>2</sub>), 5.5 (1 H, dd, J 12 and 2, CH=CHH), 5.3 (1 H, m, bridgehead), 5.1 (1 H, dd, J 7 and 2, CH=CHH), 4.5 (1 H, m, bridgehead), 4.0 (4 H, 2 q, J 7, OCH<sub>2</sub>Me), 2.4 (2 H, m, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.1 (1 H, OH), 2.0–1.5 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>) and 1.3 (6 H, 2 t, J 7, OCH<sub>2</sub>Me); *m/z* 324 (M<sup>+</sup>, 34%), 283 (37), 235 (11), 130 (100) and 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 32).

The tertiary alcohol (500 mg) and methanolic potassium hydroxide [15 cm<sup>3</sup> of a solution of potassium hydroxide (7.2 g) in methanol (37.5 cm<sup>3</sup>) and water (1 cm<sup>3</sup>)] were heated together under reflux for 8 h. After the mixture had cooled to room temperature solid sodium hydrogen carbonate (1 g) was added, the mixture was stirred for 1 h and then filtered, yellow mercury(II) oxide (4 g) was added, and the mixture was stirred for a further 3 h before being filtered through Celite; water (30 cm<sup>3</sup>) was added and the whole was extracted with dichloromethane (3 × 20 cm<sup>3</sup>). The extracts were dried with magnesium sulfate, filtered and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–light petroleum] to give *2-allyl-6,7-diazabicyclo[3.2.2]nona-3,6-dien-2-ol* (170 mg, 52%) as an off-white solid, m.p. 81–84 °C (Found: C, 67.4; H, 7.7; N, 15.8%; M<sup>+</sup>, 178.1110. C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 67.4; H, 7.9; N, 15.8%; M, 178.1106);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  3360 (OH);  $\delta_{\text{H}}$  6.05 (1 H, m, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.90 (1 H, dd, J 11 and 8, 4-H), 5.55 (2 H, m, 1- and 5-H), 5.45 (1 H, dd, J 11 and 2.5, 3-H), 5.25 (1 H, ddt, J 10, 2 and 1, C=CHH), 5.17 (1 H, ddt, J 17, 2 and 1, C=CHH), 2.40 (2 H, 2 dddt, J 14, 7 and 1, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.17 (1 H, s, OH) and 1.75–1.51 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>); *m/z* 178 (M<sup>+</sup>, 0%), 160 (M<sup>+</sup> – H<sub>2</sub>O, 47), 179 (19), 132 (M<sup>+</sup> – H<sub>2</sub>O – N<sub>2</sub>, 15), 188 (22), 117 (22), 91 (C<sub>7</sub>H<sub>2</sub><sup>+</sup>, 42) and 81 (100). An NOE difference experiment showed an interaction between the allylic CH<sub>2</sub> ( $\delta_{\text{H}}$  2.40), and the CH<sub>2</sub>CH<sub>2</sub> ( $\delta_{\text{H}}$  1.75–1.51) of the bicyclononane, confirming that the single isomer isolated had the allyl group *anti* to the –N=N–bridge. Unfortunately, attempts to dehydrate this compound produced only a mixture of low-molecular-mass products. Similarly, attempts to dehydrate the alcohol **32** and then hydrolyse the carbamate groups failed to produce a simple product.<sup>5</sup>

**Reaction of Hex-1-ynyllithium with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of butyllithium (2.25 cm<sup>3</sup>; 1.6 mol dm<sup>-3</sup>) was added to hex-1-yne (2.0 cm<sup>3</sup>) in diethyl ether (15 cm<sup>3</sup>). A solution of the enone **15**<sup>3</sup> (1 g) in diethyl ether (15 cm<sup>3</sup>) was added and the mixture was stirred for 2 h at room temperature. Saturated aq. ammonium chloride was added, the layers were separated, and the aqueous phase was extracted with diethyl ether (2 × 30 cm<sup>3</sup>). The combined organic extracts were dried with magnesium sulfate, filtered and evaporated under reduced pressure, and the residue was chromatographed on flash silica [(1:1) diethyl ether–light petroleum].

The first fraction proved to be *diethyl 4-(hex-1-ynyl)-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 19c* (stereochemistry tentatively assigned by comparison of <sup>1</sup>H NMR spectra with the ethynyl series) as a yellow oil (496 mg, 39%) (Found: M<sup>+</sup>, 364.1996. C<sub>19</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub> requires M, 364.1998);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3440 (OH), 2230 (C≡C), 1750–1680 (C=O) and 1550 (C=C);  $\delta_{\text{H}}$  6.2 (1 H, dd, J 15 and 7, 2-H), 5.7 (1 H, d, J 15, 3-H), 4.8 (1 H, m, 5-H), 4.6 (1 H, m, 1-H), 4.2 (4 H, 2 q, J 7, OCH<sub>2</sub>Me), 2.0–0.8 (13 H, m) and 1.3 (6 H, 2 t, J 7, OCH<sub>2</sub>Me); *m/z* 364 (M<sup>+</sup>, 5%), 291 (3), 158 (15), 130 (29), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 11) and 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 100).

The second fraction was the *diastereoisomer 18c* (stereochemistry tentatively assigned by comparison of <sup>1</sup>H NMR spectra with the 2-ethynyl series) as a yellow oil (504 mg, 41%)

(Found:  $M^+$ , 364.2004.  $C_{19}H_{28}N_2O_5$  requires  $M$ , 364.1998);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3440 (OH), 2230 ( $C\equiv C$ ), 1750–1680 ( $C=O$ ) and 1550 ( $C=C$ );  $\delta_H$  6.1 (1 H, dd,  $J$  15 and 7, 4-H), 5.6 (1 H, d,  $J$  15, 3-H), 4.8 (1 H, m, 1-H), 4.6 (1 H, m, 5-H), 4.2 (4 H, 2 q,  $J$  7,  $OCH_2Me$ ), 3.1 (1 H, s, OH), 2.4–0.8 (13 H, m) and 1.3 (6 H, m,  $OCH_2Me$ );  $m/z$  364 ( $M^+$ , 5%), 291 (2), 158 (16), 130 (29), 91 ( $C_7H_7^+$ , 10) and 29 ( $C_2H_5^+$ , 100).

**Reaction of Ethynyllithium with Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15.**—A solution of ethynyllithium was prepared by adding butyllithium (6.7  $\text{cm}^3$ , 1.6 mol  $\text{dm}^{-3}$ ) to a saturated solution of acetylene in dry THF (75  $\text{cm}^3$ ) at  $-78^\circ\text{C}$ .<sup>7</sup> A solution of the enone **15**<sup>3</sup> (3 g) in dry THF (25  $\text{cm}^3$ ) was rapidly added and the mixture was allowed to warm slowly to room temperature during 4–5 h. Saturated aq. ammonium chloride was added, the solids were removed by filtration, and the aqueous phase was saturated with sodium chloride and extracted with diethyl ether (2  $\times$  70  $\text{cm}^3$ ). The combined organic extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–light petroleum and then pure diethyl ether].

The first fraction was diethyl 4-ethynyl-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate **19a** (1.42 g, 47%) as a crystalline solid, m.p. 153–154  $^\circ\text{C}$  (Found: C, 58.5; H, 6.8; N, 9.2%;  $M^+$ , 308.1367.  $C_{15}H_{20}N_2O_5$  requires C, 58.4; H, 6.5; N, 9.1%;  $M$ , 308.1372);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  3440 (OH), 3300 ( $C\equiv CH$ ), 2110 ( $C=C$ ), 1740 ( $C=O$ ) and 1685 ( $C=C$ );  $\delta_H$  6.1 (1 H, dd,  $J$  13 and 6.5, 2-H), 5.8 (1 H, br d,  $J$  13, 3-H), 4.9 (1 H, m, 5-H), 4.6 (1 H, m, 1-H), 4.2 (4 H, 2 q,  $J$  7,  $OCH_2Me$ ), 3.9 (1 H, s, OH), 2.6 (1 H, s,  $C\equiv CH$ ), 2.4–1.7 (4 H, m,  $CH_2CH_2$ ) and 1.2 (6 H, 2 t,  $OCH_2Me$ );  $m/z$  308 ( $M^+$ , 9%), 134 (11), 130 (34), 105 (14), 91 ( $C_7H_7^+$ , 13), 83 (17) and 29 ( $C_2H_5^+$ , 100).

A solution of this alcohol (250 mg) in benzene (4  $\text{cm}^3$ ) with a little 4-(dimethylamino)pyridine was mixed with a solution of acetic anhydride (0.7  $\text{cm}^3$ ) and triethylamine (1.0  $\text{cm}^3$ ) in benzene (2.3  $\text{cm}^3$ ). After the mixture had been kept for 18 h at room temperature, 2 mol  $\text{dm}^{-3}$  aq. hydrochloric acid (10  $\text{cm}^3$ ) was added. The organic layer was separated and the aqueous phase was extracted with benzene (2  $\times$  10  $\text{cm}^3$ ). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure to give the acetate **19b** as a crystalline solid (280 mg, 99%), m.p. 121–123  $^\circ\text{C}$  [(from (3:1) hexane–diethyl ether) (Found: C, 58.6; H, 6.5; N, 8.1%;  $M^+$ , 350.1464.  $C_{17}H_{22}N_2O_6$  requires C, 58.6; H, 6.5; N, 8.0%;  $M$ , 350.1477);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  3300 ( $C\equiv CH$ ), 2121 ( $C=C$ ), 1750 (acetate CO) and 1720 (carbamate CO). The  $^1\text{H}$  NMR spectrum showed the presence of a pair of rotamers. Some of the main peaks were 'doubled' but on warming to  $\sim 60^\circ\text{C}$  these partially collapsed to give the expected spectrum;  $\delta_H$  6.3 and 6.2 (1 H, 2 dd,  $J$  11 and 7, 2-H), 5.9 (1 H, br d,  $J$  11, 3-H), 5.5 (1 H, 2 s or br d,  $J$  7, 5-H), 4.6 (1 H, m, 5-H), 4.2 (4 H, 2 q,  $J$  7,  $OCH_2Me$ ), 2.7 (1 H, 2 s,  $C\equiv CH$ ), 2.05 and 2.00 (3 H, 2 s, Ac), 2.2–1.8 (4 H, m,  $CH_2CH_2$ ) and 1.2 (6 H, 3 t,  $J$  7,  $OCH_2Me$ ); the stereochemistry was assigned on the basis of an NOE between the acetate Me and carbamate  $CH_2$ ;  $m/z$  350 ( $M^+$ , 3%), 163 (7), 91 ( $C_7H_7^+$ , 10), 83 (9) and 29 ( $C_2H_5^+$ , 100).

The second fraction from the column was the diastereoisomer of **19a**, the alcohol **18a** as an oil (1.56 g, 48%) (Found:  $M^+$ , 308.1363.  $C_{15}H_{20}N_2O_5$  requires 308.1372);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  3440 (OH), 3300 ( $C\equiv CH$ ), 2110 ( $C=C$ ), 1740–1710 ( $C=O$ ) and 1685 ( $C=C$ );  $\delta_H$  6.1 (1 H, dd,  $J$  13 and 7, 2-H), 5.6 (1 H, d,  $J$  13, 3-H), 4.7 (1 H, m, 5-H), 4.5 (1 H, m, 1-H), 4.2 (4 H, 2 q,  $J$  7,  $OCH_2Me$ ), 3.1 (1 H, s, OH), 2.6 (1 H, s,  $C\equiv CH$ ), 2.4–1.7 (4 H, m,  $CH_2CH_2$ ) and 1.3 (6 H, 2 t,  $J$  7,  $OCH_2Me$ );  $m/z$  308 ( $M^+$ , 6%), 134 (5), 130 (28), 105 (15), 91 ( $C_7H_7^+$ , 13), 83 (15) and 29 ( $C_2H_5^+$ , 100).

Acetylation in the same manner as before gave the acetate **18b** as an oil (Found:  $M^+$ , 350.1468;  $C_{17}H_{22}N_2O_6$  requires  $M$ , 350.1477);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  3300 ( $C\equiv CH$ ), 2120 ( $C=C$ ), 1750 (CO of acetate) and 1700 (CO of carbamate);  $\delta_H$  6.2 (2 H, m, 2- and 3-H), 5.1 (1 H, m, 5-H), 4.6 (1 H, m, 1-H), 4.2 (4 H, 2 q,  $OCH_2Me$ ), 2.8 (1 H, s,  $C\equiv CH$ ), 2.1 (3 H, Ac), 2.0–1.8 (4 H,  $CH_2CH_2$ ), and 1.3 (6 H, 2 t,  $OCH_2Me$ );  $m/z$  350 ( $M^+$ , 10%), 163 (15), 91 ( $C_7H_7^+$ , 83 (13) and 29 ( $C_2H_5^+$ , 100).

**Reduction of Diethyl 4-Oxo-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 15 with Sodium Borohydride.**<sup>18</sup>—Sodium borohydride (70 mg) was added in portions to a solution of the enone **15**<sup>3</sup> (500 mg) in 0.4 mol  $\text{dm}^{-3}$  cerium(III) chloride–methanol (3  $\text{cm}^3$ ). After the mixture had been stirred for a further 30 min, water (10  $\text{cm}^3$ ) was added and the mixture was extracted with diethyl ether (2  $\times$  10  $\text{cm}^3$ ). The extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure to give diethyl 4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate as an oil (493 mg, 98%). The product obtained in this way needed no further purification and had spectroscopic properties identical with those reported above.

**Silver Ion-catalysed Rearrangement of 4-Acetoxy-4-ethynyl-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 19b.**<sup>9</sup>—Potassium carbonate (10 mg) and silver carbonate (3 mg) were added to a solution of the acetate **19b** (74 mg) in 80% aq. acetic acid (7  $\text{cm}^3$ ) and the mixture was refluxed for 3 h and then cooled. Water (10  $\text{cm}^3$ ) was added, the layers were separated, and the aqueous layer was extracted with dichloromethane (3  $\times$  10  $\text{cm}^3$ ). The combined extracts were washed with aqueous sodium hydrogen carbonate (30  $\text{cm}^3$ ), dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–hexane] to give a yellow gum identified as a mixture of the aldehydes **20a** and **21a** (48 mg, 80%) (Found:  $M^+$ , 308.1366.  $C_{15}H_{20}N_2O_5$  requires  $M$ , 308.1372);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  1745 (aldehyde  $C=O$ ), 1710 (carbamate  $C=O$ ) and 1670 ( $C=C$ );  $\delta_H$  10.1 (1 H, d,  $J$  6, CHO), 4.5–7.2 (5 H, m, olefinics and bridgehead positions; the 3-H of the *E* isomer resolved at  $\delta$  7.2, d,  $J$  10), 4.2 (4 H, 2 q,  $J$  7,  $OCH_2Me$ ), 2.5–1.4 (4 H, m,  $CH_2CH_2$ ) and 1.2 (6 H, 2 t,  $J$  7,  $OCH_2Me$ );  $m/z$  308 ( $M^+$ , 18%), 137 (44), 134 (15), 133 (31), 109 (70), 105 (18), 91 ( $C_7H_7^+$ , 25) and 29 ( $C_2H_5^+$ , 100).

**Meyer–Schuster Rearrangement<sup>8</sup> of Diethyl 4-(Hex-1-ynyl)-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate 18c.**—A few drops of conc. sulfuric acid were added to a solution of the propargylic alcohol **18c** (55 mg) in 80% aq. acetic acid (3  $\text{cm}^3$ ). The mixture was heated under reflux for 1 h, diluted with water (10  $\text{cm}^3$ ), neutralised with 2 mol  $\text{dm}^{-3}$  aq. sodium carbonate, and extracted with diethyl ether (3  $\times$  20  $\text{cm}^3$ ). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed [(1:1) diethyl ether–hexane] to give a yellow oil identified as a 3:2 mixture of the *E* (**21b**) and *Z* (**20b**) isomers of diethyl 4-(2-oxohexylidene)-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate (52 mg, 95%) (Found:  $M^+$ , 364.1988.  $C_{19}H_{28}N_2O_5$  requires  $M$ , 364.1990);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1740–1780 (CO);  $\delta_H$  7.5–4.5 (5 H, m, olefinics and bridgeheads; the 3-H of the *E*-isomer resolved at  $\delta$  7.5, d,  $J$  13), 4.2 (4 H, m,  $OCH_2Me$ ), 2.5 (2 H, t,  $J$  7,  $COCH_2$ ), 2.4–1.3 (8 H,  $CH_2$ ), 1.2 (6 H, m,  $OCH_2Me$ ) and 0.9 (3 H, t,  $J$  7,  $[CH_2]_3Me$ );  $m/z$  364 ( $M^+$ , 14%), 191 (13), 190 (17), 189 (36), 133 (11), 105 (18), 91 ( $C_7H_7^+$ , 19) and 29 ( $C_2H_5^+$ , 100). This reaction was normally monitored by TLC and when carried out on a larger scale, with alcohols **18c**, **19c** or a mixture of **18c** and **19c** as the starting material, two 'intermediates' could be detected, and by stopping the reaction before it was complete these could be isolated by column

chromatography. The first of these was less polar than the products **20b** and **21b** and was tentatively assigned the structure **22b**. It was obtained as an oil (Found:  $M^+$ , 406.2091.  $C_{21}H_{30}N_2O_6$  requires  $M$ , 406.2103);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  2210 ( $\text{C}\equiv\text{C}$ ), 1745 (acetate  $\text{C}=\text{O}$ ) and 1710 (carbamate  $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  5.7 (2 H, m, 3- and 4-H), 4.5 (2 H, m, bridgeheads), 4.2 (4 H, 2 q,  $J$  7,  $\text{OCH}_2\text{Me}$ ), 2.3 (2 H, t,  $J$  7,  $\text{C}\equiv\text{CCH}_2$ ), 2.1 (3 H, s, Ac), 2.0–1.3 (8 H, m,  $\text{CH}_2$ ), 1.2 (6 H, 2 t,  $J$  7,  $\text{OCH}_2\text{Me}$ ) and 0.9 (3 H, t,  $J$  7,  $[\text{CH}_2]_3\text{Me}$ );  $m/z$  406 ( $M^+$ , 13%), 189 (37), 188 (63), 105 (16), 91 ( $\text{C}_7\text{H}_7^+$ ), 83 (45) and 29 ( $\text{C}_2\text{H}_5^+$ , 100). The second 'intermediate' was more polar than the products **20b** and **21b** and was identified as diethyl 2-(hex-1-ynyl)-4-hydroxy-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate **22a**. It was obtained as an oil (Found:  $M^+$ , 364.2004.  $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_5$  requires  $M$ , 364.1998);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  231 (enyne);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  3460 (OH), 2220 ( $\text{C}\equiv\text{C}$ ) and 1740–1720 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  6.0 (1 H, d,  $J$  5.5, 3-H), 4.8 (1 H, dd,  $J$  7 and 5.5, 4-H), 4.6 (1 H, m, 5-H), 4.2 (5 H, m,  $\text{OCH}_2\text{Me}$  and 1-H), 2.7 (2 H, t,  $J$  7,  $\text{C}\equiv\text{CCH}_2$ ), 2.2–1.3 (8 H, m,  $\text{CH}_2$ ), 1.3 (6 H, t,  $J$  7,  $\text{OCH}_2\text{Me}$ ) and 0.9 (3 H, m,  $[\text{CH}_2]_3\text{Me}$ );  $m/z$  364 ( $M^+$ , 3%), 190 (56), 189 (59), 188 (42), 158 (67), 130 (97), 91 ( $\text{C}_7\text{H}_7^+$ , 66), 77 (35) and 29 ( $\text{C}_2\text{H}_5^+$ , 100).

*Peterson Methylenation of Diethyl 4-(2-Oxohexylidene)-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate (20b + 21b, Z + E Isomers).*<sup>11</sup>—The reagent was generated by addition of chloromethyl(trimethyl)silane (1.2  $\text{cm}^3$ ) to magnesium (191 mg) in diethyl ether (6  $\text{cm}^3$ ) during 20 min at 0 °C. The solution was allowed to reach room temperature, a mixture of the enones **20b** and **21b** (2.49 g) in diethyl ether (15  $\text{cm}^3$ ) was added, and the reaction mixture was heated under reflux for 3 h. The solution was cooled to 0 °C and thionyl dichloride (0.5  $\text{cm}^3$ ) was added. After 1 h at room temperature the mixture was treated with saturated aq. ammonium chloride (20  $\text{cm}^3$ ) and after a further 3 h the mixture was filtered and the aqueous layer was extracted with diethyl ether (2  $\times$  40  $\text{cm}^3$ ). The combined extracts were dried with magnesium sulfate, filtered, and evaporated under reduced pressure, and the residue was chromatographed on flash silica [(1:1) diethyl ether–light petroleum] to give an *E/Z* mixture of diethyl 4-(2-butylallylidene)-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate (**20c** and **21c**) as a yellow gum (1.69 g, 68%) (Found:  $M^+$ , 362.2206.  $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4$  requires  $M$ , 362.2205);  $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$  1740–1690 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  6.8–5.7 (3 H, m, olefinics), 5.1 (1 H, m,  $\text{C}=\text{CHH}$ ), 4.8 (1 H, m,  $\text{C}=\text{CHH}$ ), 5.2–4.4 (2 H, m, 1- and 5-H), 4.2 (4 H, 2 q,  $J$  7,  $\text{OCH}_2\text{Me}$ ), 2.4–1.0 (10 H, m,  $\text{CH}_2$ ), 1.2 (6 H, 2 t,  $J$  7,  $\text{OCH}_2\text{Me}$ ) and 0.9 (3 H, m,  $[\text{CH}_2]_3\text{Me}$ );  $m/z$  362 ( $M^+$ , 22%), 289 (8), 188 (22), 186 (18), 131 (29), 91 ( $\text{C}_7\text{H}_7^+$ , 35) and 29 ( $\text{C}_2\text{H}_5^+$ , 100). This mixture of trienes, like the dienones from which it was derived, could not be separated by chromatography and the separation of *E* and *Z* isomers was left until after the next stage of the preparation.

*Hydrolysis and Oxidation of Diethyl 4-(2'-Butylallylidene)-6,7-diazabicyclo[3.2.2]non-2-ene-6,7-dicarboxylate (20c and 21c).*—The mixture of trienes obtained in the previous experiment (**20c** + **21c**) (1.01 g) was heated under reflux in methanolic potassium hydroxide [40  $\text{cm}^3$  of a solution made from potassium hydroxide (7.2 g), methanol (37.5  $\text{cm}^3$ ), and water (1  $\text{cm}^3$ )] for 8 h. After the mixture had cooled, solid sodium hydrogen carbonate (3 g) was added, the mixture was stirred for 1 h at room temperature and then filtered, yellow mercury(II) oxide (8 g) was added, and the mixture was stirred for a further 6 h. Solids were removed by filtration through Celite, the filtrate, concentrated under reduced pressure at 0 °C to remove most of the methanol, was treated with water (70  $\text{cm}^3$ ), and the mixture was extracted with dichloromethane (3  $\times$  60  $\text{cm}^3$ ). The combined organic extracts were dried with magnesium sulfate, filtered, and evaporated under reduced

pressure at 0 °C to give a dark oil (350–400 mg, ~60%). The  $^1\text{H}$  NMR spectrum showed that this crude product contained little other than the desired diazenes **23** and **24**. Since these were unstable the crude product was stored at low temperature and portions were subjected to rapid (flash) chromatography [(3:1) light petroleum–diethyl ether] as required. In a typical experiment a portion of the oil (35 mg) yielded (*E*)-4-(2'-butylallylidene)-6,7-diazabicyclo[3.2.2]nona-2,6-diene **24** (10.4 mg) and the *Z*-isomer **23** (16 mg), both as oils which were initially colourless but which became quite quickly brown.

For the *Z*-isomer **23** (Found:  $M^+$  –  $\text{N}_2$ , 188.1554.  $\text{C}_{14}\text{H}_{20}$  requires  $m/z$ , 188.1564;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  407 ( $\text{N}=\text{N}$  and 282 (triene);  $\delta_{\text{H}}$  6.21 (1 H, m, 5-H), 5.96 (1 H, d,  $J$  11, 3-H), 5.90 (1 H, s, 1'-H), 5.75 (1 H, dd,  $J$  11 and 8, 2-H), 5.45 (1 H, dd,  $J$  8 and 5, 1-H), 5.2 (1 H, m,  $\text{C}=\text{CHH}$ ), 5.1 (1 H, m,  $\text{C}=\text{CHH}$ ), 2.16 (2 H, t,  $J$  7,  $\text{CH}_2\text{C}=\text{C}$ ), 2.1–1.3 (8 H, m,  $\text{CH}_2$ ) and 0.9 (3 H, t,  $J$  7, Me);  $m/z$  210 ( $M^+$ , 0%), 188 ( $M^+$  –  $\text{N}_2$ , 42), 160 (7), 159 (12), 145 (77), 131 (83), 117 (66), 91 ( $\text{C}_7\text{H}_7^+$ , 100) and 84 (41).

For the *E*-isomer **24** (Found:  $M^+$  –  $\text{N}_2$ , 188.1559);  $\lambda_{\max}(\text{EtOH})/\text{nm}$  407 ( $\text{N}=\text{N}$ ) and 283 (triene);  $\delta_{\text{H}}$  6.5 (1 H, d,  $J$  11, 3-H), 5.98 (1 H, s, 1'-H), 5.78 (1 H, ddd,  $J$  11, 8 and 1.5, 2-H), 5.43 (2 H, m, 1- and 5-H), 5.05 (1 H, m,  $\text{C}=\text{CHH}$ ), 4.84 (1 H, m,  $\text{C}=\text{CHH}$ ), 2.07 (2 H, t,  $J$  7,  $\text{CH}_2\text{C}=\text{C}$ ), 2.0–1.2 (8 H, m,  $\text{CH}_2$ ) and 0.9 (3 H, t,  $J$  7, Me);  $m/z$  210 ( $M^+$ , 0%), 188 ( $M^+$  –  $\text{N}_2$ , 19), 173 (2), 160 (2), 145 (31), 117 (20), 91 ( $\text{C}_7\text{H}_7^+$ , 66), 84 (89) and 41 (100). The stereochemistries of these two products were assigned on the basis of COSY and NOE experiments described in detail in the preliminary communication<sup>1</sup> and the assignment was confirmed on the basis of  $^1\text{H}$  NMR chemical shifts as discussed in the main text.

*ESR Experiments.*—A sample of the diazene (~10 mg) in [(5:5:2) diethyl ether–2-methylbutane–ethanol] (EPA) or (1:1) 2-methyltetrahydrofuran–propan-2-ol in a 5 mm silica ESR tube was degassed through a series of freeze–pump–thaw cycles and sealed under vacuum (~10<sup>-3</sup> mmHg). The tube, set in a silica 'finger dewar' containing liquid nitrogen, was irradiated using an Hanovia 504/4 medium-pressure mercury vapour lamp for ca. 6 min and the resultant ESR spectrum was recorded on a Varian X-band ESR spectrometer at 77 K.

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