Preparation, Pyrolysis, and Photolysis of Three Sterically Crowded Alkenes, 3,3,3′,3′,5,5,5′,5′-Octamethyl-3,3′,5,5′-tetrahydro-4,4′-bi(4*H*-pyrazolylidene) 2,2,4,4-Tetramethyl-3-(3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazol-4-ylidene)-thietane 1,1-Dioxide and 2,2,2′,2′,4,4,4′,4′-Octamethyl-3,3′-bithietanylidene 1,1,1′,1′-Tetraoxide, Potential Precursors to the Octamethyltetramethylene-ethane (TME) Biradical

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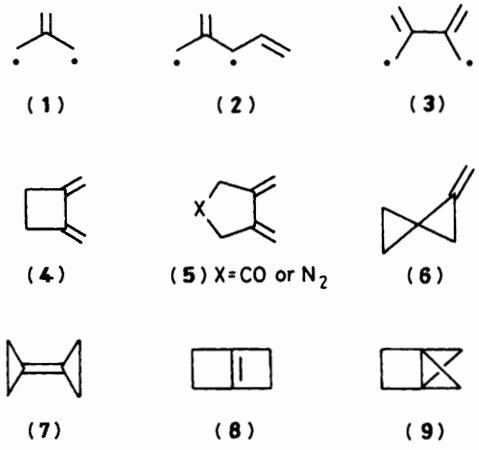
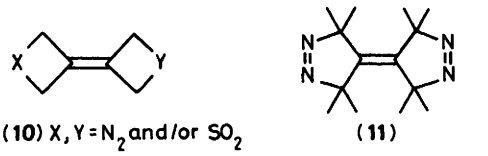
Photolysis and pyrolysis of the title compounds involve a stepwise elimination of nitrogen and/or sulphur dioxide and reactions which can be interpreted in terms of a series of trimethylenemethane (TMM) biradical intermediates. However, the photosensitised photolysis of the bi(pyrazolylidene) (**11**) gives products indicative of an elimination of both nitrogens and the generation of a tetramethylene-ethane (TME) biradical intermediate. New syntheses of a number of highly sterically crowded alkenes including 2,2,4,4-tetramethyl-3-(3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazol-4-ylidene)thietane 1,1-dioxide (**12**) and 2,2,2′,2′,4,4,4′,4′-octamethyl-3,3′-bithietanylidene 1,1,1′,1′-tetraoxide (**13**), are described. Flash vacuum pyrolysis (f.v.p.) of 3,3,3′,3′,5,5,5′,5′-octamethyl-3,3′,5,5′-tetrahydro-4,4′-bi(4*H*-pyrazolylidene) (**11**) at < 400 °C gives 3,3,5,5-tetramethyl-4-(2,2,3,3-tetramethylcyclopropylidene)-3,5-dihydro-4*H*-pyrazole (**21**), at *ca.* 400 °C 1-isopropylidene-2,2,4,4,5,5-hexamethylspiropentane (**22**), and at *ca.* 580 °C a *ca.* 5:1 mixture of 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (**23**) and 2-(2,3-dimethylbut-1-en-3-yl)-1-isopropyl-3,3-dimethylcyclopropene (**27**). Above 700 °C a complex mixture of aromatic products and low molecular weight hydrocarbons is produced which includes ethane, ethylene, propene, isobutane, and isobutene, *p*-xylene, *o*-cymene and probably *m*-cymene, and 2,5-dimethylisopropylbenzene. F.v.p. of the dihydropyrazole sulphone (**12**) gives initially 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)thietane 1,1-dioxide (**41**) and at higher temperatures similar mixtures to those obtained from the bipyrazolylidene (**11**). Similar results were also obtained for the f.v.p. of the bis-sulphone (**13**). Photolysis of the bipyrazolylidene (**11**) gave initially the dihydropyrazole (**21**) and then a 48:52 mixture of the spiro compound (**22**) and 2,2,2′,2′,3,3,3′,3′-octamethylbicyclopropylidene (**42**). Photolysis of the dihydropyrazole sulphone (**12**) gave 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)-thietane 1,1-dioxide (**41**). Benzophenone-sensitised photolysis of the bipyrazolylidene (**11**) gave 1,2-di-isopropylidene-3,3,4,4-tetramethylcyclobutane (**32**).

The TMM biradical (**1**), the vinyl TMM biradical (**2**), and the TME biradical (**3**) have 4-, 6-, and 6-π electrons respectively and are the three simplest representatives of the family of non-classical or non-Kekulé polyenes. TME Biradicals have often been implicated as intermediates in the dimerisation of allenes,[1] in the rearrangement of 1,2-dimethylenecyclobutanes (**4**),[2] and in the elimination of carbon monoxide or nitrogen from compounds of the type shown in formula (**5**).[3] In principle, at least, TME biradicals can also be derived by homolysis of two or more carbon–carbon bonds in compounds containing the carbon skeletons shown in formulae (**6**)—(**9**).[4] We chose to investigate a further group of potential TME precursors, of the type shown in formula (**10**). Our previous experience in generating TMM biradicals,[5-8] led us to choose systems where the 'leaving groups' X and Y were nitrogen and/or sulphur dioxide, namely compounds (**11**)—(**13**). The compounds in which the positions α to the 'leaving groups' were blocked with methyl substituents were specifically chosen in order to avoid problems arising from tautomerisation and double bond migration.[5]

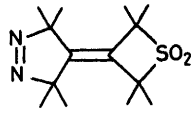


The synthesis of the bipyrazolylidene (**11**) has been described in a previous paper.[6] Those of compounds (**12**) and (**13**) followed a similar scheme in which the sterically crowded double bond was created through a thioketone–diazo compound reaction.[5,6] To prepare the dihydropyrazole sulphone (**12**) an ether solution of the hydrazone (**14c**) was oxidised at 0 °C with nickel peroxide to give the diazo compound (**14d**). This was then treated with the thioketone (**15b**). After 2 h at 0 °C the mixture was cooled to −78 °C when the white dihydrothiadiazole (**16a**) precipitated out. When this was heated (without solvent) nitrogen was eliminated to give the episulphide (**17a**) which was finally converted into the alkene (**12**) by treatment with trimethyl phosphite. The preparation of the



(10) X, Y = N_2 and/or SO_2

(11)



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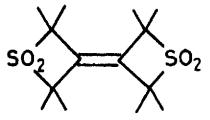

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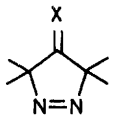

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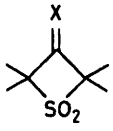
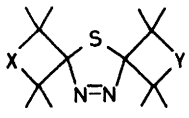


(15)

a; X = O=
b; X = S=
c; X = NNH_2
d; X = N_2



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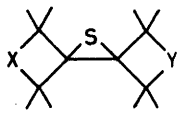
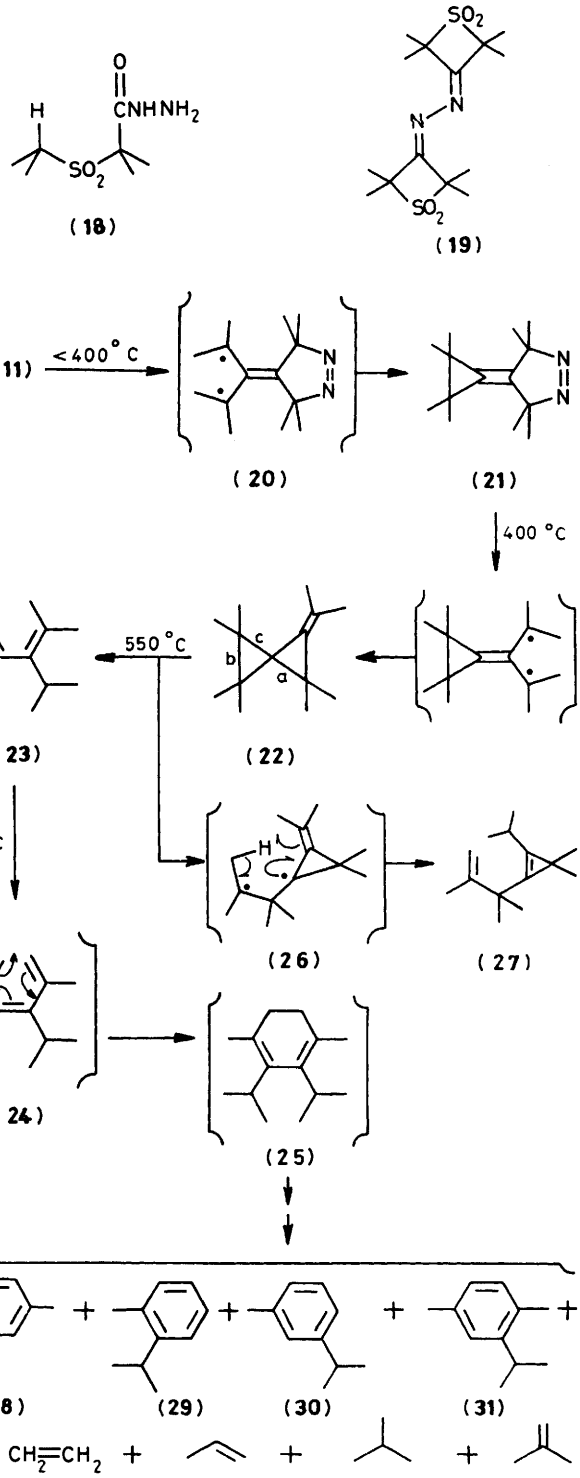


(17)

a; X = N_2, Y = SO_2
b; X = Y = SO_2

disulphone (**13**) followed a similar scheme, but first the hydrazone (**15c**) and diazo compound (**15d**) had to be obtained.[9,10] These reactions in the 'sulphone series' provided many more problems than those in the 'dihydropyrazole series'. Reaction of 2,2,4,4-tetramethylthietan-3-one 1,1-dioxide (**15a**) with hydrazine in ethanol gave, not the desired hydrazone (**15c**), but the ring-opened product (**18**). This problem could be partly overcome by using an aprotic solvent (dry dioxane), but even in this solvent the reaction was only wholly successful when carried out on a small scale in dilute solution. An attempt to scale up the reaction and to use a more concentrated solution gave a mixture of the desired hydrazone (**15c**) and the diazine (**19**) (see Experimental section). Problems were also encountered in the oxidation of the hydrazone of 2,2,4,4-tetramethylthietan-3-one 1,1-dioxide (**15c**) to the corresponding diazo compound (**15d**).[9] The diazo compound (**15d**) was considerably less stable than its dihydropyrazole counterpart (**14d**). The reaction of the diazo compound (**15d**) with the thioketone (**15b**) had, therefore, to be carried out at lower temperatures (−35 to −20 °C). The cycloaddition was, however, accomplished to give a modest yield (21%) of the dihydrothiadiazole (**16b**). This was then converted into the episulphide (**17b**) and the alkene (**13**) cleanly and without further difficulty.

To generate a TME biradical from any of the potential precursors (**11**)—(**13**) both 'leaving groups' must be removed simultaneously or, if they are lost in a stepwise manner, then the second 'leaving group' must be lost very shortly after the first so that the initially formed TMM biradical has no chance to undergo other reactions. In those cases where nitrogen is the



(18) (19) (11) (20) (21) (23) (22) (26) (27) (24) (25) (28) (29) (30) (31)

Scheme 1. Flash vacuum pyrolysis of 3,3,3′,3′,5,5,5′,5′-octamethyl-3,3′5,5′-tetrahydrobi(4*H*-pyrazolylidene) (**11**)

'leaving group' the elimination can, in principle, be achieved thermally[8] or photochemically,[7] but in the case of sulphur dioxide only flash vacuum pyrolysis (f.v.p.) can be employed.[5] The main results obtained for the f.v.p. of the bipyrazolylidene (**11**)[11] are summarised in Scheme 1. At temperatures below 300 °C mainly solid products resulted. These collected around the neck of the f.v.p. apparatus and proved to be mixtures of the

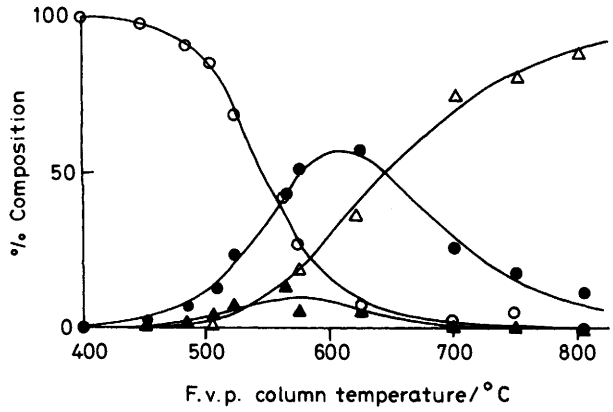
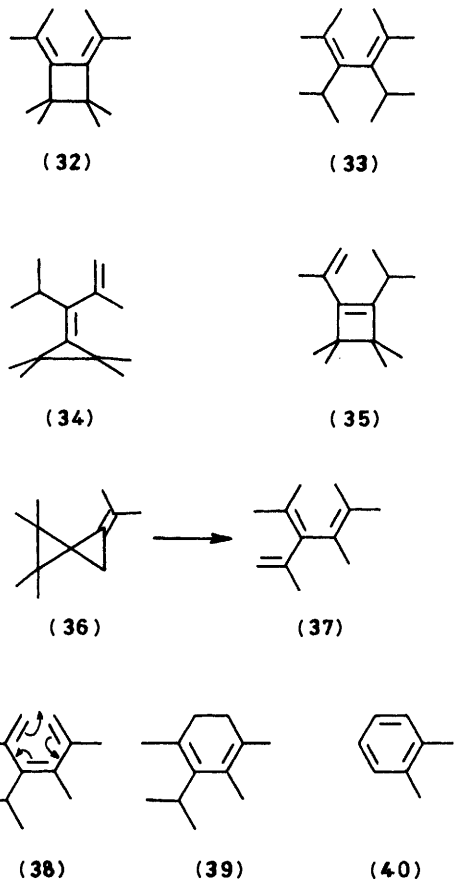
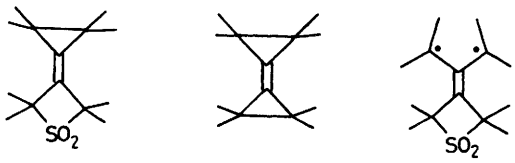


Figure 1. Composition of the mixture of liquid products obtained by f.v.p. of 3,3,3′,3′,5,5,5′,5′-octamethyl-3,3′,5,5′-tetrahydrobi(4*H*-pyrazolylidene) (**11**) as a function of the temperature of the f.v.p. column. The ratios are internally normalised and are based on g.l.c. peak areas, uncorrected for f.i.d. response. At 700 °C the 'aromatic' products comprised 69% of the total mixture; this included 33% *o*-cymene, 24% *p*-xylene and many minor components: ○, spiropentane (**22**); △, 'aromatics'; ●, compound (**23**); ▲, cyclopropene (**27**)



starting material and the monopyrazole (**21**). At higher temperatures mainly liquid products were obtained. The variation in the composition of this mixture of liquids as a function of the temperature of the f.v.p. column is shown in Figure 1. At *ca.* 400 °C essentially pure 1-isopropylidene-2,2,4,4,5,5-hexamethylspiropentane (**22**) was obtained. At 580 °C the main new products were a *ca.* 5:1 mixture of 2,5-dimethyl-4-isopropyl-3-isopropylidenehexa-1,4-diene (**23**) and 2-(2,3-dimethylbut-1-en-3-yl)-1-isopropyl-3,3-dimethylcyclopropene (**27**). At 700 °C and above a complex mixture resulted of which the main liquid components were *p*-xylene (**28**) and *o*-cymene (**29**). Identification of the triene (**23**) provided no problems, and was confirmed by the synthesis of authentic material from the thermal rearrangement of the tetramethylallene dimer (**32**), by a selective catalytic hydrogenation to the symmetrical diene (**33**), and by preparing an adduct with sulphur dioxide. The identification of the minor product formed at 580 °C proved more difficult. Initially a small sample was isolated by preparative g.l.c. The mass spectrum confirmed that this was isomeric with compounds (**22**) and (**23**), and the i.r. spectrum showed it to be an alkene and to contain no detectable C≡C stretching frequency. The ^{1}H n.m.r. spectrum showed the presence of a $CH_3C{=}CH_2$ grouping, two uncoupled inequivalent CMe_2 groupings, and a $CHMe_2$ which was attached to a double bond ($CHMe_2$, δ 2.75). This data can be fitted to three possible structures (**27**), (**34**), and (**35**). An authentic sample of compound (**34**) was, however, available from a related study[12] and so this possible assignment could be quickly discounted. An authentic sample of the diene (**35**) was prepared by photoisomerisation of the tetramethylallene dimer (**32**).[13] This also showed different spectroscopic and chromatographic properties from those of the unknown compound. It was therefore concluded, by a process of elimination, that this compound must be the cyclopropene (**27**). Positive evidence in favour of this assignment was obtained by the isolation of a larger sample by preparative g.l.c. and from its ^{13}C n.m.r. spectrum. Particularly characteristic were the ^{13}C n.m.r. chemical shifts for the olefinic carbons δ_c 151.0 and 108.5 p.p.m. ($C{=}CH_2$)[14] and δ_c 127.4 and 126.6 p.p.m. (cyclopropene C=C).[14,15] Formation of this cyclopropene from the spiro compound (**22**) is readily rationalised. Homolysis of the allylic bond c in compound (**22**) gives a diradical (**26**) which can rearrange by the mechanism shown. The fact that this compound disappears from the reaction mixture at higher temperatures is not surprising in view of the known ease with which cyclopropenes undergo thermal rearrangements.[16] However, none of the minor products obtained from high temperature f.v.p. of these materials could be identified as having arisen from this route. Most of the liquid products obtained above 700 °C seemed to be benzenoid materials derived from the triene (**23**), presumably through cyclisation of its conjugated isomer 3,4-di-isopropyl-2,5-dimethylhexa-1,3,5-triene (**24**) to the cyclohexadiene (**25**). The two major components of this mixture were isolated by preparative g.l.c. and were shown by spectroscopic comparison and by comparison of the analytical g.l.c. retention times to be *p*-xylene and *o*-cymene. The mixture also contained a number of minor components. One of these was probably *m*-cymene (**30**) (by comparison of the g.l.c. retention time with that of authentic material) and another was probably 2,5-dimethylisopropylbenzene (**31**) (by comparison of the g.l.c. retention time with that of authentic material, and a mass spectroscopy/g.l.c. confirmation of an *m/z* 148, $C_{11}H_{16}$). Comparison of the structural formulae for these aromatic compounds (**28**)—(**31**) tends to confirm the view that they are derived from the cyclohexadiene (**25**). Crandell[17] obtained rather similar results in a study of the pyrolysis of 1-isopropylidene-4,4,5,5-tetramethylspiropentane (**36**). This gave first the triene (**37**) and at higher temperatures the aromatic products (**28**) and (**40**). He postulated the intermediacy of the conjugated triene (**38**) and the cyclohexadiene (**39**). The rationale behind the aromatisation reactions seems to be that once the cyclohexadiene (**25**) or (**39**) is formed it undergoes a series of 1,5-hydrogen shifts and a fairly non-specific series of reactions in which (presumably allylic) C–Me, C–H, and C–Pr^i bonds are broken producing hydrogen, methyl, and isopropyl radicals. In an attempt to determine the



(41) (42) (43)

fate of the C_1—C_4 fragments produced in these reactions we carried out the pyrolysis of a sample of 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (**23**) at *ca.* 750 °C. The products were trapped in liquid nitrogen in the normal manner and were then allowed to warm to room temperature, and the gases evolved as the solution warmed up were collected and analysed by gas chromatography. They were mainly ethane, ethylene, propene, isobutane, and isobutene with trace amounts of methane and propane. These are the products which would be expected from a mixture of (possibly vibrationally excited) methyl and isopropyl radicals. The only slight surprise was that methane and propane were present in such small amounts, although the fact that there was so little methane may simply reflect the difficulty in trapping this material at low pressures.

The f.v.p. of the dihydropyrazole sulphone (**12**) followed a similar course to that of the bipyrazolylidene (**11**) except that slightly higher temperatures were required to effect the elimination of sulphur dioxide than for nitrogen.[18] At 400 °C and below only solid products were obtained which collected in the neck of the apparatus and proved to be mixtures of starting material and the monosulphone (**41**)[7,8] At 550 °C some liquid product was collected in the trap. This proved to be mainly the spiro compound (**22**) with some of the triene (**23**). At higher temperatures, the triene (**23**) and aromatic products were obtained [exactly as in the case of the bipyrazolylidene (Scheme 1)].

The f.v.p. of the disulphone (**13**) at 650 °C gave a solid product, the monosulphone (**41**), and a liquid product which was mainly the triene (**23**). At 770 °C the normal mixture of 'aromatic' products resulted, consisting mainly of *p*-xylene and *o*-cymene. The only significant difference between the sulphones and dihydropyrazoles was that, as a higher temperature is needed to eliminate sulphur dioxide than for nitrogen the radicals produced tend to undergo H-transfer rather than cyclisation.[18] As a result, this disulphone (**13**) gave the triene (**23**) as the first hydrocarbon product and no spiropentane (**22**) could be detected.

The photochemical reactions of the bipyrazolylidene (**11**) and the dihydropyrazole sulphone (**12**) were also investigated and the direct photolysis of these compounds has been discussed in some detail in a previous paper.[7] The bipyrazolylidene (**11**) gives first the monopyrazole (**21**) and, on more prolonged photolysis, a 48:52 mixture of the symmetrical bicyclopropylidene (**42**) and the spiro compound (**22**). This sequence is similar to that observed under f.v.p. conditions except for the observation of product (**42**). The reason that this product was not observed under f.v.p. conditions is that it isomerises thermally to the spiro compound (**22**).[7]

In terms of the original objective of this work, none of the reactions described so far need to be interpreted in terms of a TME intermediate but rather a sequence of TMM intermediates is implicated as shown in Scheme 1. The only possible exception is the conversion of the spiro compound (**22**) into the triene (**23**). Indeed, Crandell[17] has proposed a TME intermediate for the equivalent conversion of the spiro compound (**36**) into the triene (**37**) but the case for a TME intermediate in these reactions remains to be proved. The problem in generating a TME intermediate from compounds (**11**)—(**13**) seems to be that the 'leaving groups' are preferentially lost in a stepwise manner and that the TMM biradicals (**20**) and (**43**), formed after elimination of the first 'leaving group', cyclise or undergo hydrogen transfer before the second 'leaving group' departs. This is perhaps not surprising since our earlier experiments[7,8,19] had suggested that singlet tetramethylated TMM biradicals of the general type shown in formula (**44**) are generated in a bis-orthogonal geometry and that cyclisation is so rapid that it even competes with rotation about the C–C bonds. These experiments had, however, also shown[7] that the triplet tetramethylated TMM biradicals were far longer lived. In the triplet state, rotation about the C–C bonds can successfully compete with ring closure and this suggests that in the triplet state of biradicals (**20**) and (**43**) elimination of the second 'leaving group' may also compete with ring closure and a breakthrough to the TME manifold occur. For one of these two systems this indeed proved to be the case. When a triplet sensitiser, benzophenone, is used in the photolysis of the bipyrazolylidene (**11**), for the first time tetramethylallene dimer (the expected product from an intermediate octamethyl-TME biradical) was formed together with the normal direct photolysis products, the monopyrazole (**21**) and the spiro compound (**22**). The ratio of products depended on the concentration of photosensitiser. As may be seen from Figure 2, extrapolation to infinite sensitiser

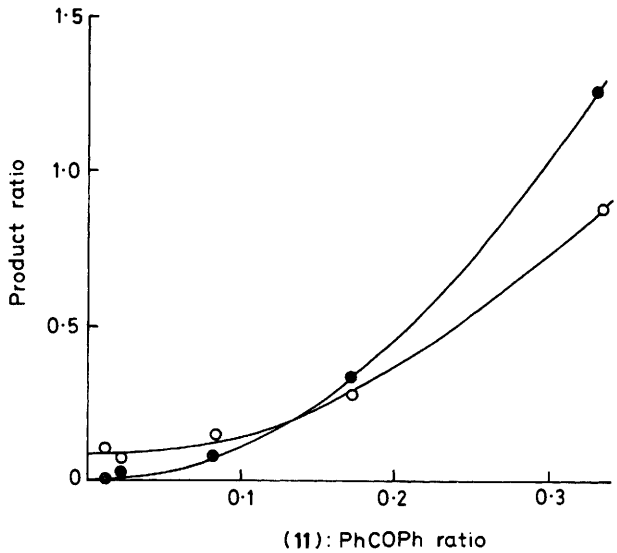
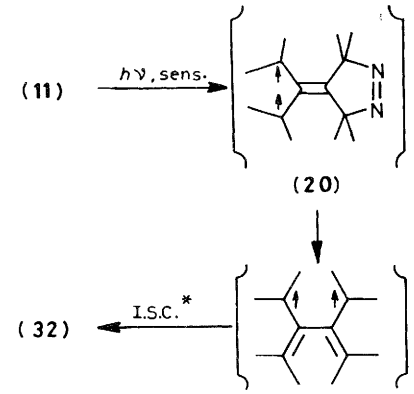
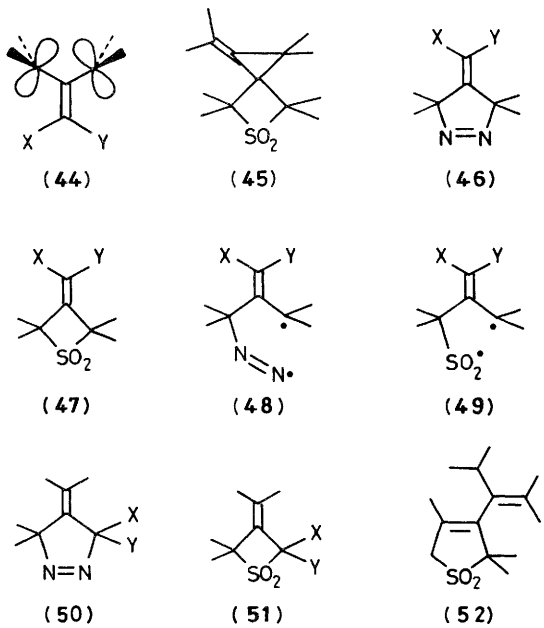


Figure 2. Photosensitised photolysis of 3,3,3′,3′,5,5,5′,5′-octamethyl-3,3′,5,5′-tetrahydrobi(4*H*-pyrazolylidene) (**11**). Plot of benzophenone/substrate ratio (weight ratio) *vs.* product ratio (g.l.c. peak area ratios uncorrected for f.i.d. response): ●, (**22**):(**32**); ○, (**21**):(**32**)

concentration (substrate:sensitiser = 0) suggests that under these conditions the ratio of products would be *ca.* 90% allene dimer (**32**), 10% spiro compound (**22**) and 0% monopyrazole (**21**). Independent studies showed that the allene dimer (**32**) did not arise from the photosensitised photolysis of compounds (**21**) or (**22**). It therefore arose from the bipyrazolylidene either directly, by simultaneous elimination of both nitrogens, or as suggested above and in Scheme 2 *via* the triplet state of the monopyrazole biradical (**20**). Among the systems we have investigated, this breakthrough to a TME biradical in the triplet series seems to be limited to the bipyrazolylidene (**11**). Two other compounds where a similar reaction might be expected are the monopyrazole (**21**) and the pyrazole sulphone (**12**), but these do not give products indicative of a TME intermediate. They do, however, give products which are consistent with the general idea that the triplet biradical intermediates are far



Scheme 2. Probable course of the photosensitised photolysis of 3,3,3',3',5,5,5',5'-octamethyl-3,3',5,5'-tetrahydrobi(4*H*-pyrazolylidene) (**11**). * I.S.C. = inter-system crossing



longer lived than their singlet counterparts. Instead of the singlet TMM product which is wholly or partly the sterically crowded 'least-motions' product, the triplet TMM's give the rearranged, more stable, spiro fused products. Whereas direct photolysis of the dihydropyrazole (**21**) gives a 48:52 mixture of the alkene (**42**) and the spiropentane (**22**), the triplet sensitised photolysis gives (within the detection limits of ^{1}H n.m.r. spectroscopy) only the spiropentane (**22**). It was also shown that, whereas the direct photolysis of the dihydropyrazole sulphone (**12**) gives only the 'least motions' product (**41**), the triplet sensitised photolysis gives mainly (75%) the rearranged spiro product 2'-isopropylidene-2,2,3',3',4,4-hexamethylthietane-3-spiro-1'-cyclopropane 1,1-dioxide (**45**).

An unresolved problem in the photolysis and pyrolysis of 4-alkylidene-3,5-dihydro-4*H*-pyrazoles (**46**) and 3-alkylidenethietane dioxides (**47**) is whether the elimination of nitrogen or sulphur dioxide involves the simultaneous homolysis of both bonds or whether intermediates such as the biradicals (**48**) and (**49**) are involved. We have discussed this problem in detail in a previous paper[8] and since then Crawford[20] and Engel[21] have both advanced further evidence for a diazenyl biradical in the decomposition of 4-alkylidene-3,5-dihydro-4*H*-pyrazoles. The most direct evidence for such intermediates is the isolation of rearranged products[22] [*i.e.* compounds (**50**) and (**51**) in the case of compounds (**46**) and (**47**)]. In our previous studies we had failed to detect any such rearrangements, but in none of the systems was there any obvious driving force for such a rearrangement. For compounds (**11**)—(**13**), however, the rearrangement would result in the formation of a spiro fused product and should result in a considerable relief on steric strain. Despite this fact, even with these compounds, no rearrangements prior to elimination of the 'leaving group' were detected, and although this is not strong evidence against stepwise bond breaking in nitrogen and sulphur dioxide elimination it may be a significant observation.

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. Photolyses were carried out in benzene solution using a Pyrex n.m.r. tube attached to the outside wall of a water-cooled Hanovia medium-pressure lamp.[7] Flash vacuum pyrolyses were performed using the apparatus previously described.[5,8] The compound was distilled or sublimed through a heated vertical silica tube. Temperatures were in the range room temp.—800 °C, pressures were in the region 10^{-3}—10^{-4} mmHg, and the contact time was estimated as *ca.* 10^{-3} s. The products were normally collected in a liquid nitrogen cooled trap and concentrated into a smaller trap by vacuum line distillation. Analytical g.l.c. was carried out at 130 °C using a 7 ft × 1/8 in column of 15% Carbowax 20M + TPA on acid-washed 80/100 Chromosorb G deactivated with Me_2Cl_2Si with a flow rate of 35 cm^3 min^{-1} and using a Perkin-Elmer F11 instrument. The retention times of the compounds in this paper were 3,3-dimethyl-2-(2,3-dimethylbut-1-en-3-yl)-1-isopropylcyclopropene (**27**), 4.2 min; *p*-xylene (**28**), 4.65 min; 1-isopropylidene-2,2,4,4,5,5-hexamethylspiro[2.2]pentane (**22**), 5.2 min; 2,5-dimethyl-4-isopropyl-3-isopropylidenehexa-1,4-diene (**23**), 6.75 min; *m*-cymene (**30**), 7.75 min; 2-isopropyl-1-isopropenyl-3,3,4,4-tetramethylcyclobutene (**35**), 8.25 min; *o*-cymene (**25**), 9.0 min; 1,2-di-isopropylidene-3,3,4,4-tetramethylcyclobutane (**32**), 10.1 min; 2,5-dimethylisopropylbenzene (**31**), 12.5 min; and 3,3,5,5-tetramethyl-4-(2,2,3,3-tetramethylcyclopropylidene)-3,5-dihydro-4*H*-pyrazole (**21**), 38.2 min. Ether refers to diethyl ether.

Reaction of 2,2,4,4-*Tetramethylthietan*-3-*one* 1,1-*Dioxide* (**15a**) *with Hydrazine in Ethanol.*—A solution of the thietanone[5] (4 g) and anhydrous hydrazine (1.2 g) in absolute ethanol (120 cm^3) was heated under reflux for 14 h in an apparatus fitted with a Soxhlet extractor containing 3A molecular sieve. The solution was poured into dichloromethane which was washed, dried, and evaporated under reduced pressure to give 2,2,4-*trimethyl*-3-*thiapentanohydrazide* 3,3-*dioxide* (**18**) (3.9 g, 83%), m.p. 120 °C, after recrystallisation from methanol (Found: C, 40.2; H, 7.6; N, 13.6; S, 15.3%; M^+, 208.0874. $C_7H_{16}N_2SO_3$ requires C, 40.4; H, 7.8; N, 13.5; S, 15.4%; M^+, 208.0882); $\nu_{max.}$ 3 390 (NH), 1 675 (C=O), 1 625, 1 310, and 1 112 cm^{-1} (SO_2); δ_H 1.35 (6 H, d, *J* 7 Hz, Me_2CH), 1.65 (6 H, s, Me_2C), 3.53 (1 H, sept, *J* 7 Hz, Me_2CH), and 6.5—4.0 (3 H, br signal removed by D_2O, $NHNH_2$); *m/z* 208 (M^+, 21%), 101 (M^+ − Pr^iSO_2, 100), and 43 (Pr^{i+}, 32).

Reaction of 2,2,4,4-*Tetramethylthietan*-3-*one* 1,1-*Dioxide* (**15a**) *with Hydrazine in Dioxane.*—A solution of the thietanone (176 mg) and anhydrous hydrazine (60 mg) in dry dioxane (40 cm^3) was heated under reflux for 40 h in an apparatus fitted with a Soxhlet extractor containing 3A molecular sieve. The solution was poured into dichloromethane, washed with brine,

dried ($MgSO_4$) and the solvent removed under reduced pressure to give the *hydrazone* (**15c**) as a pale yellow solid which was recrystallised from dichloromethane–light petroleum (120 mg, 62%), m.p. (sealed tube) 180—182 °C (Found: C, 44.3; H, 7.3; N, 14.7; S, 16.7. $C_7H_{14}N_2O_2S$ requires C, 44.2; H, 7.4; N, 14.7; S, 16.8%); $\nu_{max.}$ 3 420 (NH), 1 620, 1 308, and 1 112 cm^{-1} (SO_2); δ_H 1.62, 1.76 (each 6 H, s, CMe_2), and 5.30 (2 H, br s exchanged by D_2O, NH_2); *m/z* 190 (M^+, 1%), 126 ($M^+ - SO_2$, 35), 109 (39), 84 ($M^+ - CMe_2SO_2$, 55), and 41 ($C_3H_5^+$, 100).

In some cases it was found that the product obtained in this way was contaminated with 2,2,4-trimethyl-3-thiapentanohydrazide 3,3-dioxide (**18**) in which case separation was effected by chromatography on Kieselgel (elution with 19 : 1 chloroform–methanol). In other cases, especially when the reaction mixture was more concentrated, the diazine (**19**) was isolated. For example, the thietanone (1.76 g) and anhydrous hydrazine (640 mg) in dioxane (100 cm^3) were heated under reflux for 45 h in an apparatus fitted with a Soxhlet extractor containing 3A molecular sieve. The mixture was poured into dichloromethane, washed with brine, dried, and the solvent removed under reduced pressure. The solid residue was recrystallised from chloroform–light petroleum (b.p. 40—60 °C) to give the *diazine* (**19**) (1.2 g, 69%), m.p. (sealed tube) 295—298 °C after further recrystallisation from chloroform–methanol–ether (Found: C, 48.1; H, 6.8; N, 8.1; S, 18.6%; M^+, 348.1174. $C_{14}H_{24}N_2O_4S_2$ requires C, 48.3; H, 6.9; N, 8.0; S, 18.4%; M^+, 348.1177), $\nu_{max.}$ 1 680, 1 310, and 1 105 cm^{-1} (SO_2); δ_H 1.72 and 1.75 (each 12 H, s, CMe_2).

2″,2″,3,3,4″,4″,5,5-*Octamethyl*-3,5-*dihydro*-4H-*diazole*-4-*spiro*-2′-(2′,5′-*dihydro*[1,3,4]*thiadiazole*)-5′-*spiro*-3″-*thietane* 1″,1″-*Dioxide* (**16a**).—An ice-cold solution of 2,2,4,4-tetramethylthietane-3-thione 1,1-dioxide[5] (130 mg) (**15b**) in dry ether (3 cm^3) was added to an ice-cold solution of 4-diazo-3,3,5,5-tetramethyl-4,5-dihydro-3*H*-pyrazole (**14d**)[6] [from 3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazol-4-one hydrazone (**14c**) (100 mg) and nickel peroxide (3 g)]. After 2 h at 0 °C the mixture was cooled to −78 °C to give the *dihydrothiadiazole* (**16a**) (143 mg, 64%) as a white solid, m.p. (sealed tube) 205—210 °C (decomp.), after crystallisation from chloroform–ether (Found: C, 48.6; H, 7.0; N, 16.6; S, 18.7. $C_{14}H_{24}N_4O_2S_2$ requires C, 48.8; H, 7.0; N, 16.3; S, 18.6%); $\nu_{max.}$ 1 123 and 1 310 cm^{-1} (SO_2); δ_H 1.27, 1.37, 1.48, and 1.62 (each 6 H, s).

2″,2″,3,3,4″,4″,5,5-*Octamethyl*-3,5-*dihydro*-4H-*diazole*-4-*spiro*-2′-*thiirane*-3′-*spiro*-3″-*thietane* 1″,1″-*Dioxide* (**17a**).—The dihydrothiadiazole (**16a**) (500 mg) was heated, without solvent, at 150 °C for 1 h to give the *episulphide* (**17a**) (460 mg, 100%), m.p. (sealed tube) 206—210 °C (decomp.), after recrystallisation from chloroform–ether (Found: C, 53.3; H, 7.8; N, 8.9; S, 20.2. $C_{14}H_{24}N_2O_2S_2$ requires C, 53.1; H, 7.7; N, 8.9; S, 20.3%); $\nu_{max.}$ 1 103, 1 150, and 1 303 cm^{-1} (SO_2); δ_H 1.56 (18 H, br s) and 1.96 (6 H, s).

3-(3,3,5,5-*Tetramethyl*-3,5-*dihydro*-4H-*pyrazol*-4-*ylidene*)-2,2,4,4-*tetramethylthietane* 1,1-*Dioxide* (**12**).—The episulphide (**17a**) (400 mg) was heated with trimethyl phosphite (400 mg) at 80 °C for 1 h. The excess of reagent was removed under reduced pressure and the residue washed with cold light petroleum to give a quantitative yield of the *alkene* (**12**), essentially pure, m.p. (sealed tube) 236—239 °C, after recrystallisation from chloroform–ether (Found: C, 58.9; H, 8.5; N, 9.8; S, 11.6. $C_{14}H_{24}N_2O_2S$ requires C, 59.1; H, 8.5; N, 9.9; S, 11.8%); $\nu_{max.}$ 1 108 and 1 300 cm^{-1} (SO_2); δ_H 1.63 (12 H, s) and 1.82 (12 H, s); *m/z* 192 ($M^+ - N_2SO_2$, 14%), 177 ($C_{13}H_{21}^+$, 19), and 149 ($C_{11}H_{17}^+$, 100).

2,2,2″,2″,4,4,4″,4″-*Octamethyl*-2′,5′-*dihydro*[1,3,4]*thiadiazole*-2′,5′-*dispiro*-3,3″-*bis*(*thietane*) 1,1,1″,1″-*Tetraoxide* (**16b**).—2,2,4,4-Tetramethylthietane-3-thione 1,1-dioxide (**15b**)[5] (250 mg) in dry tetrahydrofuran (2 cm^3) was added to a solution of 3-diazo-2,2,4,4-tetramethylthietane 1,1-dioxide (**15d**) [from the hydrazone (**15c**) (250 mg) and nickel peroxide (2.5 g)] in dry tetrahydrofuran (10 cm^3) at −35 to −20 °C under nitrogen. After several days at 0 °C a solid product had formed which was removed by filtration to give the *dihydrothiadiazole* (**16b**) (103 mg, 21%), m.p. 310—312 °C (decomp.), after recrystallisation from chloroform–ether (Found: C, 44.2; H, 6.5; N, 7.7; S, 25.3%; M^+, 380.0898. $C_{14}H_{24}N_2O_4S_3$ requires C, 44.2; H, 6.4; N, 7.4; S, 25.3%; M^+, 380.0891); $\nu_{max.}$ 1 310 and 1 120 cm^{-1} (SO_2); δ_H 1.43 (12 H, s) and 1.65 (12 H, s); *m/z* 380 (M^+, < 0.1%), 352 ($M^+ - N_2$, 0.4), 246 ($M^+ - N_2$, SO_2CMe_3, 73), 182 (45), 96 (100), and 81 (64).

2,2,2″,2″,4,4,4″,4″-*Octamethylthiirane*-2′,3′-*dispiro*-3,3″-*bis*(*thietane*) 1,1,1″,1″-*Tetraoxide* (**17b**).—The dihydrothiadiazole (**16b**) (65 mg) was heated (in the absence of solvent) at 160 °C for 40 min to give a quantitative yield of the *episulphide* (**17b**), m.p., after recrystallisation from chloroform–ether, 330—338 °C (decomp.) (Found: C, 47.7; H, 7.0; S, 27.1%; M^+, 352.0837. $C_{14}H_{24}O_4S_3$ requires C, 47.7; H, 6.9; S, 27.3%; M^+, 352.0837), $\nu_{max.}$ 1 310 and 1 110 cm^{-1} (SO_2); δ_H 1.44 and 1.92 (each 12 H, s); *m/z* 352 (M^+, 0.7%), 246 ($M^+ - SO_2CMe_2$, 71), 182 (40), 96 (100), and 81 (78).

2,2,2′,2′,4,4,4′,4′-*Octamethyl*-3,3′-*bithietanylidene* 1,1,1′,1′-*Tetraoxide* (**13**).—The episulphide (**17b**) (50 mg) was heated with trimethyl phosphite at 60 °C for 1 h. N.m.r. spectroscopy showed a complete, quantitative reaction. The excess of reagent was removed under reduced pressure and the residue chromatographed on silica gel (elution with chloroform) to give the *alkene* (**13**), m.p. (sealed tube) 336—346 °C (decomp.), after recrystallisation from chloroform–ether (Found: C, 52.2; H, 7.5; S, 19.8. $C_{14}H_{24}S_2O_4$ requires C, 52.5; H, 7.6; S, 20.0%); $\nu_{max.}$ 1 110 and 1 305 cm^{-1} (SO_2); δ_H 1.75 (24 H, s); *m/z* 256 ($M^+ - SO_2$, 2%), 192 ($M^+ - S_2O_4$, 28), and 149 ($M^+ - S_2O_4C_3H_7$, 100).

1-*Isopropylidene*-2,2,4,4,5,5-*hexamethylspiropentane* (**22**).—3,3,3′,3′,5,5,5′,5′-Octamethyl-3,3′,5,5′-tetrahydro-4,4′-bi(4*H*-pyrazolylidene) (**11**) (60 mg)[6] was passed through the flash vacuum pyrolysis apparatus at 430 °C and 8 × 10^{-3} mmHg. The only significant volatile product at these temperatures is the spiropentane (**22**) which was collected in a trap cooled with liquid nitrogen and then concentrated by distillation into a smaller trap on the vacuum line. The pure *spiropentane* (**22**) was thus obtained as a water-white liquid (45 mg, 98%) (Found: C, 87.1; H, 12.6. $C_{14}H_{28}$ requires C, 87.4; H, 12.6%); δ_H 1.15 (12 H, s, ring CMe_2), 1.16 (6 H, s, ring CMe_2), and 1.78 and 1.80 (each 3 H, s, vinyl CMe_2), δ_C 20.0, 21.6, 21.8 (ring CMe_2), 22.2, 22.5 (vinyl CMe_2), 21.3, 27.5, 39.9 (C-2, -3, -4, and -5 of the spiropentane skeleton, confirmed as quaternary carbons by weak noise decoupling), and 115.2 and 130.5 (vinyl carbons); *m/z* 192 (M^+, 16%), 177 ($M^+ - CH_3$, 16), 149 ($M^+ - C_3H_7$, 89), and 108 ($C_8H_{12}^+$, 100).

2,5-*Dimethyl*-4-*isopropyl*-3-*isopropylidenehexa*-1,4-*diene* (**23**).[23]—Compound (**23**) was obtained in a similar manner by pyrolysis of 1,2-di-isopropylidene-3,3,4,4-tetramethylcyclobutane (**32**)[24] at *ca.* 600 °C and was obtained as a water white liquid, b.p. 80 °C/10 mmHg (Found: M^+, 192.1879. $C_{14}H_{24}$ requires M^+, 192.1878); δ_H 0.90, 0.99 [each 3 H, d, *J* 7 Hz, $(CH_3)_2CH$ with hindered rotation, collapsed to 2 s by irradiation of the signal at δ 2.82], 1.54, 1.70, 1.73, 1.78 (15 H, each s, vinyl Me), 2.82 [1 H, sept., *J* 7 Hz, $CH(CH_3)_2$], and 4.74, 5.0 (each 1 H, br, $C{=}CH_2$); δ_C 19.2, 19.6, 20.8, 21.9, 22.2, 22.4, 30.9

(5 × CH_3 and 1 × Pr^i), and 114.6, 126.3, 128.0, 136.9, 137.8, 146.7 p.p.m. (6 × vinyl C). Hydrogenation at atmospheric pressure in methanol using 10% palladium on charcoal as the catalyst gave 3,4-di-isopropyl-2,5-dimethylhexa-2,4-diene[23] (Found: M^+, 194.2035. $C_{14}H_{26}$ requires M^+, 194.2034); δ_H 0.95, 1.07 [each 6 H, each d, *J* 7 Hz, $(CH_3)_2CH$ with hindered rotation, collapsed to 2 s by irradiation of the signal at δ 2.71], 1.50, 1.73 (each 6 H, s, vinyl CH_3), and 2.71 [2 H, m, *J* 7 Hz, $(CH_3)_2CH$]. A sample of the triene was sealed in a tube with liquid sulphur dioxide and heated on a steam-bath for 30 h. After removal of the sulphur dioxide the residue was chromatographed on Kieselgel (elution with chloroform) to give 2,2,4-*trimethyl*-3-(2,4-*dimethylpent*-2-*en*-3-*yl*)-2,5-*dihydrothiole* 1,1-*dioxide* (**52**), m.p. 60—61 °C, after recrystallisation from light petroleum (b.p. 60—80 °C) (Found: C, 65.6; H, 9.2; S, 12.4%; M^+, 256.1497. $C_{14}H_{24}SO_2$ requires C, 65.6; H, 9.5; S, 12.5%; M^+, 256.1497); $\nu_{max.}$ ($CHCl_3$) 1460, 1 300, and 1 100 cm^{-1} (SO_2); δ_H 0.97, 1.11 [each 3 H, d, *J* 7 Hz, $(CH_3)_2CH$ with hindered rotation, collapsed to s by irradiation of the signal at δ 2.77], 1.26 (6 H, s, CMe_2), 1.59, 1.67, 1.81 (total 9 H, s, vinyl CH_3), 2.77 [1 H, m. $CH(CH_3)_2$], and 3.4—3.9 (2 H, m, CH_2); *m/z* 256 (M^+, 19%), 192 ($M^+ - SO_2$, 12), 177 (16), and 149 (100).

2-(2,3-*Dimethylbut*-1-*en*-3-*yl*)-1-*isopropyl*-3,3-*dimethylcyclopropene* (**27**).—3,3,3′,3′,5,5,5′,5′-Octamethyl-3,3′,5,5′-tetrahydro-4,4′-bi(4*H*-pyrazolylidene) (**11**)[6] (1.2 g) was subjected to f.v.p. at 570 °C and 2—6 × 10^{-3} mmHg in eight batches of 150 mg each. The volatile products were trapped using liquid nitrogen and concentrated by trap-to-trap distillation on the vacuum line. Analytical g.l.c. showed that the product contained the cyclopropene (**27**) (*ca.* 12%), spiropentane (**22**), (18%), and triene (**23**), (64%). The product was separated by preparative g.l.c. on a PYE 104 instrument equipped with a 9:1 stream splitter and using a 7 ft × 7 mm column of 15% Carbowax 20M + PTA at an oven temperature of 100 °C to yield the *cyclopropene* (**27**) as a water-white liquid (Found: M^+, 192.1879. $C_{14}H_{24}$ requires M^+, 192.1878); δ_H 1.08 (6 H, d, *J* 7 Hz, Me_2CH), 1.12, 1.25 (each 6 H, s, CMe_2), 1.76 (3 H, s, vinyl Me), 2.75 (1 H, sept., *J* 7 Hz, Me_2CH), and 4.71 and 4.78 (each 1 H, m, $C{=}CH_2$); δ_C 20.2, 20.6, 21.8, 26.1, 26.7, 26.9, 40.7, 108.5, 151.0 ($C{=}CH_2$),[14] and 127.4 and 126.6 (cyclopropene C=C).[14,15]

1,2-*Di-isopropylidene*-3,3,4,4-*tetramethylcyclobutane* (**32**).[24]—Tetramethylallene was prepared by thermal cracking of 3-hydroxy-2,2,4-trimethylpent-3-enoic acid β-lactone[25] and was redistilled, b.p. 86—91 °C, δ_H 1.65. The allene (3 g) was sealed in a base-washed 100 cm^3 Carius tube and heated at 194 °C for 24 h to give the allene dimer which was distilled, b.p. 50 °C/10 mmHg; δ_H 1.08 (12 H, s, ring CMe_2) and 1.68 (12 H, s, vinyl CMe_2). If the glassware was not base-washed the major product was 2,4-dimethylpenta-1,3-diene; δ_H 1.69, 1.84 (total 9 H, br s, vinyl CH_3), and 4.82, 5.02, and 5.77 (each 1 H, br s, vinyl H). If the pyrolysis time was increased to 80 h and the temperature to 225 °C a virtually quantitative yield of 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (**23**) was obtained, b.p. 190—195 °C.

1-*Isopropyl*-2-*isopropenyl*-3,3,4,4-*tetramethylcyclobutene* (**35**).[13]—1,2-Di-isopropylidene-3,3,4,4-tetramethylcyclobutane (1.0 g) in benzene (15 cm^3) was photolysed using a medium-pressure Hanovia lamp with a Pyrex filter until n.m.r. spectroscopy showed the reaction to be complete (4 h). The solvent was removed under reduced pressure and the residue subjected to preparative g.l.c. on a Pye 104 instrument with a 7 ft × 7 mm column packed with 15% Carbowax 20M + PTA at 100 °C. The cyclobutene was isolated as a water-white liquid, δ_H 1.09, 1.13 (each 6 H, s, CMe_2), 1.10 [6 H, d, *J* 7 Hz, $(CH_3)_2CH$], 1.90 (3 H, t, *J* 1 Hz, vinyl CH_3), 2.88 [1 H, sept., J 7 Hz, $(CH_3)_2CH$], and 4.81 (2 H, m, $C{=}CH_2$).

o-*Cymene*.[26]—*o*-Toluic acid was converted into the acid chloride which was treated with methylmagnesium iodide to give 2-(2-methylphenyl)propan-2-ol; $\nu_{max.}$(film) 3 350 cm^{-1} (OH). Acid-catalysed dehydration gave 2-(2-methylphenyl)-propene; δ_H 2.03 (3 H, br s, vinyl CH_3), 2.32 (3 H, s, $ArCH_3$), 4.90, 5.22 (each 1 H, br s, $C{=}CH_2$), and 7.2 (4 H, s, ArH), which was hydrogenated at atmospheric pressure in methanol solution using 10% palladium on carbon as a catalyst to give *o*-cymene, δ_H 1.23 [6 H, d, *J* 7 Hz, $CH(CH_3)_2$], 2.33 (3 H, s, ArMe), 3.13 [1 H, sept., *J* 7 Hz, $CH(CH_3)_2$], and 7.0—7.3 (4 H, m, ArH).

m-*Cymene*.[26]—*m*-Toluic acid was converted into the acid chloride which was treated with methylmagnesium iodide. Acid work-up gave 2-(3-methylphenyl)propan-2-ol, δ_H 1.57 (6 H, s, CMe_2), 1.95 (1 H, br s, OH), 2.34 (3 H, s, ArMe), and 6.9—7.5 (4 H, m, ArH). Acid-catalysed dehydration gave 2-(3-methylphenyl)propene, δ_H 2.14 (3 H, br s, vinyl Me), 2.35 (3 H, s, ArMe), 5.05, 5.33 (each 1 H, br s, $C{=}CH_2$), and 7.0—7.5 (4 H, m, ArH), which was hydrogenated at atmospheric pressure in methanol solution using 10% palladium on carbon as the catalyst to give *m*-cymene, δ_H 1.24 [6 H, d, *J* 7 Hz, $CH(CH_3)_2$], 2.31 (3 H, s, ArMe), 2.88 [1 H, m, $CH(CH_3)_2$, and 7.0—7.4 (4 H, m, ArH).

2,5-*Dimethylisopropylbenzene*.[27]—Reaction of *p*-xylene with acetyl chloride–aluminium trichloride in carbon disulphide gave 2,5-dimethylacetophenone, b.p. 227—230 °C, $\nu_{max.}$ (film) 1 685 cm^{-1} (C=O); δ_H 2.34, 2.48, 2.55 (each 3 H, s, Ar*Me* and CO*Me*), 7.16 (2 H, AB quartet, aryl 3- and 4-H), and 7.52 (1 H, br s, aryl 6-H). Reaction with methylmagnesium iodide and acid work-up gave 2-(2,5-dimethylphenyl)propan-2-ol, $\nu_{max.}$(film) 3 380 cm^{-1} (OH); δ_H 1.57 [6 H, s, $C(CH_3)_2$], 1.77 (1 H, s, OH), 2.27, 2.48 (each 3 H, s, ArMe), 6.93 (2 H, AB quartet, aryl 3- and 4-H), and 7.20 (1 H, br s, aryl 6-H). Reaction with hydrogen iodide and red phosphorus in glacial acetic acid gave a mixture of reduction and dehydration products which was fully hydrogenated to 2,5-dimethylisopropylbenzene using 10% palladium on carbon as the catalyst; δ_H 1.27 [6 H, d, *J* 7 Hz, $CH(CH_3)_2$], 2.30 (6 H, s, ArMe), 3.13 (1 H, septet, *J* 7 Hz, $CHMe_2$), and 6.8—7.2 (3 H, m, ArH).

High-temperature F.V.P. of 4-*Isopropyl*-3-*isopropylidene*-2,5-*dimethylhexa*-1,4-*diene* (**23**).—A sample of the triene (**23**) (1.0 g) was subjected to f.v.p. at *ca.* 750 °C and 3 × 10^{-3} mmHg. The volatile products were collected in a liquid nitrogen cooled trap and concentrated by trap-trap distillation on the vacuum line in the usual manner. The cold trap was detached from the vacuum line, allowed to warm to room temperature, and the gases evolved (*ca.* 70 cm^3) collected by downward displacement of water. The mixture of gases was analysed* by gas chromatography on a Perkin-Elmer 900 GLC instrument using a 2 m × 3 mm Porapak Q column using a standard temperature programmed routine starting at 80 °C, and the components were identified by a comparison of the retention times with those of standard mixtures of gases (methane, ethane, ethylene, acetylene, allene, propane, propene, butane, isobutane, all butene isomers, and isobutene). The liquid products were separated by preparative g.l.c. using a Pye 104 instrument with a 7 ft × 7 mm (4 mm i.d.) column packed with Carbowax 20M on 80/100 mesh Chromosorb at 100 °C. Three major components were isolated pure. Recovered triene (**23**) was identified by g.l.c.

* Experiments performed by Mr D. G. Mills, Department of Physical Chemistry.

retention time and ^{1}H n.m.r. spectroscopy; *p*-xylene (**28**) by its g.l.c. retention time and ^{1}H and ^{13}C n.m.r. spectra; and *o*-cymene (**29**) by its g.l.c. retention time and ^{1}H n.m.r. spectrum. A portion of the liquid product was also analysed by mass spectroscopy by g.l.c. which showed components with *m/z* 192 ($C_{14}H_{24}$, isomer of starting material), 148 ($C_{11}H_{16}$, dimethylisopropylbenzene isomer), 134 ($C_{10}H_{14}$, cymene isomer), and 106 (C_8H_{10}, xylene isomer).

Photosensitised Photolysis of 3-(3,3,5,5-*Tetramethyl*-3,5-*dihydro*-4H-*pyrazol*-4-*ylidene*)-2,2,4,4-*tetramethylthietane* 1,1-*Dioxide* (**12**).—The dihydropyrazole sulphone (**12**) (66 mg) and benzophenone (600 mg) in benzene (4 cm^3) was photolysed in the normal manner until n.m.r. spectroscopy showed that all of the starting material had gone (45 min). The solvent was removed and the residue chromatographed on silica eluting with 1:2 chloroform–light petroleum to give a *ca.* 1:3 mixture of 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)-thietane 1,1-dioxide (**41**)[7] and 2′-isopropylidene-2,2,3′,3′,4,4-hexamethylthietane-3-spiro-1′-cyclopropane 1,1-dioxide (**45**) (40 mg, 67%), $\nu_{max.}$ 1 110 and 1 295 cm^{-1} (SO_2); δ_H [peaks attributable to compound (**45**)] 1.22, 1.29, 1.76 (each 6 H, s, ring Me's), and 1.81, 1.95 (each 3 H, s, vinyl Me's); δ_C [peaks attributable to compound (**45**)] 21.6, 21.9, 22.0, 23.0, 23.2 (methyls), 23.9, 39.4, 80.7 (C-2, -4, and -3′, confirmed as arising from quaternary carbon by the INEPT technique), and 145.0 (vinyl C); *m/z* 256 (M^+, 0.2%), 192 ($M^+ - SO_2$, 29), 177 (21), and 149 (100). Repeated chromatography using a variety of solvents and stationary phases resulted in material from which some of the minor product had been removed, but a complete separation of the two components was never achieved.

Pure 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)thietane 1,1-dioxide (**41**) was prepared by direct photolysis of the dihydropyrazole sulphone (**12**). This showed spectroscopic and other physical properties identical with those previously reported;[7] also δ_C 21.5, 23.9 (CMe_2 groups), 22.2 (cyclopropyl CMe_2; confirmed as quaternary C by the INEPT technique), 81.7 (thietane CMe_2), and 128.3 and 139.6 p.p.m. (C=C). This material was stable to photolysis in the presence of benzophenone.

Photosensitised Photolysis of 3,3,3′,3′5,5,5′,5′-*Octamethyl*-3,3′,5,5′-*tetrahydro*-4,4′-*bi*(4H-*pyrazolylidene*) (**11**).[11]—A mixture of the bi(pyrazole) (**11**)[6] and benzophenone (50—150 mg; 50—300 mg; 50—600 mg; 10—600 mg; and 5—600 mg) in benzene (2 cm^3) was photolysed in an n.m.r. tube in the usual manner. The progress of the reaction was periodically monitored both by n.m.r. spectroscopy and by g.l.c. In the ^{1}H n.m.r. spectrum the starting material in benzene showed a singlet at δ 1.39, the product monopyrazole (**21**) signals at δ 1.39 and 0.96, the spiropentane (**22**) signals at δ 1.2 and 1.8 (br) and the allene dimer (**32**) signals at δ 1.07 and 1.62 (br). Both n.m.r. and g.l.c. confirmed that compounds (**21**), (**22**), and (**32**) were the only significant products in the initial stages, but on prolonged photolysis a broad envelope corresponding to a complex mixture of products developed in the n.m.r. spectrum. The dependence of product ratio on the ratio of starting bis(pyrazole) to sensitiser is shown in Figure 2. This data is based on initial product ratios (formed after 5—10 min photolysis) and is based on g.l.c. peak areas uncorrected for (f.i.d.) detector response ratios. On prolonged photolysis the allene dimer (**32**) was slowly destroyed and in the g.l.c. a slow increase was noted in the spiro compound (**22**) to allene dimer (**32**) ratio. In separate experiments under comparable conditions it was shown that sensitised photolysis of compounds (**21**) and (**22**) did not give rise to any allene dimer (**32**).

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