Making a Vinyl-Trimethylenemethane Precursor through the Addition of Diethyl Azodicarboxylate to Tropone.[1]

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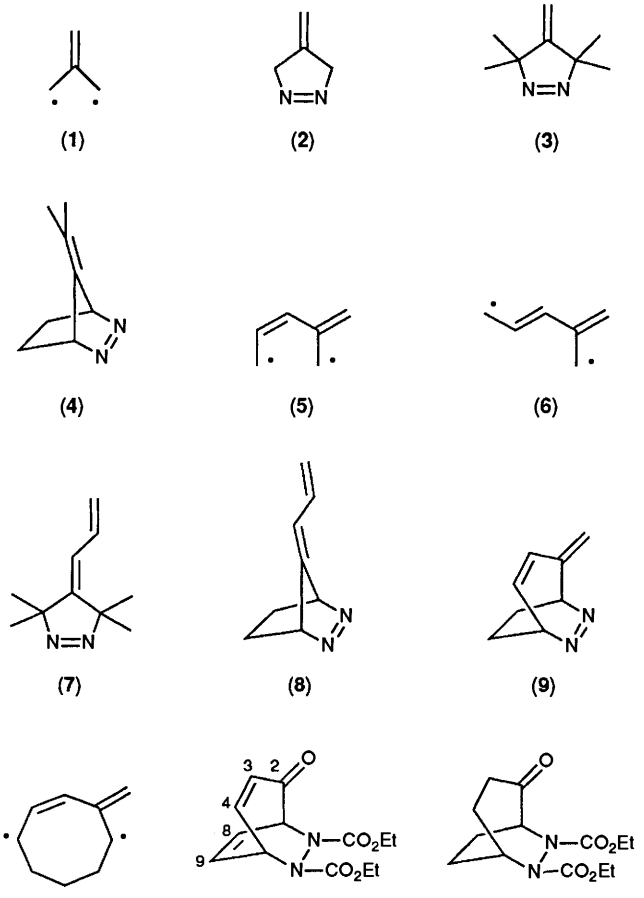
Diethyl 2-oxo-6,7-diazabicyclo[3.2.2]nona-3,8-diene-6,7-dicarboxylate (**11**) has been prepared by the addition of diethyl azodicarboxylate to tropone. The 3,4-double bond was protected by reaction with triethyl orthoformate–ethanol–tosic acid (toluene-*p*-sulphonic acid), the 8,9-double bond reduced, and the enone unit deprotected with water–dioxane–tosic acid. The resultant enone was converted into the conjugated diene by reaction with methyl-lithium and dehydration. Hydrolysis of the carbamate groups (KOH–MeOH) and oxidation (HgO) gave 2-methylene-6,7-diazabicyclo-[3.2.2]nona-3,6-diene (**9**). UV irradiation of a glassy solution of this diazene at 77 K gave the first observable triplet ESR spectrum of a vinyl-trimethylenemethane biradical, 2-methylenecyclohept-3-ene-1,5-diyl (**10**). Despite the fact that this non-Kekulé polyene has a triplet ground state, the singlet biradical reacts as such to give a mixture of 7-methylenebicyclo[4.1.0]hept-2-ene (**28**), 2-methylenebicyclo[3.2.0]hept-3-ene (**29**), and 3-methylenehepta-1,4,6-triene (**30**) faster than it undergoes intersystem crossing. Several interesting contrasts exist between the chemistry of the bridged vinyl-TMM precursor (**9**) and the equivalent bridged TMM precursor, 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (**4**). In the former case, pyrolysis proceeds *via* the singlet biradical to give mainly monomeric products. There is no CIDNP effect and trapping with alkenes gives low yields of cycloadducts (Scheme 1). In the latter case, pyrolysis gives dimeric products *via* the triplet biradical. There is a strong CIDNP effect and in the presence of alkenes high yields of cyclo-adducts are obtained (Scheme 2).

The three simplest non-Kekulé polyenes are TMM, TME,† and vinyl-TMM.[2] Of these TMM is by far the best understood. The parent TMM biradical (**1**) can be made from the pyrazoline (**2**).[3] However, since this pyrazoline is subject to N=N–CH→NH–N=C tautomerism[3,4] workers have concentrated on α-methylated (**3**)[5] and bicyclic (**4**)[6–9] diazene precursors for which such tautomerism is impossible. Compared to TMM, vinyl-TMM is little understood although its chemistry should be more varied and more interesting. Whereas TMM (**1**) is a simple 1,3-biradical, vinyl-TMM [*Z*-(**5**), or *E*-(**6**)] is both a 1,3-biradical and a 1,5-biradical. This difference suggests new chemistry and new synthetic routes. The vinyl-TMM precursors (**7**)[10] and (**8**)[11] (and simple derivatives thereof) are based on the known TMM precursors (**3**) and (**4**). They solve the tautomerism problem but give mixtures of *Z*- and *E*-biradicals. They are based on the perception of vinyl-TMM as a 1,3-biradical, whereas the route developed in this paper is based on the 1,5-biradical character of vinyl-TMM and makes use of the precursor (**9**).[1] This precursor not only solves the tautomerism problem but also gives rise to a single, sterically defined *Z*-vinyl-TMM (**10**).

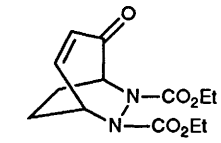
When a mixture of tropone and diethyl azodicarboxylate in xylene is refluxed for 24 h the adduct (**11**) is obtained in 67% yield.[12] This adduct has the desired skeleton but selective reduction of the 8,9 double bond proved to be difficult. Attempted selective reduction with 1 mol equiv. of hydrogen using 5% Pd on C, Pd on $BaSO_4$, or Wilkinson's catalyst gave mixtures. NMR analysis showed that these contained starting material (**11**), the fully reduced product (**12**), but none of the desired half-reduced product (**13**).

The first attempt to solve this problem was to use an α-substituted tropone that would give an adduct with a tri-



(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12)

† TMM = 'trimethylenemethane'; TME = 'tetramethylene-ethane.'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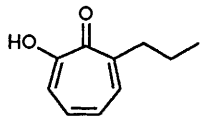
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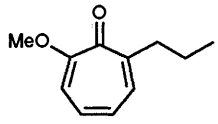
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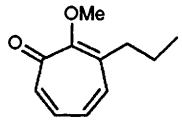
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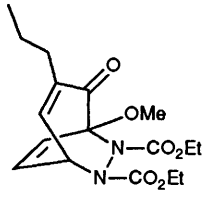
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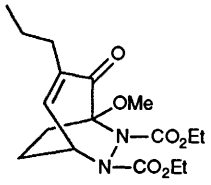
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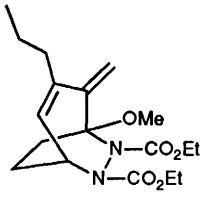
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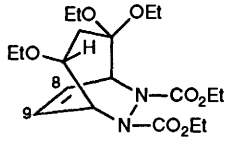
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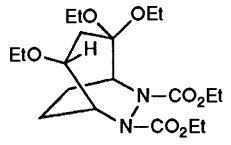
substituted 3,4-double bond and for which selective reduction should be straightforward. Three different tropones were tried. The results for all three were similar[13] and only one will be described in detail. Tropolone was treated with allyl bromide and base. A Claisen rearrangement of the resultant allyl ether followed by selective reduction of the terminal double bond gave 3-propyltropolone (**14**).[14] Methylation with diazomethane in ether gave a mixture of isomers (**15**) and (**16**). Since $2\pi + 4\pi$ cycloaddition reactions of α-alkoxytropones normally give products with a bridgehead alkoxy substituent,[13,15] only the first of these isomers is of use (*i.e.* only this isomer will give an adduct with a 3-propyl substituent). Unfortunately, this was the minor product from the methylation reaction but it was found that the overall yield and the proportion of the desired isomer (**15**) could be improved by the addition of methanol to the reaction mixture. In this way, enough was isolated to continue the reaction sequence: CH_2N_2 in pure ether, yield *ca.* 70%, ratio (**15**)–(**16**) *ca.* 1:3; in 8% methanol–ether, yield 81%, ratio 1:2.3; in 14% methanol–ether, yield 90%, ratio 1:1.9. When the α,α′-disubstituted tropone (**15**) was heated with diethyl azodicarboxylate in benzene at 145 °C (sealed tube) for 4 h the expected adduct (**17**) was obtained in 75% yield and this could be selectively hydrogenated using 1 mol equiv. of hydrogen and Pd on $BaSO_4$. However, the resultant enone (**18**) resisted all attempts to convert it into the diene (**19**) using either Wittig reagents or a methyl lithium–dehydration sequence. Later, experience showed that these reactions are far from easy, even for the enone (**13**), and it seems that the presence of substituents in the 1 and 3 positions renders the reactions impossible.

The next attempt to convert the adduct (**11**) into the enone (**13**) involved making the fully hydrogenated ketone (**12**) and then trying to reintroduce the 3,4-double bond through α-halogenation or α-selenation. However, these routes also proved unsuccessful.[13] A far simpler solution to the problem was discovered by accident.

It was argued that, if the keto group in compound (**11**) was converted into a suitable acetal, this might provide sufficient steric hindrance to facilitate a selective reduction of the 8,9 double bond. However, when the adduct (**11**) was treated with triethyl orthoformate–ethanol–tosic acid the product was not a simple acetal but the triethoxy derivative (**20**). In a single step, both the carbonyl and 3,4-double bonds were protected. Hydrogenation of the 8,9-double bond (10% Pd on C catalyst and 20–30 atm pressure) gave compound (**21**), and acid catalysed deprotection (water–dioxane–tosic acid) and chromatographic purification gave the desired enone as a crystalline solid and in good yield (63% on the last three steps).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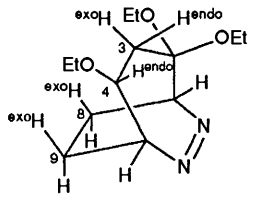
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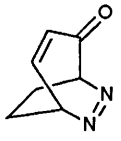
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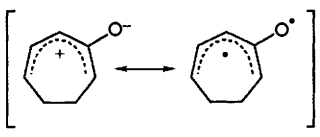
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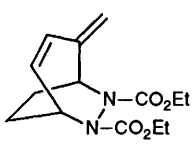
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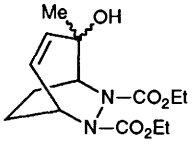
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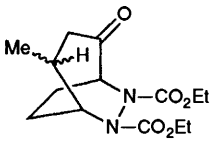
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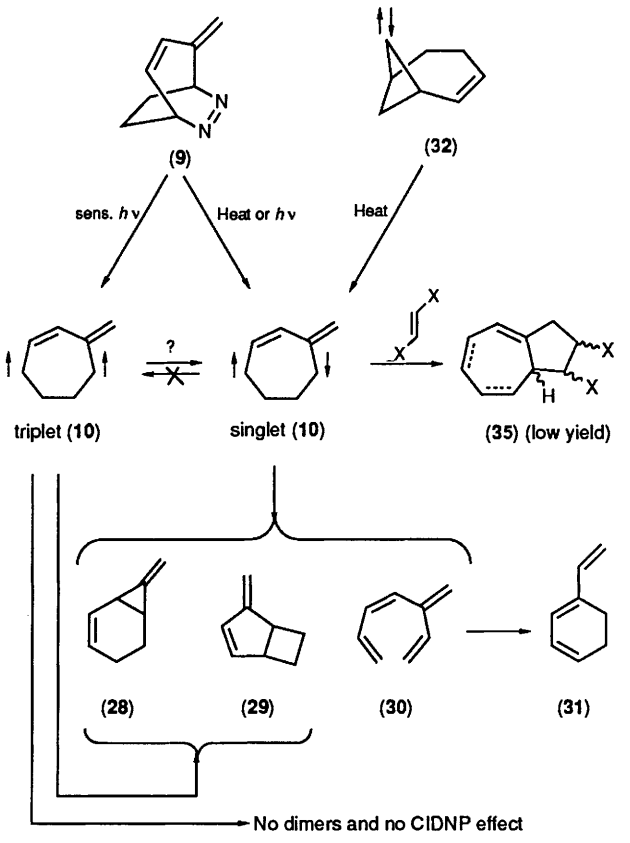
The stereochemistry shown for compounds (**20**) and (**21**), with the ethoxy group at C-4 over the $-CH_2CH_2-$ bridge rather than the –N–N– bridge, is based on NMR experiments on the corresponding diazene (**22**). A constant problem in this work was that the carbamates (**11**)–(**13**), (**17**)–(**21**), and (**25**)–(**27**) show hindered rotation on the ^1H NMR time scale. As a result, signals in the ^1H NMR spectrum are sometimes very broad, the spectra themselves are field-dependent, and generally the ^1H NMR spectra are less informative than is normally the case. When the $-N(CO_2Et)-N(CO_2Et)-$ bridge is converted into an –N=N– bridge, however, normal sharp ^1H NMR spectra, containing all of the expected spin-coupling information, and for which NOE experiments are straightforward, are obtained. In the case of compound (**22**), the stereochemistry was established by a combination of COSY and 1-D difference-NOE experiments. The crucial information is the presence of an NOE between 3-H^{exo} and 8-H^{exo}, 9-H^{exo} together with an 11.5 Hz coupling between 3-H^{exo} and 4-H^{endo}. It was also found that there was no NOE between 4-H^{endo} or 3-H^{endo} and positions 8 and 9. J(3-H^{endo}, 4-H^{endo}) is 5 Hz. Part of the reason for preparing compound (**22**) was the hope that, through the diazene (**23**), it would act as a precursor to the interesting oxypentadienyl zwitterion–biradical (**24**). However, acid treatment of the diazine (**22**) gave only complex mixtures of low molecular weight products.

Conversion of the enone (**13**) into the desired diene (**9**) was initially attempted through a Wittig reaction but this gave a poor yield (*ca.* 23%).[16] However, the diene (**25**) could be obtained in fairly good yield by a methylation–dehydration sequence. Treatment of the enone (**13**) with 1.25 equivalents of methyl-lithium at −15 °C in diethyl ether gave 59% of the 1,2-adduct (**26**) and 8% of the 1,4-adduct (**27**). (These may have been mixtures of stereoisomers. As usual, the ^{1}H NMR spectra were complicated by hindered rotation of the carbamate groups and attempts to hydrolyse these groups failed to give identifiable products.) The 1,2-adduct (**26**) was dehydrated using tosic acid–4 Å molecular sieves–benzene to give the diene (**25**) in 70–83% yield. Base catalysed hydrolysis of the carbamate groups (KOH–MeOH) and oxidation (yellow mercuric oxide) proceeded without difficulty to give the desired diazene (**9**) (70–80% yield on the last two steps). It was isolated as a pale brown mobile oil which gave white crystals on storage at −40 °C. The overall route from tropone to the vinyl-TMM precursor (**9**) involves eight steps, most proceeding in good yield, and there are no problems in preparing multigram quantities.

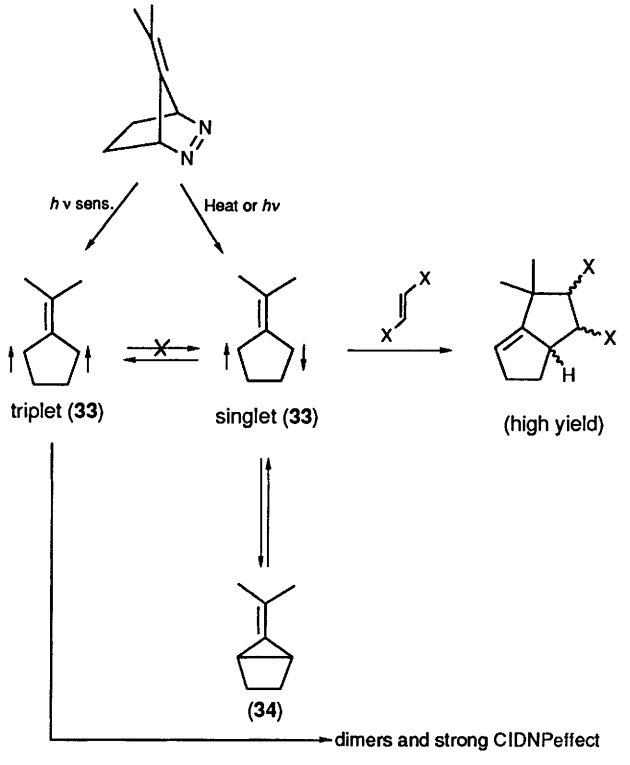
UV irradiation of the diazene (**9**) in an EPA glass [diethyl ether–2-methylbutane–ethanol (5:5:2)] or in a 2-methyltetrahydrofuran–isopropyl alcohol (1:1) glass at 77 K gave the same triplet ESR spectrum.[1] This showed a four line $\Delta m = 1$ region, $|D/hc| = 0.019$ cm^{-1} and $|E/hc| = 0.006$ cm^{-1}, and a strong $\Delta m = 2$ transition at half field. The value of $|D/hc|$ corresponds to that calculated for the triplet *Z*-vinyl-TMM biradical (**10**)[1,17] and this constituted the first ESR observation of a vinyl-TMM triplet. Such a triplet spectrum can arise either if the biradical has a triplet ground state or if it has a singlet ground state and the triplet state is thermally populated. However, in this case, the biradical is expected to be a ground state triplet,[18] and a study of the temperature dependence of the intensity of the $\Delta m = 2$ transition confirmed that this is the case.[19] Despite this, all of the evidence we have collected suggests that when the biradical (**10**) is generated in its singlet state, it reacts as the singlet rather than crossing to the ground state triplet (*i.e.* reaction of the singlet is fast relative to intersystem crossing).

Pyrolysis of the diazene (**9**) proceeds very cleanly and gives a mixture of four C_8H_{10} hydrocarbons which was analysed by GLC (Table). The three major products (**28**)–(**30**) are all derived directly from the biradical (**10**) whereas the dihydrostyrene (**31**) arises by electrocyclisation of the tetraene (**30**).[20] (Scheme 1). Dimeric products are formed in trace quantitities but could be detected by both GLC[20] and mass spectroscopy. When the total crude product was subjected to mass spectroscopy, the initial spectrum was dominated by a parent ion *m/z* 106 (C_8H_{10}). As the temperature of the probe was raised, however, an ion *m/z* 212 ($C_{16}H_8$) could be observed. We believe that the C_8 products arise from singlet (**10**) as shown in Scheme 1. Previous workers have suggested that this same biradical is produced by rearrangement of the carbene (**32**)[20] and although it is not possible to make a direct comparison with their product ratios, the general distribution of primary products (**28**) ⩾ (**29**) ⩾ (**30**) is similar in both cases.

An interesting comparison can also be made between the pyrolysis of the diazene (**9**), which gives mainly monomeric products, probably *via* the singlet vinyl-TMM (**10**) (Scheme 1) and that of the related diazene (**4**) which gives mainly dimeric products *via* the triplet TMM (**33**) (Scheme 2).[6,8] This major difference in reactivity occurs despite the fact that both biradicals (**10**) and (**33**) have triplet ground states! Berson has argued[8] that this is because the primary product of the singlet biradical (**33**), the bicyclic compound (**34**), is highly strained and reverts to the biradical (**33**) at low temperatures. At these low temperatures, intersystem crossing competes effectively with recyclisation (because ISC has a low pre-exponential factor) giving rise to triplet and eventually dimers. However,



Scheme 1.



Scheme 2.

the bicyclic compound (**28**) only reverts to biradical (**10**) at high temperatures (> 120 °C);[20] conditions where ISC cannot compete effectively with other processes. Ultimately, the dif-

Table. Products of the pyrolysis and photolysis of the diazene (**9**).

	% Products			
	(**28**)	(**29**)	(**30**)	(**31**)
Thermolysis of (**9**), 120 °C[a]	98.9	1.1	0.5	0.5
Thermolysis of (**9**), 25 °C[b]	99.5	0.3	0.1	0.1
Photolysis of (**9**), 25 °C[a]	83.1	9.5	7.4	0
Sensitised photolysis of (**9**), 25 °C[a,c]	96.4	3.4	0	0

[a] Since the product ratios were somewhat time dependent, results have been extrapolated to $t = 0$. [b] Extrapolated product ratios from 120 °C on the assumption [log(ratio at T_1)]/log(ratio at T_2] = T_2/T_1. [c] Benzophenone sensitiser. Essentially the same results were obtained for molar ratios of Ph_2CO to (**9**) of 2:1 and of 5:1.

ference relates to the fact that compound (**34**) is more highly strained than compound (**28**)!

Whereas the monomeric products from the pyrolysis of diazene (**9**) seem to arise from singlet (**10**) the detection of traces of C_{16} dimer by mass spectroscopy suggest that these arise through triplet (**10**). To investigate this possibility, a CIDNP experiment was performed in which the pyrolysis of diazene (**9**) was once again compared to that of the equivalent TMM precursor (**4**). When a solution of the diazene (**4**) in $[^2H]_8$-toluene is inserted into the probe of an NMR spectrometer at 105 °C it decomposes with a 'half life' of *ca.* 30 s (under these conditions the kinetics are not strictly first order and the exact value of the 'half-life' depends on how quickly the solution reaches probe temperature). The dimers produced show a very strong emission CIDNP effect,[6] characteristic of a triplet reaction.[21] This effect is so strong (peak heights up to 10^3 times their normal value) that we argued that, even if only a little triplet dimerisation occurred in the equivalent pyrolysis of diazine (**9**), it should be possible to observe the CIDNP. However, under comparable conditions, *i.e.* a solution of diazene (**9**) in $[^2H]_{10}$-xylene, a probe temperature of 144 °C, and with a 'half life' of *ca.* 30 s, no effect was observed. This makes it very unlikely that triplet (**10**) is involved in the formation of these dimers. They may well be secondary products, perhaps arising from the tetraene (**30**).

Direct (unsensitised) photolysis of the diazine (**9**) should also give the singlet biradical (**10**) and the observed product distribution, (**28**) ⩾ (**29**) > (**30**) (Table), is consistent with this. The slightly lower proportion of the [4.1.0]bicyclic product (**28**) compared with the pyrolytic reaction may be because photolysis produces a vibrationally hot singlet but, in the absence of further experimental results, other explanations cannot be discounted.[22]

Triplet sensitised photolysis of the diazene (**9**) should generate triplet (**10**) directly[8] (Scheme 1). This photolysis gave mainly the [4.1.0]bicyclic hydrocarbon (**28**) and a little of the [3.2.0]bicyclic hydrocarbon (**29**) but no (**30**) or (**31**) (Table). As shown in Scheme 1, we believe that, triplet (**10**) gives rise to these hydrocarbons directly. This would imply that ISC accompanies cyclisation. If ISC of triplet (**10**) occurred before cyclisation it would be difficult to explain the absence of product (**30**). Once again, it is interesting to contrast the triplet TMM (**33**) (Scheme 2) that dimerises and the triplet vinyl-TMM (**10**) that gives monomeric products (Scheme 1). The difference, once again, probably relates to the strained nature of the TMM cyclisation product (**34**).

As shown in Scheme 2 the bridged singlet TMM biradical (**33**) adds efficiently to olefins.[7–9] These additions seem to be FMO controlled;[8] they are regioselective and stereoselective, and have been used in the synthesis of several polycyclic natural products.[9] At the outset of this work, simple analogy between the bridged TMM (**33**) and the bridged vinyl-TMM (**10**) suggested that the latter biradical should also add to olefins to give products of the bicyclo[5.3.0], bicyclo[4.2.1], or bicyclo-[3.2.2] type. As the work progressed, it became clear that there were more contrasts than parallels between the reactivities of the two biradicals and this was also true of the cycloaddition reactions.

A mixture of the diazene (**9**) (200 mg) and dimethyl fumarate (*ca.* 10 equivalents) was sealed *in vacuo* and heated at 120 °C for 30 min. The products obtained were then compared (GLC, TLC, and HPLC) to those obtained by heating diazene (**9**) or dimethyl fumarate on their own. Attempted isolation of the cross products by preparative GLC gave four fractions (total *ca.* 10 mg), each of which proved to be a mixture. The largest and purest of these fractions gave a parent ion in the mass spectrum M^+, 250.1206, $C_{14}H_{18}O_4$ and an NMR spectrum consistent with a bicyclo[5.3.0] structure (**35**) but also appeared to be a mixture of stereo- and regio-isomers. Similar results were obtained with butadiene and with 1,1-diethoxyethylene.[13] In all cases, a complex mixture of cross products was obtained with a combined yield < 10%. Although the results of these intermolecular cycloadditions were disappointing, they do suggest that a suitably designed intramolecular trapping experiment would be successful[11,13] and work on systems of this type is in progress.

Overall, the route developed has succeeded in producing the first observable vinyl-TMM biradical. It is capable of variation and has already been used to generate other types of non-Kekulé polyene.[13,23] Although poor yields were obtained in intermolecular cycloaddition reactions, equivalent intramolecular cycloadditions may prove to be useful. Some interesting contrasts have also emerged between the bridged vinyl-TMM (**10**) (Scheme 1) and the bridged TMM (**33**) (Scheme 2).

Experimental

Instrumentation.—M.p.s were determined on a Reichert hot-stage and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1420 ratio recording spectrometer, and UV spectra were recorded on a Pye–Unicam PU8800 UV–VIS spectrometer using 1 cm cells. All NMR spectra were recorded in deuteriochloroform (unless otherwise stated). ^1H NMR spectra, recorded at low field, were obtained either from a Perkin–Elmer R32 or a JEOL FX90Q. ^1H NMR spectra recorded at 400 MHz and all 2-D spectra were obtained from a Brüker AM400 spectrometer. Low resolution mass spectra were recorded on a Kratos MS25 mass spectrometer, whereas high resolution measurements were determined on a Kratos MS9/50 mass spectrometer.

General Procedures.—All reactions were conducted under a positive pressure of dry nitrogen and for procedures which required anhydrous conditions, the apparatus was oven-dried and/or flame-dried prior to use. The term *in vacuo* refers to the removal of solvent using a Büchi rotary evaporator at water aspirator pressure, followed by evacuation of the flask (*ca.* 0.5 mmHg) for 1–3 h. TLC was performed on Camlab pre-coated TLC plates, with a layer thickness of 0.2 mm (Merck Kieselgel 5174 Type 60, F_{254}). Compounds were visualised first under UV light (254 nm), then were sprayed either with 10% ceric ammonium nitrate in 2M sulphuric acid or dipped in 10% sulphuric acid in methanol before heating. Column chromatography was performed on Merck Kieselgel 'G' Type 60 (0.04–0.063 mm) unless stated otherwise. Flash silica refers to Camlab Kieselgel 60G 230–400 mesh ASTM, 0.04–0.063 mm, and 'Sorbsil' refers to Crossfields Sorbsil M60. 'Light petroleum' refers to the 30–40 °C fraction, and was distilled prior to use,

though AnalaR grade was used directly. Diethyl ether and THF were distilled either from sodium benzophenone ketyl (if dry solvent was required) or distilled directly prior to use. Benzene was dried over sodium, whereas ethanol and methanol were distilled from their respective magnesium alkoxides. The terms 'methanolic KOH' and 'KOH in methanol' refer to a solution comprising of KOH (7.2 g), methanol (37.5 ml), and water (1 ml).

Diethyl 2-Oxo-6,7-diazabicyclo[3.2.2]*nona-3,8-diene-6,7-dicarboxylate* (**11**).[12]—Tropone (5 g, 47 mmol, 1 equiv.) and diethyl azodicarboxylate (8.2 g, 47 mmol, 1 equiv.) were heated under reflux in xylene (20 ml) for 24 h. Concentration of the product *in vacuo* afforded a dark gum. The bulk of the product was isolated as an off-white solid by trituration of the gum with diethyl ether (3 × 30 ml). Further product was isolated by column chromatography (100% diethyl ether) of the residue from the ether extracts, again as an off-white solid (8.84 g, 67%), m.p. 101–102 °C (lit.,[12] 102–103 °C); ν_{max}(Nujol) 1 740–1 690 cm^{-1} (C=O); δ_H 7.0 (1 H, ddd, *J* 8, 2, and < 1 Hz), 6.8 (1 H, dd, *J* 11 and 8 Hz), 6.2 (1 H, dt, *J* 8, 8 and 1.5 Hz), 5.8 (1 H, dd, *J* 11 and < 1 Hz), 5.4 (1 H, ddd, *J* 8, 6, and < 1 Hz, bridgehead), 5.1, (1 H, dd, *J* 8 and < 1 Hz, bridgehead), 4.2 (4 H, two q, *J* 7 Hz, carbamate $-CH_2CH_3$), and 1.3 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_3); *m/z* 280 (M^+, 100%), 208 (24, $M^+ - C_2H_4$, $-CO_2$), 162 (25), 107 (95, $C_7H_7O^+$), and 105 (46, $C_7H_5O^+$).

Diethyl 2-Oxo-6,7-diazabicyclo[3.2.2]*nonane-6,7-dicarboxylate* (**12**).[16]—To a solution of diethyl 2-oxo-6,7-diazabicyclo-[3.2.2]nona-3,8-diene-6,7-dicarboxylate (3.89 g, 13.9 mmol) in ethanol (50 ml) was added a small quantity of 10% palladium on charcoal. The mixture was stirred vigorously in the presence of hydrogen (atmospheric pressure) for 18 h (until no more hydrogen was absorbed). The product was filtered through Celite and concentrated *in vacuo* to yield a dark viscous oil. Purification by column chromatography on 'Sorbsil' (100% ethyl acetate) gave a viscous orange oil (2.70 g, 70%) (Found: M^+, 284.1369. $C_{13}H_{20}N_2O_5$ requires 284.1372); $\nu_{max}(CCl_4)$ 1 730 and 1 710 cm^{-1} (C=O); δ_H 4.9 (2 H, br m, bridgeheads), 4.4 (4 H, br q, *J* 7 Hz, carbamate CH_2CH_3), 2.9–1.6 (8 H, m, CH_2), and 1.3 (6 H, two t, *J* 7 Hz, carbamate $-CH_2CH_3$); *m/z* 284 (M^+, 19%), 184 (38, $M^+ - 2 \times C_2H_4$, $-CO_2$), 139 (46), 111 (100, $C_7H_{11}O^+$), 105 (50, $C_7H_5O^+$), and 83 (57, $C_5H_7O^+$).

2-Allyloxytropone.[14]—To tropolone (5.0 g, 41 mmol, 1 equiv.) in DMF (50 ml) was added potassium carbonate (6.79 g, 50 mmol), 1.2 equiv.) and allyl bromide (18.75 ml, 41 mmol, 1 equiv.). The solution was heated at 50–60 °C for 40 h. Water (150 ml) was added to the solution, followed by continuous extraction with diethyl ether (500 ml) for 18 h. Concentration *in vacuo* afforded 2-allyloxytropone (7.36 g) as an orange oil; ν_{max}(film) 1 590 (C=O), 1 280 and 1 230 cm^{-1} (O–C); δ_H 7.0 (5 H, m, ring protons), 6.2 (1 H, m, $CH=CH_2$), 5.5 (2 H, m, $CH=CH_2$), and 4.8 (2 H, d, *J* 5 Hz, OCH_2CH); *m/z* 162 (38, M^+, 9%), 147 (9, $M^+ - CH_3$), 133 (54, $M^+ - CHO$), 105 (100, $C_7H_7O^+$), and 41 (21, $C_3H_5^+$).

Allyltropolone.[14]—2-Allyloxytropone (7.36 g, 45.4 mmol) was heated under reflux in nonane (50 ml) for 4 h. Concentration *in vacuo* (bath temperature *ca.* 70–80 °C led to the formation of tarry products, so the product was isolated by cooling to −40 °C for 18 h. The resulting dark crystalline solid was collected and dried. A second crop was isolated by cooling the mother liquor for a further 18 h at −40 °C. Recrystallisation from pentane at −40 °C, afforded allyltropolone as off-white flakes (5.64 g, 85%), m.p. 41–43 °C (lit.[14] 44–45 °C); ν_{max} 1 600 cm^{-1} (C=O); δ_H 7.7–6.8 (4 H, m, ring protons), 6.1 (1 H, m, $CH_2CH=CH_2$), 5.5–5.1 (2 H, m, $CH_2CH=CH_2$), and 3.6 (2 H, br d, *J* 7 Hz, $CH_2CH=CH_2$); *m/z* 162 (M^+, 52%), 147 (100, $M^+ - CH_3$), 144 (22, $M^+ - H_2O$), 115 (42), 105 (11, $C_7H_5O^+$), 91 (17, $C_7H_7^+$), 77 (17, $C_6H_5^+$), and 51 (10).

3-Propyltropolone (**14**).[14]—Allyltropolone (859.3 mg, 5.30 mmol, 1 equiv.) in ethanol (*ca.* 30 ml) was hydrogenated in the presence of a small quantity of 10% palladium on charcoal at 1 atm at room temperature. When 127 cm^3 (5.30 mmol, 1 equiv.) of hydrogen had been consumed, the solution was filtered through Celite and concentrated *in vacuo* to yield 3-propyltropolone (**14**) (831.4 mg, 96%) as an orange oil; δ_H 9.5 (1 H, br s, OH, exchanges with D_2O), 7.7–6.8 (4 H, m, ring protons), 2.85 (2 H, t, *J* 7 Hz, CH_2CH_2), 1.7 (2 H, sextet, *J* 7 Hz, $CH_2CH_2CH_3$), and 1.0 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 164 (M^+, 68%), 149 (100, $M^+ - CH_3$), 136 (32, $M^+ - C_2H_4$), 122 (14, $M^+ - C_3H_6$), 105 (1, $C_7H_5O^+$), 91 (6, $C_7H_7^+$), 77 (16, $C_6H_5^+$), and 51 (5).

2-Methoxy-7-propyltropone (**15**) *and 2-Methoxy-3-propyltropone* (**16**).—To a solution of 3-propyltropolone (825 mg, 5.03 mmol, 1 equiv.) in diethyl ether (*ca.* 25 ml) and methanol (2 ml) at 0 °C, was added an ether solution of diazomethane (53 ml, 12.6 mmol, 2.5 equiv.) over a period of 1 h. After 18 h at room temperature the mixture was concentrated *in vacuo*. Column chromatography (100% diethyl ether) afforded *2-methoxy-7-propyltropone* (**15**) (242.5 mg, 24%) and *2-methoxy-3-propyltropone* (**16**) (550.1 mg, 57%) as pale yellow oils. For compound (**15**) (Found: M^+, 178.0998. $C_{11}H_{14}O_2$ requires 178.0994); ν_{max}(film) 1 580 cm^{-1} (C=O); δ_H 7.1 (4 H, m, ring protons), 3.9 (3 H, s, OCH_3), 2.7 (2 H, t, *J* 7 Hz, CH_2CH_2), 1.6 (2 H, br sextet, *J* 7 Hz, $CH_2CH_2CH_3$), and 1.0 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 178 (M^+, 95%), 163 (97, $M^+ - CH_3$), 147 (22, $M^+ - CH_3O$), 133 (26, 163 − CH_2O), 121 (53, 163 − C_3H_6), 91 (100, $C_7H_7^+$), and 77 (25, $C_6H_5^+$). For compound (**16**) (Found: M^+, 178.0991. $C_{11}H_{14}O_2$ requires 178.0994); ν_{max}(film) 1 580 cm^{-1}, (C=O); δ_H 7.4 (1 H, br d, $CH=CHC=O$), 6.9 (3 H, m, ring protons), 3.9 (3 H, s, OCH_3), 2.8 (2 H, t, *J* 7 Hz, CH_2CH_2), 1.6 (2 H, br sextet, *J* 7 Hz, $CH_2CH_2CH_3$), and 0.9 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 178 (M^+, 63%), 163 (100, $M^+ - CH_3$), 145 (18), 131 (11), 121 (17, 163 − C_3H_6), 105 (13, $C_7H_5O^+$), 91 (54, $C_7H_7^+$), and 77 (18, $C_6H_5^+$).

Diethyl 1-Methoxy-2-oxo-3-propyl-6,7-diazabicyclo[3.2.2]*nona-3,8-diene-6,7-dicarboxylate* (**17**).—2-Methoxy-7-propyltropone (246.5 mg, 1.138 mmol, 1 equiv.), diethyl azodicarboxylate (241 mg, 1.138 mmol, 1 equiv.) and $[^2H]_6$benzene (0.2 ml) were degassed, sealed *in vacuo* and heated for 4 h at 145 °C. The reaction was monitored by ^1H NMR spectroscopy. Column chromatography on flash silica (light petroleum–diethyl ether) (3:1) gave a pale yellow oil (360 mg, 75%) identified as *the adduct* (**17**) (Found: M^+, 352.1636. $C_{17}H_{24}N_2O_6$ requires 352.1634); ν_{max}(film) 1 730–1 710 (C=O enone and carbamate) and 750 cm^{-1} (C=C); $\delta_H([^2H]_6$benzene) 6.9 (1 H, br d, *J* 7 Hz), 6.8 (1 H, dd, *J* 11 and 7 Hz), 5.8 (1 H, d, *J* 11 Hz), 5.3 (1 H, br t, *J* 7 Hz, bridgehead), 4.2 (4 H, two q, *J* 7 Hz, carbamate CH_2CH_3), 3.5 (3 H, s, OCH_3), 2.5–1.5 (4 H, m, $CH_2CH_2CH_3$), 1.3 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_3), and 0.9 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 352 (M^+, 14%), 279 (57, $M^+ - C_2H_5$, $-CO_2$), 251 (94, 279 − C_2H_4), 207 (100), 179 (81), 91 (30, $C_7H_7^+$), and 77 (14, $C_6H_5^+$).

Diethyl 1-Methoxy-2-oxo-3-propyl-6,7-diazabicyclo[3.2.2]*non-3-ene-6,7-dicarboxylate* (**18**).—Diethyl 1-methoxy-2-oxo-3-propyl-6,7-diazabicyclo[3.2.2]nona-3,8-diene-6,7-dicarboxylate (**17**) (144.5 mg, 0.41 mmol, 1 equiv.) in ethanol (5 ml) was hydrogenated under 1 atm at RT in the presence of a small

quantity of palladium on barium sulphate. Once 1 mol equiv. of hydrogen had been consumed, the solution was filtered through Celite and the *product* was isolated by concentration of the solution *in vacuo*, to yield a pale yellow oil (101.5 mg, 70%) (Found: M^+, 354.1793. $C_{17}H_{26}N_2O_6$ requires 354.1791); ν_{max}(film) 1 730–1 710 (C=O), 1 460, 1 370 (CCH_3), and 700 cm^{-1} (CH=C); δ_H 6.7 (1 H, br dd, *J* 7 and <1 Hz), 4.9 (1 H, m, bridgehead), 4.3 (4 H, two q, *J* 7 Hz, carbamate CH_2CH_3), 3.4 (3 H, s, OCH_3), 2.8–1.3 (8 H, m, bicyclic and propyl CH_2), 1.3 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_3), and 0.9 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 354 (M^+, 4%), 225 (43), 209 (26, $M^+ - C_2H_5$, $-C_2H_4$, $-2 \times CO_2$), 181 (18), 153 (100), and 91 (4, $C_7H_7^+$).

Diethyl 2,2,4-*Triethoxy*-6,7-*diazabicyclo*[3.2.2]*non*-8-*ene*-6,7-*dicarboxylate* (**20**).—To a solution of the tropone–diethyl azodicarboxylate adduct (**11**) (1.75 g, 6.25 mmol, 1 equiv.) in dry ethanol (150 ml), was added triethyl orthoformate (2.6 ml, 16.2 mmol, 2.5 equiv.) and a small quantity of toluene-*p*-sulphonic acid. This mixture was heated under reflux for 18 h. After cooling, the mixture was concentrated *in vacuo*, redissolved in diethyl ether (*ca.* 70 ml), treated successively with 5% Na_2CO_3 (3 × 50 ml) and water (1 × 50 ml), and then dried ($MgSO_4$). Concentration *in vacuo* gave a brown oil, identified as *the triethoxy compound* (**20**) (2.205 g, 91%) (Found: C, 56.8; H, 7.9; N, 7.0%; M^+, 400.2215. $C_{19}H_{32}N_2O_7$ requires C, 57.0, H, 8.0, N, 7.0%; M^+, 400.2209); ν_{max}(film) 1 750, 1 700 (C=O), 1 420, 1 380 (CCH_3), and 1 095 cm^{-1} (OC); δ_H 6.7 (1 H, br ddd, *J* 8,6 and 1 Hz, olefinic), 6.2 (1 H, ddd, *J* 8, 6 and <1 Hz, olefinic), 4.9 (2 H, m, bridgeheads), 4.2 (4 H, two q, *J* 7 Hz, carbamate CH_2CH_3), 3.7 [4 H, two q, *J* 7 Hz, $C(OCH_2CH_3)_2$], 3.6 [2 H, q, *J* 7 Hz, $CH(OCH_2CH_3)$], 3.6 [1 H, m, CH(OEt)], 2.3 [1 H, dd, *J* 14 and 6 Hz, $CH(OEt)CHHC(OEt)_2$], 1.6 [1 H, dd, *J* 14 and 10 Hz, $CH(OEt)CHHC(OEt)_2$], and 1.2 (15 H, m, carbamate and ethoxy CH_2CH_3); *m/z* 400 (M^+, 12%), 355 (11, $M^+ - C_2H_5O$), 325 (13, $M^+ - C_2H_5O$, $-C_2H_5$), 181 (23), 145 (100, $C_7H_{13}O_3^+$), 109 (17, $C_7H_9O^+$), 107 (16, $C_7H_7O^+$), and 81 (79, $C_5H_5O^+$).

Diethyl 2,2,4-*Triethoxy*-6,7-*diazabicyclo*[3.2.2]*nonane*-6,7-*dicarboxylate* (**21**).—The triethoxy adduct (**20**) (2.205 g, 5.51 mmol,) in ethanol (*ca.* 50 ml) was hydrogenated at room temperature at 20–30 atm in the presence of a small amount of 10% palladium on charcoal. When hydrogen uptake had ceased (after 3–4 h), the solution was filtered through Celite. Concentration *in vacuo* gave the *title compound* as a viscous yellow oil (2.18 g, 100%) (Found: C, 56.9; H, 8.5; N, 7.0%; M^+, 402.2366. $C_{19}H_{34}N_2O_7$ requires C, 57.0; H, 8.5; N, 7.0%; M^+, 402.2365); ν_{max}(film) 1 740, 1 700 (C=O), 1 415, 1 380 (C–CH_3), 1 100, and 1 075 cm^{-1} (OC); δ_H 4.6 (1 H, m, bridgehead), 4.3 (5 H, m, bridgehead and carbamate CH_2CH_3), 3.7 (6 H, three q, ethoxy CH_2CH_3), 3.6 [1 H, m, $CHCH(OEt)CH_2$], 2.6–1.5 [6 H, m, bicyclic CH_2 and $CH(OEt)CH_2C(OEt)_2$], and 1.2 (15 H, m, carbamate and ethoxy CH_2CH_3); *m/z* 402 (M^+, 4%), 357 (9.6, $M^+ - C_2H_5O$), 173 (59, $C_6H_9N_2O_4^+$), 145 (100, $C_7H_{13}O_3^+$), 117 (27), and 83 (14, $C_5H_7O^+$).

Diethyl 2-*Oxo*-6,7-*diazabicyclo*[3.2.2]*non*-3-*ene*-6,7-*dicarboxylate* (**13**).—A solution of the triethoxy compound (**21**) (15.4 g, 38.2 mmol, 1 equiv.), in 1,4-dioxane (40 ml), water (160 ml), and toluene-*p*-sulphonic acid (7.2 g, 38.2 mmol, 1 equiv.), was heated at 60–70 °C for 48 h. The solution was poured into water, extracted with diethyl ether (2 × 230, 1 × 150 ml) and the extract dried ($MgSO_4$). Concentration of the mixture *in vacuo*, followed by column chromatography (diethyl ether–light petroleum (1:1) gave the *enone* (**13**) as a white crystalline solid (7.48 g, 69%), m.p. 62–64 °C (Found: C, 55.2; H, 6.4; N, 10.0%; M^+, 282.1219. $C_{13}H_{18}N_2O_5$ requires C, 55.3, H, 6.4; N, 9.9%; M^+, 282.1216); ν_{max}(film) 1 750–1 680 cm^{-1} (C=O carbamate and enone); δ_H 7.3 (1 H, br dd, *J* 11, 8, and <1 Hz, $CHCH$=CHC=O), 6.4 (1 H, dd, *J* 11 and 1 Hz, CH=CHC=O), 5.3 (1 H, br t, *J* 8 and <1 Hz, bridgehead), 4.7 (1 H, m, bridgehead), 4.2 (4 H, two q, *J* 7 Hz, carbamate CH_2CH_3), 2.8–1.5 (4 H, m, bicyclic CH_2), and 1.3 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_3); *m/z* 282 (M^+, 16%), 210 (52, $M^+ - C_2H_4$, $-CO_2$), 137 (45, $M^+ - C_2H_5$, $-C_2H_4$, $-2 \times CO_2$), 109 (100, $C_7H_9O^+$), 81 (73, $C_5H_5O^+$), and 53 (34).

Also isolated was a small quantity of by-product (*ca.* 5–10%), which was identified as *diethyl* 4-*ethoxy*-2-*oxo*-6,7-*diazabicyclo*[3.2.2]*nonane*-6,7-*dicarboxylate* (Found: M^+, 328.1630. $C_{15}H_{24}O_6$ requires 328.1634); ν_{max}(film) 1 720 (C=O ketone and carbamate), 1 460, 1 380 (CCH_3), and 1 260 cm^{-1} (OC); δ_H 4.8 (1 H, m, bridgehead), 4.2 [6 H, m, $CHCH$(OEt), bridgehead and carbamate $-CH_2CH_3$], 3.6 (2 H, q, *J* 7 Hz, ethoxy CH_2CH_3), 2.9 [1 H, dd, *J* 18 and 9 Hz, $-CH(OEt)CHHCO$], 2.6 [1 H, dd, *J* 18 and 4 Hz, $CH(OEt)CHHCO$], 2.5–1.5 (4 H, m, bicyclic CH_2), and 1.2 (9 H, three t, *J* 7 Hz, ethoxy and carbamate CH_2CH_3); *m/z* 328 (M^+, 4%), 228 (10, $M^+ - 2 \times C_2H_4$, $-CO_2$), 183 (10, $M^+ - C_2H_5$, $-C_2H_4$, $-2 \times CO_2$), 155 (52), 137 (23), 111 (36, $C_7H_{11}O^+$), 109 (30, $C_7H_9O^+$), and 83 (100, $C_5H_7O^+$).

2,2,4-*Triethoxy*-6,7-*diazabicyclo*[3.2.2]*non*-6-*ene* (**22**).—The triethoxy compound (**21**) (1.2 g, 2.98 mmol) was dissolved in methanolic KOH (15 ml), and heated under reflux for 18 h. Solid $NaHCO_3$ (*ca.* 1 g) was added, and the mixture stirred for 1 h; the solid was then filtered off. The filtrate was stirred in the presence of yellow mercuric oxide (*ca.* 6 g) for 18 h, filtered through Celite, and the filtrate concentrated *in vacuo* at 0 °C. The residue was dissolved in water, and extracted with dichloromethane (2 × 20, 1 × 15 ml). The combined dichloromethane extracts were dried ($MgSO_4$) and concentrated *in vacuo* at 0 °C. Column chromatography of the residue on flash silica (diethyl ether–light petroleum) (1:1), gave a white crystalline solid, identified as the *title compound*, (**22**) (596 mg, 78%), m.p. 50–53 °C (Found: C, 61.0; H, 9.6; N, 10.9%; M^+, 256.1787. $C_{13}H_{24}N_2O_3$ requires C, 60.9; H, 9.4; N, 10.9; M^+, 256.1787); ν_{max}($CHCl_3$) 1 560 (N=N), 1 470, 1 440 (C–CH_3), 1 070 (CO), and 1 030 cm^{-1} (CO); δ (400 MHz) 5.22 (2 H, m, bridgeheads), 3.7–3.5 (6 H, m, ethoxy CH_2CH_3), 3.25 [1 H, ddd, *J* 11.5, 5, and <1 Hz, CH(OEt)–CH_2], 2.3 [1 H, dddd, *J* 13, 5, 1.5, and 1.5 Hz, $CH(OEt)CHHC(OEt)_2$], 1.9, 1.6 (4 H, m, bicyclic CH_2), 1.75 [1 H, dd, *J* 13 and 11.5 Hz, $CH(OEt)CHHC(OEt)_2$], and 1.1–1.3 (9 H, m, ethoxy CH_2-CH_3). The full assignment of this spectrum was achieved with the help of COSY and NOE experiments as described in the text; *m/z* 256 (M^+, 5%), 228 (2, $M^+ - N_2$), 211 (30, $M^+ - C_2H_5O$), 173 (28), 145 (32), 109 (37, $C_7H_9O^+$), and 55 (100, $C_4H_7^+$).

Diethyl 2-*Methylene*-6,7-*diazabicyclo*[3.2.2]*non*-3-*ene*-6,7-*dicarboxylate* (**25**), via *Wittig Methylenation*.[24]—The ylide was generating by the addition of 1.55M butyl-lithium (1.4 ml, 2.13 mmol, 3 equiv.) to dry triphenylphosphonium bromide (840 mg, 2.34 mmol, 3.3 equiv.), in diethyl ether (20 ml). To the ylide solution, was added a solution of the enone (**13**) (194 mg, 0.688 mmol, 1 equiv.) in diethyl ether (4.0 ml), at room temperature. The solution was stirred at room temperature for 5 h, and then treated with water (3 × 30 ml), dried ($MgSO_4$), and concentrated *in vacuo*. Column chromatography of the residue (diethyl ether–light petroleum) (1:1), afforded a pale yellow oil, identified as the *diene* (**25**) (44.3 mg, 23%) (Found: M^+, 280.1423. $C_{14}H_{20}N_2O_4$ requires 280.1423); ν_{max}(film) 1 720 (C=O), 1 600 (C=C), 890 (=CH_2), and 660 cm^{-1} (*cis* HC=CH); δ_H 6.5–6.0 (2 H, m, bicyclic olefinics), 5.3–4.8 (3 H, =CH_2 and 1 bridgehead), 4.1 (1 H, m, bridgehead), 4.2 (4 H, two q, *J* 7 Hz,

carbamate CH_2CH_3), 2.5–1.5 (4 H, m, bicyclic CH_2), and 1.3 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_2); *m/z* 280 (M^+, 50%), 208 (28, $M^+ - C_2H_4$, $-CO_2$), 207 (32, $M^+ - C_2H_5$, $-CO_2$), 135 (100, $C_8H_{11}N_2^+$), 105 (72, $C_8H_9^+$), 91 (72, $C_7H_7^+$), and 77 (22, $C_6H_5^+$).

Diethyl 2-Hydroxy-2-methyl-6,7-diazabicyclo[3.2.2]*non-3-ene-6,7-dicarboxylate* (**26**).—To a solution of the enone (**13**) (403 mg, 1.44 mmol, 1 equiv.) in diethyl ether, at −15 °C, was added 1.55M MeLi (1.16 ml, 1.8 mmol, 1.25 equiv.) over 2 min. The solution was stirred for 5 min at −15 °C and then diluted with water (10 ml), and allowed to warm to room temperature. The layers were separated, and the aqueous phase was extracted with diethyl ether (2 × 10 ml). The combined diethyl ether extracts were dried ($MgSO_4$), and concentrated *in vacuo*. Column chromatography of the residue (100% diethyl ether), gave a colourless oil, identified as the *tertiary allylic alcohol* (**26**) (254.4 mg, 59%) (Found: C, 56.4; H, 7.6; N, 9.7%; M^+, 298.1520. $C_{14}H_{22}N_2O_5$ requires C, 56.4; H, 7.4; N, 9.4%; M^+, 298.1529); ν_{max}(film) 3 500–3 400 (OH), 1 730–1 700 (C=O), 1 470, 1 380 (CCH_3), and 760 cm^{-1} (*Z* HC=CH); δ_H 6.0 (1 H, dd, *J* 10.5 and 6.5 Hz, CHC*H*=CH), 5.5 (1 H, br d, *J* 10.5 Hz, CH=C*H*C), 4.4 (2 H, m, bridgeheads), 4.2 (4 H, two q, *J* 7 Hz, carbamate CH_2CH_3), 1.9 (4 H, m, bicyclic CH_2), 1.6 (1 H, br s, OH, exchanges with D_2O), 1.2 (6 H, two t, *J* 7 Hz, carbamate CH_2CH_3), and 1.2 (3 H, s, CH_3); *m/z* 298 (M^+, 11.9%), 165 (14.2), 153 (12.8), 109 (22.9, $C_7H_9O^+$), 83 (21.7, $C_5H_7O^+$), 81 (23.7, $C_5H_5O^+$), and 29 (100, $C_2H_5^+$).

Also isolated was a small quantity of a by-product (*ca.* 8%) identified as *diethyl 4-methyl-2-oxo-6,7-diazabicyclo*[3.2.2]*nonane-6,7-dicarboxylate* (**27**) (Found: M^+, 298.1523. $C_{14}H_{22}N_2O_5$ requires 298.1529); δ_H 4.7–4.1 (6 H, m, bridgeheads and carbamate CH_2CH_3), 2.8–1.7 [7 H, m, bicyclic CH_2 and −C*H*(Me)], and 1.2 [9 H, m, CH(CH_3), and carbamate CH_2CH_3]; *m/z* 298 (M^+, 64%), 198 (84, $M^+ - 2 \times C_2H_4$, $-CO_2$), 197 (52), 153 (98, $M^+ - C_2H_5$, $-C_2H_4$, $-2 \times CO_2$), 125 (70), and 83 (100, $C_5H_7O^+$).

Diethyl 2-Methylene-6,7-diazabicyclo[3.2.2]*non-3-ene-6,7-dicarboxylate* (**25**) via *the Dehydration of* (**26**) *with Toluene-p-sulphonic Acid and* 4 Å *Molecular Sieves*.—To a solution of the tertiary allylic alcohol (**26**) (254.4 mg, 0.854 mmol, 1 equiv.) in sodium-dried benzene (30 ml), was added anhydrous toluene-*p*-sulphonic acid (147 mg, 0.854 mmol, 1 equiv.) and 4 Å type molecular sieves (*ca.* 0.5–1.0 g). The solution was heated for 3–4 h at 80–90 °C, and then filtered through Celite and poured into water (*ca.* 50 ml). The layers were separated, and the aqueous phase was extracted further with benzene (2 × 30 ml). The combined organic extracts were washed with dilute $NaHCO_3$ (*ca.* 70 ml), dried ($MgSO_4$), and then concentrated. Column chromatography of the residue on flash silica (diethyl ether–light petroleum) (1:1) afforded the *diene* (**25**) (198 mg, 83%) as a pale yellow oil. This had identical spectroscopic properties to the compound obtained from the Wittig methylenation of (**13**).

2-Methylene-6,7-diazabicyclo[3.2.2]*nona-3,6-diene* (**9**).—The diene (**25**) (650 mg, 2.32 mmol) in methanolic KOH, was heated under reflux for 8 h. The mixture was cooled, solid $NaHCO_3$ (*ca.* 1 g) was added to it and it was then stirred for 1 h at room temperature. The solid was filtered off and the filtrate was stirred in the presence of yellow mercuric oxide (*ca.* 4–5 g) at room temperature for 3–4 h. The solution was then filtered through Celite and concentrated at 0 °C *in vacuo*. The residue was dissolved in water (10 ml) and extracted with dichloromethane (2 × 7, 1 × 5 ml), and the extract dried ($MgSO_4$) and concentrated at 0 °C *in vacuo*. Flash chromatography of the residue (diethyl ether–light petroleum) (1:1) afforded a mobile brown liquid, identified as *the diene* (**9**) (262.1 mg, 84%) (Found: M^+, 134.0840. $C_8H_{10}N_2$ requires 134.084); λ_{max}(EtOH) 400 and 254 nm (log ε 2.60 and 3.82); ν_{max}(film) 1 690 (C=C), 1 590 (N=N), 1 440 (=CH_2), and 890 cm^{-1} (=CH_2); δ_H 6.05 (1 H, ddd, *J* 10.5, 1.5, and <1 Hz, CH=C*H*C=CH_2), 5.8 (1 H, dddd, *J* 10.5, 9.0, 1.5, and <1 Hz, CHC*H*=CHC=), 5.58 (1 H, m, bridgehead), 5.4 (1 H, ddd, 9.0, 5.5, and <1 Hz, bridgehead), 5.17 (1 H, br s, C=C*H*H), 4.92 (1 H, br s, −C=CH*H*), and 2.0–1.67 (4 H, m, bicyclic methylenes); *m/z* 134 (M^+, 0%), 106 (18, $M^+ - N_2$), 105 (27, $C_7H_5O^+$), 91 (100, $C_7H_7^+$), and 77 (18, C_6H_5).

Thermolysis of 2-Methylene-6,7-diazabicyclo[3.2.2]*nona-3,6-diene* (**9**)*: Initial Investigation of the Products by Analytical GLC*.—The instrument used for this experiment, was a Pye–Unicam GCD analytical gas chromatograph with a flame ionisation detector (FID). It was fitted with a 2.1 m × 4 mm column, containing 10% Apiezon L, supported on 80/100 Chromasorb. Conditions established for the separation of cyclo-octa-1,3-diene (C_8) and hexadecane (C_{16}) were: column temperature, 240 °C; injection and detector temperatures, 290 °C; carrier gas, N_2. The retention times for the two components were: C_8, 2 min; C_{16}, 14.5 min. A sample of (**9**) (*ca.* 10 mg) was degassed, sealed down, then pyrolysed at 120 °C for 20 min. GLC analysis of the products under the conditions described above, showed significant quantities of two 'C_8' components (t_R 2.2 and 2.4 min) and a small amount (<0.1%) of 'C_{16}' products, (t_R 15 min).

Thermolysis of 2-Methylene-6,7-diazabicyclo[3.2.2]*nona-3,6-diene* (**9**)*: Isolation and Analysis of the Products by NMR*.—Attempted isolation of the monomeric products from the thermolysis was performed on a Pye 104 preparative gas chromatograph (with an FID) fitted with a 2 m × 6 mm column, containing 15% Apiezon L supported on 80/200 'Chromasorb AW'. The temperature of the column was set at 150 °C, with the injection port and detector at *ca.* 200–300 °C. The pressure of the carrier gas (N_2) was set at 7 psi. A sample of (**9**) (35 mg) was thermolysed in the usual manner. The total product from the thermolysis was dissolved in dichloromethane (75 μl), and injected onto the preparative column. Two products were isolated, with t_R values of 4.7 (fraction 1) and 6.5 min (fraction 2), respectively; both were analysed by 400 MHz ^1H NMR. Decoupling experiments were used extensively to assist in the interpretation of the ^1H NMR spectra. Fraction 1 contained two components in approximately equal quantities, identified as 7-methylenebicyclo[4.1.0]hept-2-ene (**28**), and 2-methylenebicyclo[3.2.0]hept-3-ene (**29**).[20] 7-Methylenebicyclo-[4.1.0]hept-2-ene (**28**);[20] δ(400 MHz) 6.13 (1 H, dd, *J* 10 and 1 Hz, CH=C*H*CH), 5.61 (1 H, ddd, *J* 10, 7, and 2.5 Hz, CHC*H*=CH), 5.35 (1 H, m, *J* <1 Hz, methylene C=C*H*H), 5.33 (1 H, t, *J* <1 Hz, methylene C=CH*H*), 2.05–1.90 (4 H, m, ring CH_2CH_2), 1.65 (1 H, m, bridgehead), and 1.25 (1 H, ddt, *J* 13, 5, and 3 Hz, bridgehead). 2-Methylenebicyclo[3.2.0]hept-3-ene (**29**);[20] δ(400 MHz) 6.3 (1 H, br d, *J* 5 and <1 Hz, CH=C*H*C=CH_2), 6.2 (1 H, m, CHC*H*=CH), 4.82 (1 H, br s, methylene =CC=C*H*H), 4.68 (1 H, m, *J* <1 Hz, methylene =C–C=CH*H*), 3.37 (1 H, m, bridgehead), 3.25 (1 H, m, bridgehead), and 2.4–1.75 (4 H, m, ring $CHCH_2CH_2CH$). Fraction 2 consisted of a single component, identified as 2,3-dihydrostyrene (**31**)[20] δ(400 MHz) 6.43 (1 H, dd, *J* 17.5 and 11 Hz, C*H*=CH), 5.23 (1 H, d, *J* 17.5, *E* CH=C*H*H), 5.05 (1 H, d, *J* 11 Hz, *Z* CH=CH*H*), 5.98 (1 H, dddd, *J* 9.5, 5.5, 1.5, and 1.5 Hz, ring CH_2CH=C*H*CH=C), 5.88 (2 H, m, ring CH_2CH=CHC*H*=C), and 2.3 (4 H, m, ring methylene CH_2CH_2; upon irradiation at δ 5.88, this multiplet collapses to an AA'BB' pattern).

Product Ratio Studies.—All GLC analyses for these

experiments were performed on a Perkin-Elmer F.11.A analytical chromatograph (with FID), fitted with a 30 m capillary column, OV 101, set at 60 °C,[20] with an injection port temperature of 150 °C.

Preliminary experiments; establishment of retention times of the thermolysis products on the F.11.A chromatograph. A sample of the diazene (**9**) (41.7 mg) was thermolysed in the usual manner. The C_8 components were isolated by preparative GLC, on the Pye 104 preparative gas chromatograph in the usual manner, after which the product was analysed by both ^{1}H NMR and analytical GLC (Perkin-Elmer F.11.A). ^{1}H NMR showed that 7-methylenebicyclo[4.1.0]hept-2-ene (**28**) was the major product. GLC analysis showed 4 products; the major component by GLC had a retention time of 16.0 min, and this was assigned as (**28**) on the basis of the NMR analysis (lit.,[20] t_R 24.2 min, 80 m capillary column). From data available in the literature,[20] the remaining components observed by GLC were assigned as: (**30**) (t_R 9.9 min; lit.,[20] 16.9 min, 80 m column); 2-methylenebicyclo[3.2.0]hept-3-ene (**29**) (t_R 13.2 min; lit.,[20] 21.0 min, 80 m column), and 2,3-dihydrostyrene (**31**) (t_R 18.5 min; lit.,[20] 27.8 min, 80 m column).

Establishment of product ratios at t = 0. All samples used in this study were degassed and sealed down in Pyrex tubes *in vacuo* prior to thermolysis and photolysis. Samples of the diazene (**8**) (*ca.* 5 mg) were thermolysed 'neat' at 120 °C and photolysed (Hanovia 1 medium pressure mercury UV lamp) in [^{2}H]$_6$benzene, both with (sensitised *hν*) and without (direct *hν*) benzophenone sensitiser, for measured periods of time. The thermolysis products were analysed by analytical GLC (Pye F.11.A), whereas the photolysis samples were examined by ^{1}H NMR and then analysed by analytical GLC. The product ratios were established for each time period by cutting and weighing triplicate GLC traces. Product ratios for $t = 0$ were calculated by extrapolation.

Intermolecular Trapping Reactions.—All trapping reactions were carried out by thermolysis of a neat mixture of the diazene (**9**) (1 equiv.) and trap (*ca.* 10–20 equiv.) in a degassed sealed tube at 120 °C for 20 min to 1 h. Also, thermolysis reactions were performed on separate samples of the diazene (**9**) and trap under the same conditions. Analysis (by TLC or GLC) immediately provided an indication as to whether new 'cross' products were present.

Reaction of diazene (**9**) *with dimethyl fumarate.* All GLC experiments were performed on a Pye 104 gas chromatograph (with a FID) using columns packed with 10% OV101 on 'WHP Chromasorb 80/100,' at *ca.* 200 °C. For analysis, a 2 m × 2 mm column was used, and a 1.5 m × 6 mm column was used for preparative purposes. For all HPLC experiments, a Varian 5000 LC instrument with a Varian Vari-Chrom UV detector set at 230 nm was used. The instrument was fitted with an analytical Zorbax CN column, and this was used throughout.

Isolation of products by GLC. A mixture of the diazene (**9**) (*ca.* 200 mg, 1 equiv.) and dimethyl fumarate (*ca.* 2.4 g, 10 equiv.) were thermolysed in the usual manner. The excess of trap was removed by precipitation from cold diethyl ether (× 3). GLC analysis of the products indicated that perhaps new cross products were present. Five products were isolated by preparative GLC. Three of these (all *ca.* 2–3 mg) were analysed by 400 MHz ^{1}H NMR and all gave complex spectra. However, two of the three fractions analysed (fractions 2 and 3) showed that an azulene type structure (**35**) may have been present. For fraction 2 (Found: M^+, 250.1206. $C_{14}H_{18}O_4$ requires 250.1205); δ(400 MHz) 5.76 (1 H, m, olefinic), 5.65 (2 H, m, olefinics), 3.62 (6 H, two s, CO_2CH_3), and 3.3–1.5 (*ca.* 9 H, m, aliphatic and bridgehead protons); *m/z* 250 (M^+, 12%), 218 (28, $M^+ - CH_3OH$), 190 (38, $M^+ - CH_3CO_2H$), 158 (28, $M^+ - CH_3CO_2H$, $-CH_3OH$), 131 (100, $M^+ - CH_3CO_2H$, $-CH_3CO_2$), 130 (96), 105 (25, $C_7H_5O^+$), and 91 (82, $C_7H_7^+$). For fraction 3 δ(400 MHz) 5.70 (*ca.* 3 H, m, olefinics), 3.70 (*ca.* 6 H, m, CO_2CH_3), 3.0–1.5 (*ca.* 9 H, m, aliphatic and bridgehead protons); *m/z* 250 (M^+, 4), 218 (3, $M^+ - CH_3OH$), 190 (12, $M^+ - CH_3CO_2H$), 158 (3, $M^+ - CH_3CO_2H$, $-CH_3OH$), 131 (18, $M^+ - CH_3CO_2H$, $-CH_3CO_2$), 130 (22), 129 (100), 105 (26, $C_7H_5O^+$), and 91 (27, $C_7H_7^+$).

Isolation of products by HPLC. The diazene (150 mg, 1 equiv.) and dimethyl fumarate (1.6 g, 10 equiv.) were thermolysed in the usual manner. Most of the excess of the trap was removed by precipitation from cold diethyl ether (× 3) and the residue (187 mg) was halved. One half (93.5 mg) was injected through the HPLC column (eluting with 17% chloroform in hexane) in 5 mg, 30 μl^{-1} quantities. Two fractions were isolated: fraction 1, 31 mg, dimethyl fumarate; fraction 2, 4.8 mg, possible cross products (total recovery 35.8 from 93.5 mg, 38%). Analysis of fraction 2 by ^{1}H NMR, showed a highly complex spectrum, which contained olefinic protons (δ 7–4), and methoxy singlets at 3.7 (Found: M^+, 250.1210. $C_{14}H_{18}O_4$ requires 250.1205). The remaining half of the original crude product (93.5 mg) was chromatographed on flash silica (diethyl ether–light petroleum) (1:1). Two fractions were isolated: the major component was identified as dimethyl fumarate (74.7 mg), and the minor (12.9 mg) was believed to be composed of cross products. From this data, it was estimated that the trapping of dimethyl fumarate by the diyl (**10**) occurred in approximately 7% yield. These studies were pursued no further.

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