Use of the Diazoalkane–Thione Reaction in the Synthesis of a Vinyltrimethylenemethane Precursor

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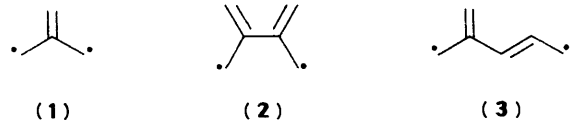
Previous studies have shown that the reaction of diazoalkanes with 3,5-dihydro-3,3,5,5-tetramethylpyrazole-4-thione (**6**) provide a flexible route for the synthesis of precursors to trimethylenemethane (TMM) (**1**) and tetramethylene-ethane (TME) (**2**) biradicals. We now show that this route can be adapted for the synthesis of a precursor to another type of non-Kekulé polyene, a vinyl-TMM biradical (**3**). The thermal isomerisation of 1-(2,4-dimethylpent-1-en-3-ylidene)-2,2,3,3-tetramethylcyclopropane (**27**) to 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (**11**) which involves a vinyl-TMM intermediate (3-isopropyl-4-isopropylidene-2,5-dimethylhex-2-ene-1,5-diyl) was shown by deuterium labelling to involve a 1,6-hydrogen shift. It is suggested that such sigmatropic rearrangements of non-Kekulé polyenes may involve orbital symmetry control. Related examples are discussed. Two reactions discovered incidentally in the course of this work are of some interest, one involving the synthesis of an allylic amine through the thermal rearrangement of an aziridine (2-isopropyl-3,3-aziridine) (**16**) and the other the formation of an oxathiole (**20**) through the reaction of a thione (**6**) and an α-diazo ketone (3-diazo-4-methylpentan-2-one) (**18**).

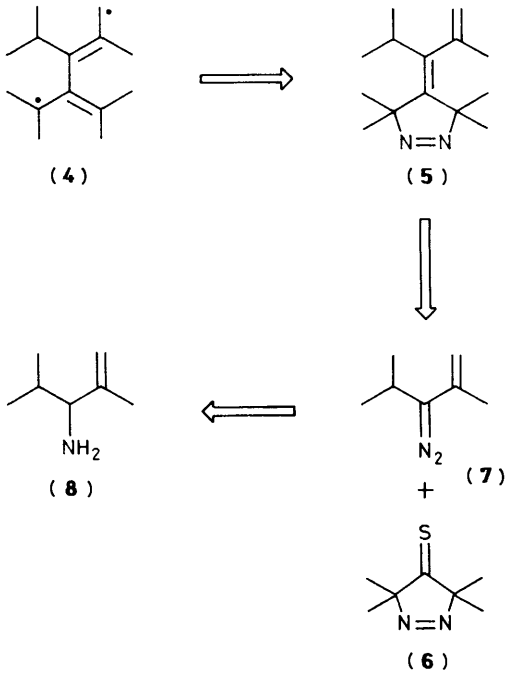
Trimethylenemethane (TMM) (**1**)[1,2] has 4 π electrons and is isomeric with butadiene. Since it is not possible to write a structure for TMM in which all 4 π electrons are paired, it is known as a non-Kekulé polyene[2] and as no 'closed shell' structure can be written, it seems reasonable to suppose that TMM will behave as a biradical. This simple expectation is confirmed both by experiment[1,2] and by molecular orbital calculations.[3] TMM is in fact the simplest member of a whole family of non-Kekulé polyenes. There are two non-Kekulé polyenes which have 6 π electrons and which are isomeric with hexatriene [tetramethylene-ethane TME (**2**), and vinyl-TMM (**3**)] and seven non-Kekulé polyenes which have 8 π electrons



(**1**) (**2**) (**3**)

which are isomeric with octatetraene. In previous papers in this series we have shown that precursors to TMM[4,5] and TME[6] biradicals [for example compound (9)] could be elaborated from the thione (**6**). In the present paper we show that this same thione can be used to make a precursor to the less well known type of 6 π electron non-Kekulé polyene, a vinyl-TMM.[7] The particular vinyl-TMM biradical which we wanted to study was 3-isopropyl-4-isopropylidene-2,5-dimethylhex-2-ene-1,5-diyl (**4**). Our interest in this particular biradical arose since it may well be an intermediate in the thermal isomerisation of the spiropentane (**10**) to the triene (**11**).[6]

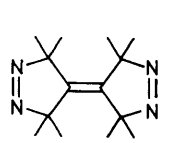
Retrosynthetic analysis (Scheme 1) suggests that the vinyl-TMM (**4**) could be derived from the dihydropyrazole (**5**), which it should be possible to obtain from the addition reaction between the thione (**6**) and the diazoalkane (**7**).[4-6] The initial objective was therefore the preparation of a precursor to the diazoalkane, the allylic amine (**8**). There are not many general routes to allylic amines but the synthesis of compound (**8**) was achieved in two ways. The first made use of a well established route, a 3,3-sigmatropic rearrangement of a trichloroacetimidate. Reaction of 1-ethoxycarbonylethylidene-(triphenyl)phosphorane[8] with 2-methylpropanal gave ethyl



(**4**) (**5**) (**8**) (**7**) + (**6**)

Scheme 1. Retrosynthetic analysis for the vinyl-TMM biradical (**4**)

2,4-dimethylpent-2-enoate which was reduced with lithium aluminium hydride.[9] The alcohol formed was added to trichloroacetonitrile to give the allylic trichloroacetimidate (**12**). This was rearranged by heating in refluxing xylene,[10] and the trichloroacetamide formed hydrolysed in ethanolic sodium hydroxide to give the amine (**8**). An interesting alternative synthesis for this amine was based on a route which, to the best of our knowledge, has only been used once before, but which may be of general utility. Fanta and Deutsch[11] showed that when the aziridine (**13**) was heated with isopropenyl acetate, the allylic amide (**14**) was produced, presumably *via* the *N*-acetylaziridine (**15**). In a similar manner we found that when the aziridine (**16**)[12-14] was heated with isopropenyl acetate, an



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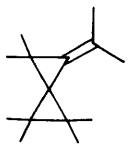

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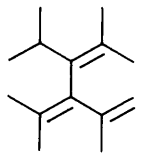

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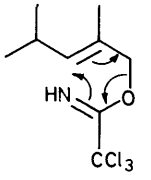

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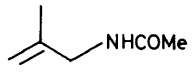

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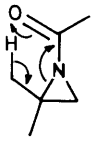

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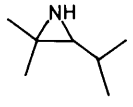

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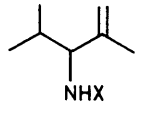

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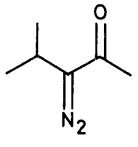
a; X = $SO_2C_6H_4Me$

b; X = $CONH_2$



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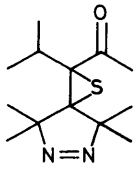

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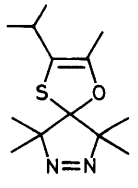
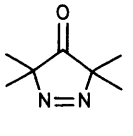


(20)

allylic amide was formed which on hydrolysis gave the amine (**8**). Whilst this amine was readily available by either route, we were not successful in converting it into the diazo compound (**7**). It could be readily converted into the tosylate (**17a**) or the urea (**17b**) but treatment of either of these with a variety of nitrosating agents gave either recovered starting material or compounds in which the double bond had been destroyed. The problem in obtaining the *N*-nitroso derivatives of these compounds is not just the presence of the double bond but also the highly hindered nature of the nitrogen, requiring rather forcing reaction conditions. An obvious synthetic equivalent to the allylic diazo compound (**7**) is the diazo ketone (**18**) which is readily available from the reaction between 2-methyldiazopropane and acetyl chloride.[15] This reacted cleanly with the thione (**6**) to give a crystalline adduct analysing correctly for $C_{13}H_{22}N_2OS$. Previous experience of the reaction of the thione (**6**) with a wide range of diazo compounds led us to assume that this was the episulphide (**19**).[4–6] Closer examination, however, showed that the product was not the episulphide (**19**) but the oxathiole (**20**). Chemically it was found that the adduct was inert towards trialkoxy- and triaryl-phosphines but was hydrolysed with dilute hydrochloric acid to give the pyrazolone (**21**). The i.r. spectrum showed a C=C bond absorption at rather high wavenumbers (1 678 cm^{-1}),[16–20] but the ^{13}C n.m.r. spectrum showed the characteristic resonances of the oxathiole ring (δ_C 138.4, 112.1, 102.3)[17,18] and that there were only two magnetically distinct types of dihydropyrazole methyl. Although this is the first time that we have found a reaction between the thione (**6**) and a diazo compound that does not give a simple episulphide or thiadiazine, the reaction of thiones with diazoketones to give oxathiols is by no means unknown[19] and there has previously been confusion in the literature over the structure of such adducts.[18] In some literature examples it has been shown that the oxathiole and keto episulphide interconvert and prolonged treatment of the equilibrating mixture with a desulphurising agent results in the α,β-unsaturated ketone.[18,20] This could not be achieved in the present case. Another synthetic equivalent to the allylic diazo compound (**7**) is the diazo ester (**22**). This is readily available by a literature method.[21] It adds to the thione (**6**) to give the desired episulphide (**23**) which with trimethyl phosphite gives the alkene (**24**). Treatment of this with an excess of methyl-lithium gave *N*-methylated products[22] but photolysis cleanly gave product (**25**) which, as expected, possesses a non-rearranged carbon skeleton.[5,6] On treatment with an excess of methyl-lithium this gave the alcohol (**26**). This was dehydrated by heating for 10 min at 70 °C with potassium hydrogen sulphate, the product being directly distilled from the mixture under reduced pressure and collected in a solid CO_2 cooled trap. The diene (**27**) obtained in this way was always found to be contaminated with a little of the triene (**11**) and further experimentation showed that this arose from an acid-catalysed rearrangement. Hence the need to minimise the contact between the acid reagent and the product. One of the initial objectives of this work had been to discover whether the diene (**27**) and biradical (**4**) were intermediates in the thermal isomerisation of the spiropentane (**10**) to the triene (**11**) or whether, as suggested by Crandell for a related system,[23] a TME biradical (**28**) was involved. The two possible routes are shown in Scheme 2. In this respect the work was inconclusive. Under flash vacuum pyrolysis conditions[6,24] and when thermolysis was studied in *o*-dichlorobenzene under rigorously acid-free conditions (see Experimental section), both



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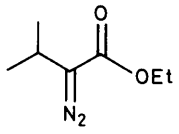

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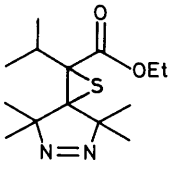

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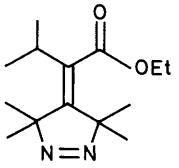

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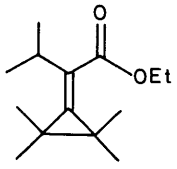

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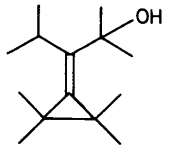

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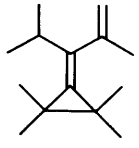

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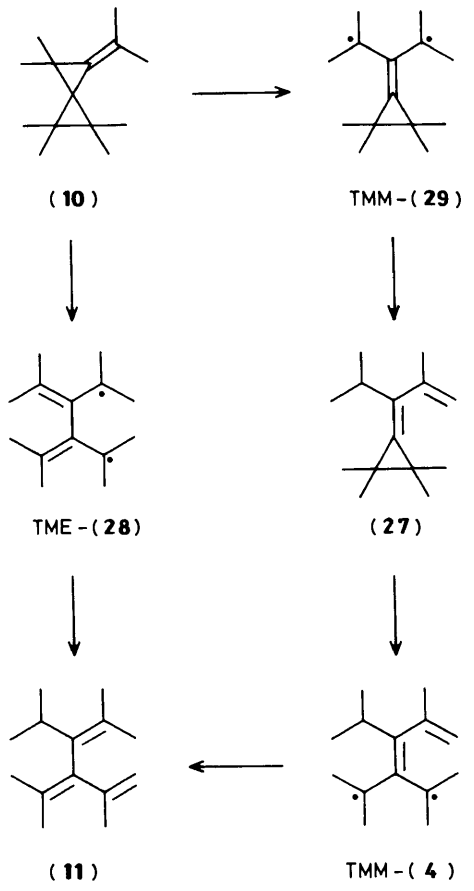
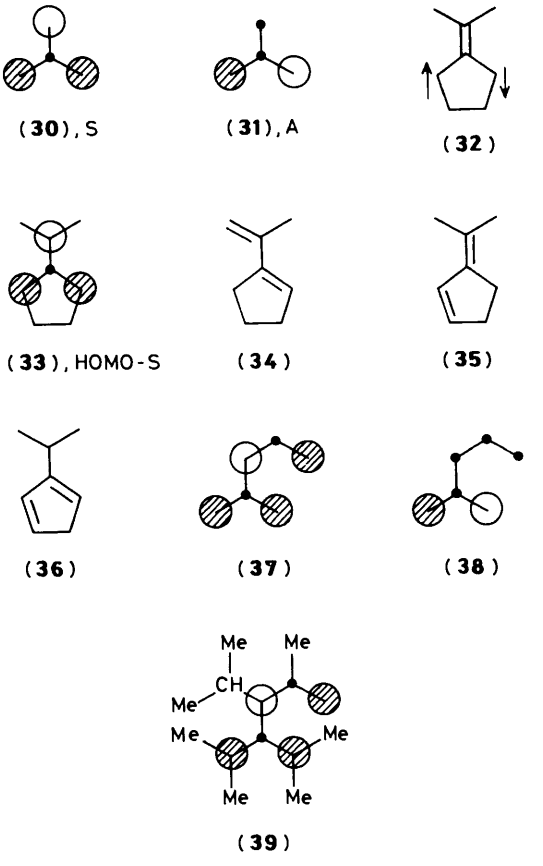


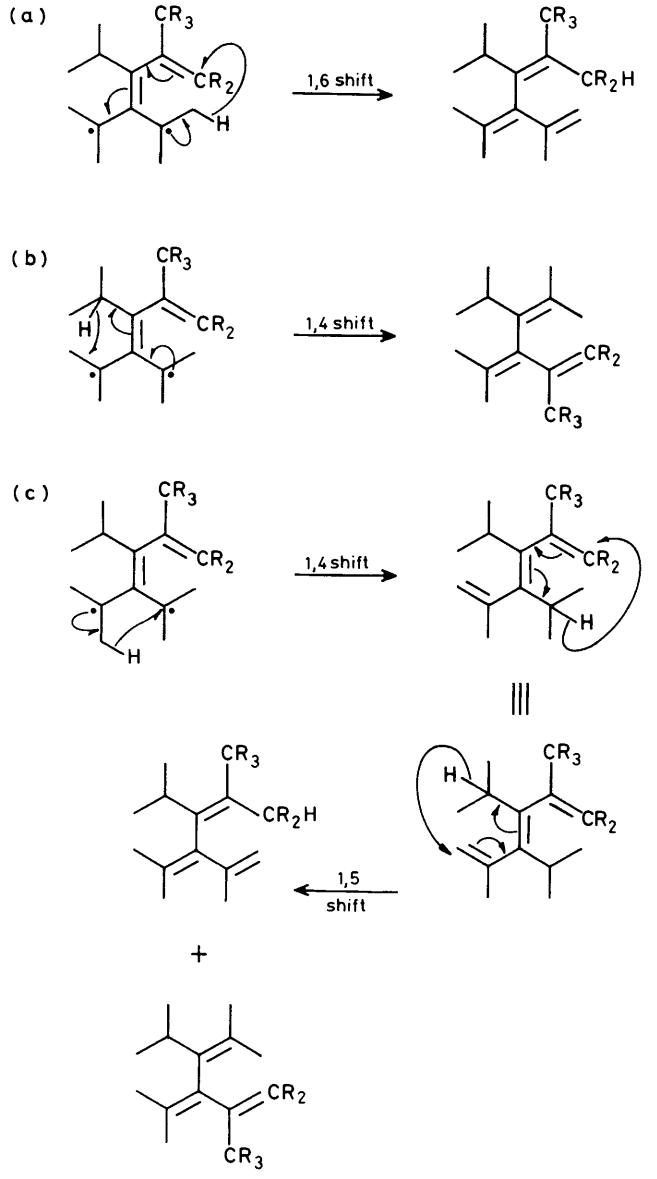
Scheme 2. Two most probable mechanisms for the isomerisation of the spiropentane (10) to the triene (11)

the spiropentane (**10**) and diene (**27**) were converted into the triene (**11**). However, the reaction of the diene was substantially the faster of the two. It is therefore possible that the diene (**27**) is an intermediate in the spiropentane thermolysis but the case for its intermediacy has not been proved. Of more interest in the mechanism of the thermal isomerisation of the diene (**27**) itself. As suggested by analogies to other alkylidenecyclopropane pyrolyses [25] and as shown in Scheme 2, this is best formulated as involving the initial homolysis of the cyclopropyl bond to give a vinyl-TMM biradical but from this point there are three possible routes to the triene. These are shown in Scheme 3. The first two mechanisms involve formal 1,6- and 1,4-hydrogen shifts and lead directly to the triene. The third, indirect, route involves a 1,4-followed by a 1,5-hydrogen shift. The second step here involves the conversion of a linear triene into a cross-conjugated triene, an unlikely process in planar systems but one which cannot be discounted *a priori* in these sterically crowded, probably non-planar, alkenes. As suggested by Scheme 3, these three possible mechanisms were easily distinguished by a simple deuterium-labelling experiment. The required deuterium-labelled triene was simply obtained by using CD_3Li in place of CH_3Li in the last but one stage of the synthesis. This was then thermolysed under flash vacuum pyrolysis conditions and in *o*-dichlorobenzene (base-washed sealed tube). The result in both cases was the same. The undeuteriated triene (**11**) showed five vinyl methyl resonances $\delta_H(CDCl_3)$ 1.52, 1.54, 1.67, 1.72, and 1.77 of which the signal at 1.67 shows allylic coupling and is assigned to $CMe{=}CH_2$. In the product from the deuteriated precursor, the integrals for the signals at 1.52 and 1.72 were reduced to one and zero hydrogens, respectively. In the ^2H n.m.r. spectrum the corresponding signals integrated for two and three deuteriums, respectively. There were no deuterium resonances in the δ 4—6 region. These studies show that, within limits of detection, the only mechanism for this isomerisation is that involving the 1,6-hydrogen shift [mechanism (a) in Scheme 3].

The most common reactions of singlet non-Kekulé polyenes are electrocyclisation reactions and reactions involving addition to alkenes,[1,2] but a signficant number of examples of sigmatropic rearrangements, reactions where the shift of a hydrogen converts the unstable non-Keukulé structure into a stable classical structure, are now known.[2,5,7] It is interesting to speculate that like the cycloaddition reactions[2,26] the sigmatropic rearrangements of these biradicals proceed under orbital symmetry control.[27] The HMO calculations for a non-Kekulé polyene always result in a pair of degenerate NBMOs, S (**30**) and A (**31**) in the case of TMM. In an unsymmetrically substituted derivative of TMM such as biradical (**32**)[28] the degeneracy of these orbitals is lifted. In the case of the TMM derivative (**32**),[28] the lower energy oribital 'HOMO' is the symmetrical orbital shown in structure (**33**).[2] For this TMM derivative 1,4-sigmatropic hydrogen shifts could lead to three products (**34**)—(**36**). The observed product is the diene (**34**).[2] Under orbital symmetry control, it is seen that compounds (**34**) and (**36**) could be formed from this biradical in a suprafacial manner but that the formation of the diene (**35**) would require

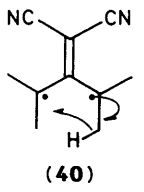


an antarafacial hydrogen shift. When it is further considered that the formation of the diene (**36**) involves migration across a 'transoid' system, it seems that FMO considerations can at least begin to help us understand why the diene (**34**) is formed. In the case of planar vinyl-TMM the non-bonding orbitals (**37**) and (**38**) are degenerate. In the biradical (**4**), however, this degeneracy is lifted and the HOMO is that shown in formula (**39**).[29] Reference to Scheme 3 shows that the 1,6-shift 'a' would



Scheme 3. The three possible routes from the biradical (**4**) to the triene (11) and the consequences of deuterium labelling. R = H or D

be antarafacial, the 1,4-shift 'b' suprafacial, and the 1,4-shift 'c' antarafacial. The last two appear to be geometrically unlikely. In the case of the suprafacial shift 'b,' the presence of the isopropyl group makes it very difficult to obtain anything approaching a planar geometry. This leaves the observed 1,6-shift as the most accessible reaction pathway. The dangers of pursuing this type of FMO argument too far, however, are seen in the case of the rearrangement of the cyano-substituted TMM biradical (**40**) to the diene (**41**). Consideration of the HOMO (**42**)[29] for this biradical suggests that this reaction must involve a 1,4-antarafacial hydrogen shift. A problem is that most examples of sigmatropic shifts in non-Kekulé polyenes, including the biradicals (**4**) and (**42**), involve highly sterically crowded systems which are certainly non-planar.[30] A clear-cut decision on whether such reactions are indeed orbital symmetry controlled must await further experimentation, particularly involving cyclic near-planar systems. In the meantime, the importance of the FMO factor *versus* other factors such as the transition state ring size remains in doubt.



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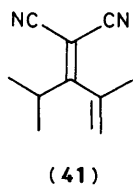

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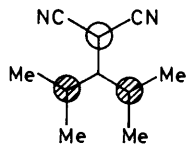

(**42**), HOMO

Experimental

Unless otherwise stated, i.r. spectra were recorded in $CHCl_3$ and n.m.r. spectra in $CDCl_3$ solution. Light petroleum refers to the fraction with b.p. 40—60 °C and ether to diethyl ether. New compounds whose elemental compositions were established through accurate mass determination were shown to be homogeneous by spectroscopic and chromatographic methods.

2,4-Dimethylpent-1-ene-3-amine (**8**) via *the Trichloroacetimidate.*[10]—Reaction of ethyl 2-bromoproprionate with triphenylphosphine followed by sodium hydroxide gave 1-ethoxycarbonylethylidene(triphenyl)phosphorane[8] which with 2-methylpropanal gave ethyl 2,4-dimethylpent-2-enoate[9] (80%, b.p. 72—74 °C/17 mmHg); δ_H 1.08 (6 H, d, *J* 8 Hz, CH*Me*$_2$), 1.30 (3 H, t, *J* 8 Hz, OCH$_2$*Me*), 1.85 (3 H, d, *J* 3 Hz, CH=C*Me*), 2.5 (3 H, m, C*H*Me$_2$ and OC*H*$_2$Me), and 6.75 (1 H, m, C*H*=CMe). This ester was reduced with lithium aluminium hydride to 2,4-dimethylpent-2-en-1-ol[9] (80%); δ_H 0.9 (6 H, d, *J* 8 Hz, CH*Me*$_2$), 1.7 (3 H, d, *J* 2 Hz, CH=C*Me*), 2.8 (1 H, m, C*H*Me$_2$), 3.0 (1 H, s, OH), 4.0 (2 H, s, C*H*$_2$OH), and 5.3 (1 H, m, C*H*=CMe). The remaining steps were based on the methods of Overman[10] and the intermediates, which were spectroscopically homogeneous, were used without purification. A small, cleaned piece of sodium (1.7 g) was added to a stirred solution of 2,4-dimethylpent-2-ene-1-ol (8.44 g) in sodium-dried ether (80 cm^3) at 0 °C. After 1 h at this temperature trichloroacetonitrile (21.3 g) was added dropwise over 25 min. After a further 1.5 h the solvent was evaporated under reduced pressure to give the crude allylic trichloroacetimidate (**12**) as an orange oil (17.2 g, 89%); δ_H 0.95 (6 H, d, *J* 7 Hz, CH*Me*$_2$), 1.72 (3 H, s, CH=C*Me*), 2.6 (1 H, m, C*H*Me$_2$), 4.6 (2 H, br s, C*H*$_2$O), 5.35 (1 H, m, C*H*=CMe), and 8.2 (1 H, br s, NH). A solution of this total crude product was refluxed in sodium-dried xylene (80 cm^3) under an atmosphere of nitrogen for 36 h. The solvent was evaporated under reduced pressure to give the crude allylic trichloroacetamide as a black solid (16 g, 93%); δ_H 0.9 (6 H, d, *J* 7 Hz, CH*Me*$_2$), 1.75 (3 H, br s, CH$_2$=C*Me*), 1.9 (1 H, m, C*H*NH), 4.1 (1 H, m, *J* 7 Hz, C*H*Me$_2$), and 4.95 (2 H, m, C*H*$_2$=CMe). Sodium hydroxide (47 g), ethanol (250 cm^3), and water (250 cm^3) were added to this crude product and the resultant mixture stirred for 2 days at room temperature. After acidification (conc. HCl, 25 cm^3), the ethanol was evaporated under reduced pressure and the aqueous solution washed with ether (3 × 50 cm^3) to remove neutral impurities. The aqueous layer was rendered basic using solid sodium hydroxide and extracted with ether (3 × 30 cm^3). The ether extracts were dried ($MgSO_4$), filtered, and fractionally distilled to give the *amine* (**8**) as a colourless oil (3.3 g, 47%), b.p. 70—73 °C (Found: M^+, 133.1201. $C_7H_{15}N$ requires 133.1204); δ_H 0.85 and 0.95 (each 3 H, d, *J* 7 Hz, CH*Me*$_2$ diasteriotopic methyls), 1.73 (3 H, s, CH$_2$=C*Me*), 1.8 (1 H, m, C*H*Me$_2$), 3.0 (1 H, d, *J* 6 Hz, C*H*NH$_2$), 4.87 (2 H, s, C*H*$_2$=CMe), 6.4 (2 H, br s, removed by D_2O, NH$_2$).

2,4-*Dimethylpent*-1-*ene*-3-*amine* (**8**) via *the Aziridine*.[11]—2,4-Dimethylpenta-2-ol (58 g) and iodine (1 g) in ether (100 cm^3) was refluxed for 30 min and fractionally distilled to give 2,4-dimethylpent-2-ene[12] as a colourless liquid (19 g, 38%), b.p. 92—94 °C; δ_H 0.9 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.65 (6 H, s, $CH{=}CMe_2$), 2.4 (1 H, m, $CHMe_2$), and 4.9 (1 H, d, *J* 8 Hz, $CH{=}CMe_2$). Iodine monochloride (31.7 g) was added dropwise to a stirred solution of sodium azide (26 g) in acetonitrile (170 cm^3) at 0 °C over 15 min. After a further 10 min at 0 °C 2,4-dimethylpent-2-ene (17 g) was added dropwise. The mixture was allowed to warm to room temperature and stirred for a further 18 h. The resultant red-brown slurry was poured into water (400 cm^3) and extracted with ether (3 × 100 cm^3). The ether extracts were washed with thiosulphate solution (3 × 100 cm^3) and brine, dried ($MgSO_4$), and the ether evaporated under reduced pressure to give the crude 3-iodo-2,4-dimethylpentan-2-azide as a yellow oil (45 g, 97%) which was used without further purification,[13] δ_H 0.9 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.55 (6 H, s, CN_3Me_2), 1.8 (1 H, m, $CHMe_2$), and 4.15 (1 H, d, *J* 6 Hz, CHI). The crude azide (45 g) was added dropwise to a stirred mixture of lithium aluminium hydride (3 g) in dry ether (200 cm^3) at 0 °C under a nitrogen atmosphere. After allowing the mixture to warm to room temperature, it was stirred for a further 18 h, poured into 20% aqueous sodium hydroxide (50 cm^3), and extracted with ether (2 × 100 cm^3). The ether extracts were dried ($MgSO_4$), filtered, and the solvent evaporated under reduced pressure to give the *aziridine* (**16**) as a pale yellow oil (11.3 g, 60%). A small sample was bulb distilled (b.p. 130 °C). **CAUTION**: An attempt to distil a 2 g sample of this compound resulted in a violent explosion[14] (Found: C, 74.4; H, 13.6%; M^+, 113.1198. $C_7H_{15}N$ requires C, 74.3; H, 13.3%; M^+, 113.1204); δ_H 0.9 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.15 and 1.20 (each 3 H, s, Me), 1.8 (1 H, m, $CHMe_2$), 3.4 (1 H, d, *J* 6 Hz, CHNH), and 4.8 (1 H, br s, NH); *m/z* 113 (M^+, 2%), 112 ($M^+ - 1$, 2), 98 (100), 84 (9), 56 (34), and 42 (60). 3-Isopropyl-2,2-dimethylaziridine (**16**) (265 mg) and isopropenyl acetate (231 mg) were heated together in a sealed, base-washed Pyrex tube at 220 °C for 4 h. Chromatography of the product on silica eluting with ether–light petroleum (5:1) gave the *amide* as a white crystalline solid (335 mg, 100%), m.p. 40—44 °C (Found: M^+, 115.1310. $C_9H_{17}NO$ requires M^+, 155.1310); δ_H 0.88, 0.89 (each 3 H, d, *J* 6 Hz, $CHMe_2$ with hindered rotation), 1.7 (3 H, d, *J* 1 Hz, $CMe{=}CH_2$), 2.0 (3 H, s, *Me*CO), 1.9 (1 H, m, $CHMe_2$), 4.18 (1 H, m, CHNH), 4.85 (2 H, br s, $CMe{=}CH_2$), and 5.8 (1 H, br s, NH). A solution of 3-acetamido-2,4-dimethylpent-1-ene (335 mg) in 75% aqueous sodium hydroxide–ethanol (1:1, 10 cm^3) was refluxed for 3 days. The mixture was acidified and the ethanol removed under reduced pressure. The solution was washed with ether (2 × 10 cm^3), basified with aqueous sodium hydroxide, and extracted with ether (2 × 10 cm^3). The ether extracts were dried ($MgSO_4$), filtered, and fractionally distilled to give the *amine* (**8**) as a water-white liquid (110 mg, 45%), the physical and spectroscopic properties of which were identical with those of the material prepared *via* the trichloroacetonitrile route.

N-(2,4-*Dimethylpent*-1-*en*-3-*yl*)*toluene*-p-*sulphonamide* (**17a**).—A mixture of 2,4-dimethylpent-1-en-3-amine (290 mg), tosyl chloride (504 mg), sodium hydroxide (100 mg), water (10 cm^3), and ethanol (3 cm^3) was heated under reflux for 2 h, cooled, and filtered to give the *tosylate* (**17a**) as a white crystalline solid (420 mg, 62%), m.p. 71—72 °C (Found: C, 62.8; H, 8.0; N, 5.3%; M^+, 267.1296. $C_{14}H_{21}NO_2S$ requires C, 62.9; H, 7.8; N, 5.2%; M^+, 267.1293); δ_H 0.8 and 0.95 (each 3 H, d, *J* 7 Hz, $CHMe_2$ with hindered rotation), 1.45 (3 H, s, $CMe{=}CH_2$), 1.75 (1 H, m, $CHMe_2$), 2.4 (3 H, s, Ar*Me*), 3.4 (1 H, t, *J* 6 Hz, CHNH), 4.6 (2 H, s, $CMe{=}CH_2$), 5.3 (1 H, d, *J* 6 Hz, NH), and 7.4 (4 H, AB quartet, ArH); *m/z* 267 (M^+, 2%), 224 ($M^+ - C_3H_7$, 95), 155 (59), 91 ($C_7H_7^+$, 100), and 43 (13).

N-(2,4-*Dimethylpent*-1-*en*-3-*yl*)*urea* (**17b**).—An acidified solution of 2,4-dimethylpent-1-en-3-amine (**8**) (2.5 g) and urea (8 g) in water (30 cm^3) was heated under reflux for 6 h, cooled in ice, and filtered to give the *urea* (**17b**) as a white crystalline solid (3.06 g, 89%) m.p. 130 °C (decomp.) (Found: C, 61.7; H, 10.3; N, 18.0. $C_8H_{16}N_2O$ requires C, 61.5; H, 10.3; N, 17.9%); $\nu_{max.}(CHCl_3)$ 1 655 (CO), 3 300 and 3 400 cm^{-1} (NH); δ_H 0.9, 1.1 (each 3 H, d, *J* 7 Hz, $CHMe_2$ with hindered rotation), 1.81 (3 H, s, $CMe{=}CH_2$), 2.1 (1 H, m, $CHMe_2$), 3.75 (1 H, t, *J* 8 Hz, CHNH), 4.5 (3 H, br s, NH and NH_2), 4.8 (br s, $CMe{=}CH_2$); *m/z* 156 (M^+, 6%), 141 (M^+ − Me, 2), 113 (63), 96 (6), 81 (3), 70 (100), and 43 (11).

4-*Isopropyl*-3′,3′,5,5′,5′-*pentamethyl*-2H-1,3-*oxathiole*-2-*spiro*-4′,3′,5′-*dihydropyrazole* (**20**).—A solution of 3-diazo-4-methylpentan-2-one (**18**)[15] (2.07 g) in pentane (25 cm^3) was added to a stirred solution of 3,5-dihydro-3,3,5,5,-tetramethylpyrazole-4-thione (**6**)[4] (2.39 g) in pentane (20 cm^3) at room temperature. After 12 h at room temperature the pink colour of the thione had disappeared. The solvent was evaporated under reduced pressure and the residue chromatographed on silica eluting with ether–light petroleum (1:4) to give the *oxathiole* (**20**) (2.7 g, 70%) as a white solid which was recrystallised from ether–light petroleum, m.p. 68—70 °C (Found: C, 61.3; H, 8.6; N, 10.9%; M^+, 254.1446. $C_{13}H_{22}N_2OS$ requires C, 61.4; H, 8.6; N, 11.0%: M^+, 254.1452); $\nu_{max.}(CHCl_3)$ 1 678 cm^{-1} (C=C);[16–20] δ_H 1.09 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.26, 154 (each 6 H, s, dihydropyrazole Me), 1.50 (3 H, s, vinyl Me), and 2.7 (1 H, septet, *J* 7 Hz, $CHMe_2$); δ_C 138.4, 112.1, 102.3 (carbons of the oxathiole ring),[17,18] 92.6, 26.5, 25.3, 22.5, 21.0, and 11.5; *m/z* 254 (M^+, 9%), 226 ($M^+ - N_2$, 13), 184 (26), 96 (48), 81 (100), and 43 (29). A portion of the oxathiole (**20**), (40 mg) in 2M aqueous hydrochloric acid (3 cm^3) and dioxane (3 cm^3) was heated on a steam-bath for 2 h, cooled, and extracted with methylene dichloride (2 × 10 cm^3), the extract dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The crude extract smelt strongly of 'thiol' but the residue obtained after removal of solvent was essentially pure 3,5-dihydro-3,3,5,5,-tetramethylpyrazol-4-one (**21**)[4] (15 mg, 61%). This was shown to be identical with an authentic sample by ^1H n.m.r. and g.l.c. comparison.

3′-*Ethoxycarbonyl*-3′-*isopropyl*-3,3,5,5,-*tetramethyl*-3,5-*dihydropyrazole*-4-*spiro*-2′-*thi-irane* (**23**).—Ethyl 2-diazo-3-methylbutanoate (**22**)[21] (4.0 g) was added to a solution of 3,5-dihydro-3,3,5,5-tetramethylpyrazole-4-thione (**6**)[4] (2.0 g) in dry ether (30 cm^3). After 2 days at room temperature the colour had changed from pink to pale yellow. The solvent was evaporated under reduced pressure and the residue chromatographed on silica eluting with ether–light petroleum (1:9) to give the *thi-irane* (**23**) as a pale yellow oil which was distilled, b.p. 100 °C/10 mmHg (2.6 g, 79%) (Found: C, 58.8; H, 8.7; N, 9.9%; M^+, 284.1558. $C_{14}H_{24}N_2SO_2$ requires C, 59.1; H, 8.4; N, 9.8%; M^+, 284.1558), $\nu_{max.}$(film) 1 720 cm^{-1} (CO); δ_H 1.20 (6 H, d, *J* 8 Hz, $CHMe_2$), 1.30 (3 H, t, *J* 7 Hz, CH_2Me), 1.37, 1.45, 1.52, and 1.59 (each 3 H, s, dihydropyrazole Me), 1.75 (1 H, septet, *J* 8 Hz, $CHMe_2$), and 4.25 (2 H, q, *J* 7 Hz, CH_2Me); *m/z* 284 (M^+, <0.1%), 256 ($M^+ - N_2$, 4), 183 (13), 96 (56), 81 (100), and 41 (38).

3,5-*Dihydro*-3,3,5,5-*tetramethyl*-4-(1-*ethoxycarbonyl*-2-*methylpyropylidene*)*pyrazole* (**24**).—A solution of the pyrazole-spiro-thi-irane (**23**) (3.2 g) and sodium-dried trimethyl phosphite (4 cm^3) in chloroform (20 cm^3) was heated under

reflux under an atmosphere of nitrogen for 2 days. The solvent was evaporated under reduced pressure and the residue chromatographed on silica eluting with ether–light petroleum (1:4) to give the alkene (**24**) as a white solid which was recrystallised from light petroleum at low temperature (2.5 g, 88%) m.p. 45—49 °C (Found: C, 66.6; H, 9.2%; $M^+ - N_2$, 224.1775. $C_{14}H_{24}N_2O_2$ requires C, 66.6; H, 9.5; $M^+ - N_2$, 224.1776); $\nu_{max.}$($CHCl_3$) 1 725 cm^{-1} (CO); δ_H 1.1 (6 H, d, *J* 8 Hz, $CHMe_2$), 1.35 (3 H, t, 8 Hz, CH_2Me), 1.42 and 1.52 (each 6 H, s dihydropyrazole Me) 2.9 (1 H, septet, *J* 8 Hz, $CHMe_2$), and 4.25 (2 H, q, *J* 8 Hz, CH_2Me); *m/z*, 224 ($M^+ - N_2$, 100%), 207 (37), 181 (23), 135 (90), 67 (17), and 43 (14).

1-(1-*Ethoxycarbonyl*-2-*methylpropylidene*)-2,2,3,3-*tetramethyl-cyclopropane* (**25**).—A solution of 3,5-dihydro-3,3,5,5-tetramethyl-4-(1-ethoxycarbonyl-2-methylpropylidine)pyrazole (**24**) (300 mg) in benzene (3 cm^3) in a sealed n.m.r. tube was photolysed using a water-cooled Hanovia medium-pressure u.v. lamp. The progress of the reaction was monitored by n.m.r. spectroscopy and it was complete in 18 h. The benzene was evaporated under reduced pressure and the residue bulb distilled (b.p. 70 °C/10 mmHg) to give the *cylclopropane* (**25**) as a colourless oil (200 mg, 75%) (Found: M^+, 224.1777. $C_{14}H_{24}O_2$ requires M^+, 224.1776); $\nu_{max.}$(film) 1 720 cm^{-1} (C=O); δ_H 1.10 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.19 and 1.17 (each 6 H, s, ring Me), 1.31 (3 H, t, *J* 8 Hz, $MeCH_2O$), 2.9 (1 H, septet, *J* 7 Hz, $CHMe_2$), and 4.20 (1 H, q, *J* 8 Hz, $MeCH_2O$); δ_C 167.7 (CO), 156.9 and 127.2 (C=C), 59.9 (OCH_2Me), 29.5, 22.3, 21.6, 20.0, and 14.5; *m/z* 224 (M^+, 100%), 209 (6), 196 (12), 181 (10), 135 (74), 91 (15), 81 (31), 67 (23), 43 (38), and 41 (39).

1-(2-*Hydroxy*-2,4-*dimethylpent*-3-*ylidene*)-2,2,3,3-*tetramethylcyclopropane* (**26**).—A solution of methyl-lithium in ether (5 cm^3, 12.5 mmol) was added to a stirred solution of the cyclopropane (**25**) (1.18 g, 5.3 mmol) in dry ether under an atmosphere of nitrogen. After 90 min the solution was poured into water. The mixture was extracted with ether (2 × 20 cm^3), the ether extracts dried, filtered, and the solvent evaporated under reduced pressure to give the *alcohol* (**26**) as a white solid which was further purified by chromatography on silica eluting with ether–light petroleum (1:1) (860 mg, 78%), m.p. 46—48 °C (Found: C, 78.6; H, 12.5. $C_{14}H_{26}O$ requires C, 79.9; H, 12.5%); $\nu_{max.}$($CHCl_3$) 3 200 cm^{-1} (OH); δ_H 1.1 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.15 (12 H, s, ring Me), 1.35 [3 H, s, $C(OH)Me_2$], 2.0 (1 H, br s, removed by D_2O, OH), and 2.5 (1 H, septet, *J* 7 Hz, $CHMe_2$).

The equivalent hexadeuteriated alcohol [$(CD_3)_2C(OH)R$] was prepared in an identical manner using CD_3Li (from CD_3I and lithium wire) 89%, m.p. 47—48 °C, ^1H n.m.r., no signal at δ 1.35.

1-(2,4-*Dimethylpent*-1-*en*-3-*ylidene*)-2,2,3,3-*tetramethylcyclopropane* (**27**).—A mixture of ground freshly fused potassium hydrogen sulphate (200 mg) and 1-(2-hydroxy-2,4-dimethylpent-3-ylidene)-2,2,3,3-tetramethylcyclopropane (**26**) (100 mg) was heated for 30 min in a Kügelröhr apparatus at 80 °C and 10 mmHg. Volatile products were trapped in a U-tube cooled at −78 °C. The product was dried with calcium sulphate and found to be a 9:1 mixture of the *diene* (**27**) and 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (**11**) (Found: M^+, 192.1870. $C_{14}H_{24}$ requires M^+, 192.1877); $\nu_{max.}$(film) 885 and 3 095 cm^{-1} (C=CH_2); δ_H 1.10 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.14 and 1.16 (each 6 H, s, ring Me), 1.90 (3 H, br s, vinyl Me), 2.80 (1 H, septet, *J* 7 Hz, $CHMe_2$), 4.85 and 4.98 (1 H, m, C=CH_2); *m/z* 192 (M^+, 9%), 177 (4), 149 (16), 91 (22), 81 (22), and 43 (100).

The equivalent pentadeuteriated alkene CD_2=C(CD_3)R was prepared from the hexadeuteriated alcohol in an identical manner, ^1H n.m.r. no signals at δ 1.90, 4.85, and 4.98.

Flash Vacuum Pyrolysis of the Diene (**27**).[5,6,24]—The diene was distilled through a heated vertical silica tube at 400—500 °C and a pressure of 10^{-3}–10^{-4} mmHg. The contact time was estimated as *ca.* 10^{-3} s. The product was collected in a liquid nitrogen-cooled trap and concentrated into a smaller trap by vacuum line distillation. The product triene (**11**) was identified by ^1H n.m.r. and g.l.c. comparison with an authentic sample. The pentadeuteriated diene was pyrolysed in the same manner and the product investigated by g.l.c. ^1H and ^2H n.m.r. spectroscopy.

Study of the Kinetics of the Isomerisation of the Diene (**27**) *to the Triene* (**11**).—A solution of the diene (**27**) in *o*-dichlorobenzene was allowed to stand for a few minutes with a pellet of sodium hydroxide before being transferred into a base-washed tube (soaked in concentrated aqueous sodium hydroxide overnight and then washed many times with distilled water and dried in the oven) which was of a suitable size to fit inside a standard 5-mm n.m.r. tube. A little *o*-dimethoxybenzene was added, the solution de-gassed (3—4 freeze-pump-thaw cycles) and the tube sealed under vacuum. The tube was heated for measured periods of time in a fluidised sand-bath and the progress of the reaction monitored by n.m.r. spectroscopy measuring the integral of the vinyl methyl *versus* the methoxy signal. The formation of the triene (**11**) was quite clean and the disappearance of the starting material followed first-order kinetics (T/K, $10^5k/s^{-1}$; 477.15, 0.89; 488.15, 3.0; 503.15, 6.09; 522.15, 38.4). E_a = 39.6 ± 4.0 kcal mol^{-1}, $\log_{10} A$ = 13.1 ± 1.8. Reproducible kinetics were only obtained when base-washed apparatus was employed. A similar attempt to study the kinetics of the isomerisation of the spiropentane (**10**) in solution showed that the reaction was negligibly slow at < 240 °C and at higher temperatures, the formation of the triene (**11**) in solution was accompanied by general decomposition. Under flash vacuum pyrolysis conditions,[5,6,24] both the diene (**27**) and the spiropentane (**10**) were cleanly converted into the triene (**11**) but the diene, once again, required milder reaction conditions.

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