The Effects of Methyl Substituents on the Trimethylenemethane† Diradical

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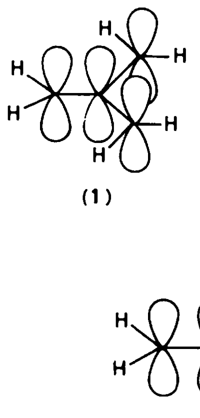
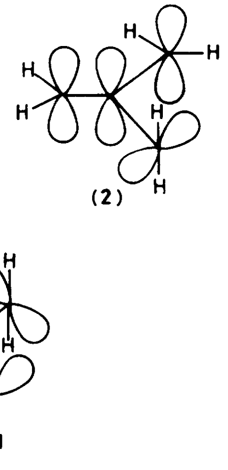
A simple, semiquantitative model for the effect of methyl substituents on the trimethylenemethane (TMM) diradical is advanced. In this, as in previous models, each methyl substituent is assumed to stabilise the diradical by *ca.* 2.8 kcal mol^{-1} per odd electron. It is further proposed that the steric factors associated with methyl substituents can be estimated from the same parameters as are used in the conformational analysis of cyclohexane derivatives. One prediction of this model is that the chemistry of singlet hexamethyl-TMM should be dominated by species adopting mono- and bis-orthogonal geometries. Existing evidence in support of the prediction is surveyed and further supporting evidence is drawn from studies of the flash vacuum pyrolysis of 4-isopropylidene-3,3,5,5-tetramethyl-4,5-dihydro-3*H*-pyrazole (**9b**), 3-isopropylidene-2,2,4,4-tetramethylthietane 1,1-dioxide (**12b**), and their deuteriated derivatives. The kinetic product ratio for thermal dediazenation of 4-([$^2H_6$]isopropylidene)-3,3,5,5-tetramethyl-4,5-dihydro-3*H*-pyrazole (**9a**) is *ca.* 71 : 29 {3-[$^2H_6$]isopropylidene-1,1,2,2-tetramethylcyclopropane (**10a**) to [1,1-*dimethyl*-$^2H_6$]-3-isopropylidene-1,1,2,2-tetramethylcyclopropane (**11a**)}.

Many theoreticians have been attracted to the problems posed by the π-diradical trimethylenemethane. Theoretical work in this area has been summarised in a number of reviews[1] and papers[2,3] and more recent studies include those by Borden[4] and by Pitzer.[5] Because of the difficulties involved most workers have concentrated on the parent system, although some calculations on the related 2-methylenecyclopentane-1,3-diyl[5–8] and on the effects of methyl[5,6] and vinyl[3,7,9,10] substituents have been reported. By way of contrast to the theoretical studies, most experimental work has been concerned with ethylene-bridged[11] and methyl-substituted[12–17] TMM derivatives; these experimental studies suggest that the effect of substituents is profound. The effect of ethylene bridging (as in 2-methylenecyclopentane-1,3-diyl) has recently been summarised and discussed by Berson;[11] in the present paper we present a simple semiquantitative treatment of the effect of methyl substituents as well as further experimental evidence concerning the geometry of hexamethyl-TMM.‡



(1)



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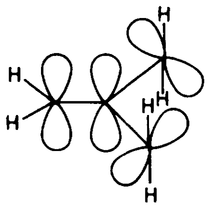

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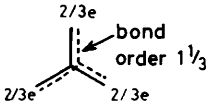
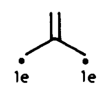


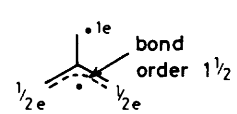
planar $^3A_2'$ ($^3B_2$)

(4)



planar $^1A_1$

(5)



planar $^1B_2$
mono-orthogonal
$^1B_1$ and $^3B_1$

(6)

The behaviour of the TMM diradical has usually been discussed in terms of three key geometries, planar (**1**), mono-orthogonal (**2**),[18] and bis-orthogonal (**3**).[13–17,19] The planar and mono-orthogonal geometries encompass many of the significant maxima and minima on the singlet and triplet energy surfaces. Singlet TMM in its bis-orthogonal geometry is usually presumed to collapse directly to methylenecyclopropane. Calculations on planar D_{3h} TMM (all C–C bond lengths and all C–C–C bond angles equal) predict that the ground state should be a triplet (**4**) ($^3A_2'$ in D_{3h} symmetry but often referred to as $^3B_2$ according to its C_{2v} classification) and that the two lowest-energy components of the singlet state ($^1E'$) should be degenerate. The Jahn-Teller theorem, however, applies to this state. In-plane distortion from D_{3h} to C_{2v} symmetry lifts this degeneracy and gives rise to two singlet states ($^1A_1$ and $^1B_2$). The lower-energy $^1A_1$ state in its optimum geometry has one short and two long C–C bonds and can be thought of as ethylene interacting weakly with two radical centres (**5**). The higher-energy $^1B_2$ state in its optimum (planar) geometry has one long and two short C–C bonds and can be thought of as an allyl radical plus an electron localised in a *p* orbital (**6**). This planar $^1B_2$ state can, however, be stabilised by rotating the unique CH_2 group by 90°. This gives the mono-orthogonal $^1B_1$ singlet. The energy of the mono-orthogonal $^3B_1$ triplet is calculated to lie just below this $^1B_1$ singlet. Whereas there seems to be a degree of agreement as to the ordering of energies of these various states (planar $^3B_2$ < mono-orthogonal $^3B_1$ < mono-orthogonal $^1B_1$ < planar $^1A_1$ < planar $^1B_2$) there has been considerable discussion of some of the actual energy differences; particularly that between $^3B_2$ and $^1B_1$ states[20,21] and that between the $^1B_1$ and $^1B_2$ states.[3,21] For the purposes of this paper we will make use of the results of Davidson and Borden's STO-3G (SDQ-CI) calculations[21] on the parent system together with an assumed $^1B_1/^3B_1$ separation of 1.2 kcal

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† Systematic name: 2-methylenepropane-1,3-diyl.

‡ Systematic name: 3-isopropylidene-2,4-dimethylpentane-2,4-diyl.

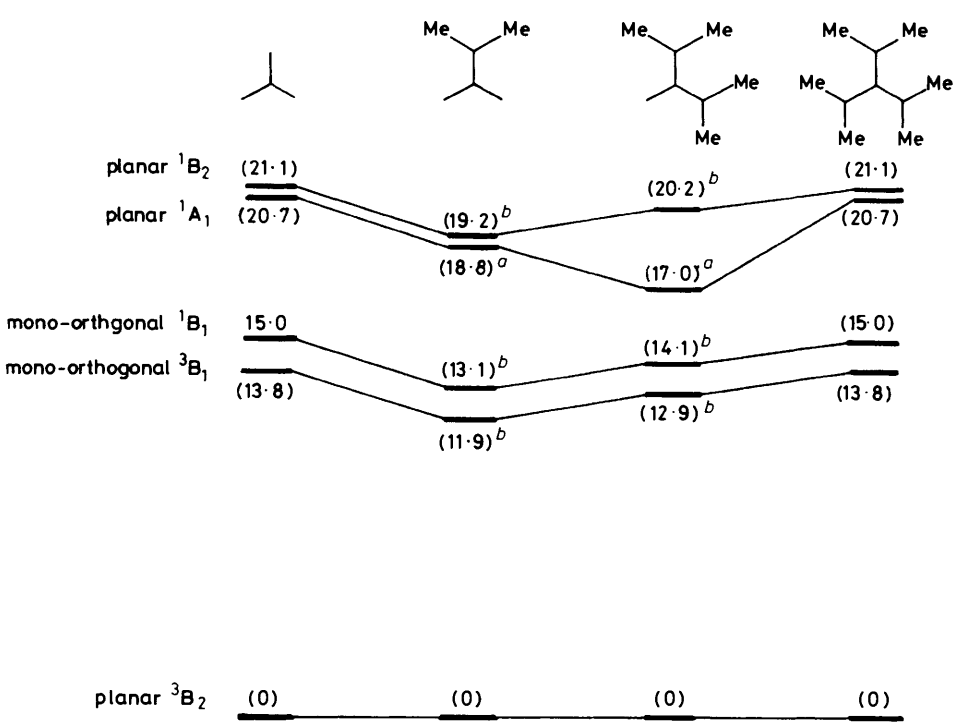

Figure 1. Effect of substituents on the relative energies (kcal mol^{-1}) of the various states of TMM; 'electronic effect' only.[5] [a] CH$_2$ unique or orthogonal carbon. [b] CMe$_2$ unique or orthogonal carbon.

mol^{-1}.[3,5] This gives a set of relative energies for the states which are fairly typical, namely $^3B_2$ (0 kcal mol^{-1}), $^3B_1$ (13.8), $^1B_1$ (15.0), $^1A_1$ (20.7), and $^1B_2$ (21.1). The effect of methyl substituents on this system may be divided into a steric and and an electronic component. The electronic component can be roughly accounted for by using the method suggested by Borden and Davidson,[6] which assumes a stabilisation factor of 2.8 kcal mol^{-1} per odd electron for methyl substitution at radical centres.[5] For a series of di-, tetra-, and hexa-methylated TMMs the 'electronic' effect on the relative energies of the states is as shown in Figure 1. The steric effect is more difficult to account for. However, since the separation of the two substituents on a planar TMM (**7**) (2.48 Å at a C–C bond length of 1.43 Å[*])[3,6,22] is similar to the separation of 2.51 Å for two 1,3-diaxial substituents on a chair cyclohexane (**8**), we suggest that, as a first approximation, the well established steric parameters that are used in cyclohexane conformational analysis can be extrapolated to the TMM series. For this paper we have adopted relative values for *cis*-1,3-interactions of H/H = 0, H/Me = 0.9, and Me/Me = 4.0 kcal mol^{-1}.[23] Inclusion of these steric factors substantially modifies the scheme in Figure 1 and gives the relative energies shown in Figure 2. Whereas some of the detailed changes shown in this Figure are dependent on the choice of parameters and may not be significant the gross trends are reasonably independent of this choice. In particular Figure 2 suggests that permethylation should significantly stabilise mono-orthogonal relative to planar geometries. This should apply *a fortiori* to the bis-orthogonal geometry. This means that: (i)[†] although the triplet should still be planar[24–26] the barrier to C–C bond rotation should be much less than in the parent system; (ii) permethylation destabilises the planar singlet species to an extent that the chemistry of singlet hexamethyl-TMM should be dominated by mono-orthogonal (and probably bis-orthogonal) species; (iii) permethylation should reduce the separation between the lowest singlet and triplet states.

Experimental evidence to some extent supports these conclusions. Triplet-sensitised photolysis of the pyrazoline (**9a**)[13,16] gives a 1:2 mixture of the cyclopropanes (**10a**) and (**11a**). The reaction is thought to go through the triplet hexamethyl-TMM and the product distribution is consistent with a planar intermediate although other geometries in which all three carbon atoms are equivalent or kinetically equivalent are also possible. So far as the singlet diradicals are concerned many studies of 'lightly' substituted TMM derivatives have been successfully interpreted in terms of a mixture of planar and mono-orthogonal geometries,[27,28] whereas those on hexa- and penta-substituted singlet TMM seem to point to a mixture of mono- and bis-orthogonal geometries.[12–17,19] Evidence comes from the kinetics of thermal dediazenation of pyrazolines of the type shown in formula (**9**) (X,Y = H, alkyl, aryl, ester, cyano, and/or chloro)[15,17] and from the product ratio (**10**):(**11**) obtained on photolysis of these pyrazolines.[16] In particular the tendency to form the least-motions product (**10**) on photolysis can only be interpreted in terms of a predominantly bis-orthogonal geometry for the singlet. The aim of the present paper is to discover whether, like the photochemical reactions,

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[*] This C–C bond length is roughly that found in the TMM–Fe(CO)$_3$ complex[22] and that calculated for triplet TMM.[3,6] For singlet TMM some bonds are calculated to be shorter and this would lead to greater steric repulsion.

[†] Consideration of only two or three key geometries is a simplification. More realistically we would perhaps expect this triplet to be close to planarity but the steric repulsion between *cis*-1,3-substituents would probably be partly relieved by a small conrotation of each CMe$_2$ group to give a geometry analogous to that found in other tetramethylallyl species.[24] Unfortunately attempts to obtain the e.s.r. spectrum of the hexamethyl-TMM triplet (which might provide some direct evidence concerning its geometry) by low-temperature photolysis of the corresponding pyrazoline or cyclobutanone, or by γ-irradiation of the methylenecyclopropane,[25] have so far failed.[26]

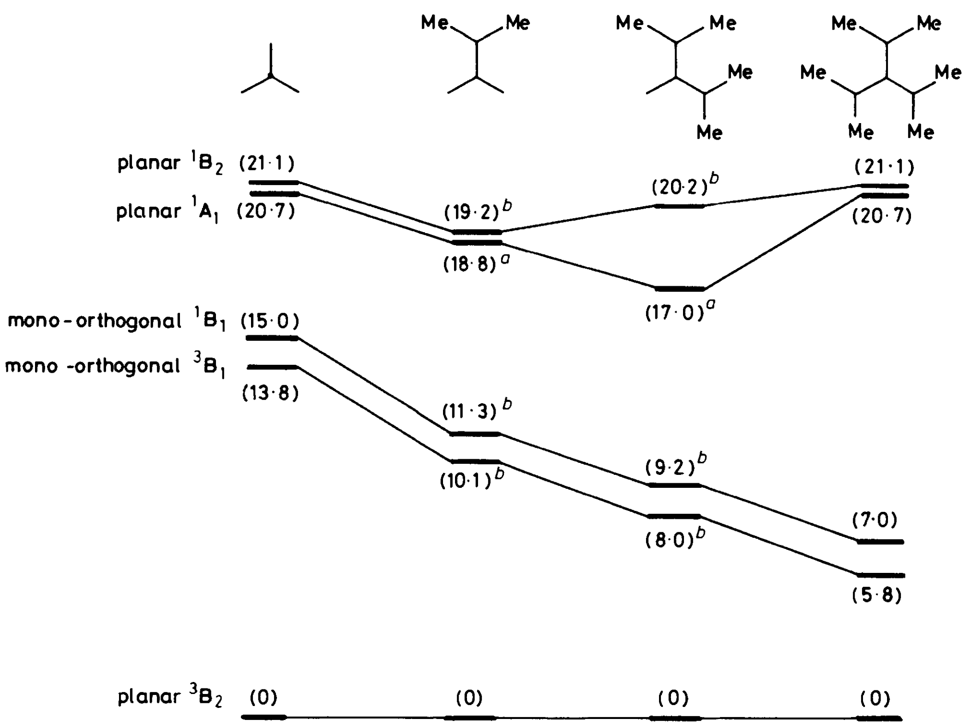
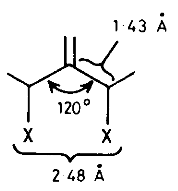


Figure 2. Effect of substituents on the relative energies (kcal mol^{-1}) of the various states of TMM; 'electronic' + 'steric' effects (see text). ^{a} CH_2 unique or orthogonal carbon. ^{b} CMe_2 unique or orthogonal carbon.



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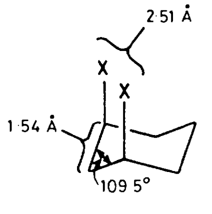

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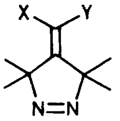

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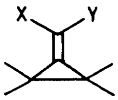

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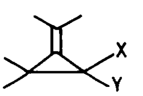

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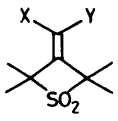
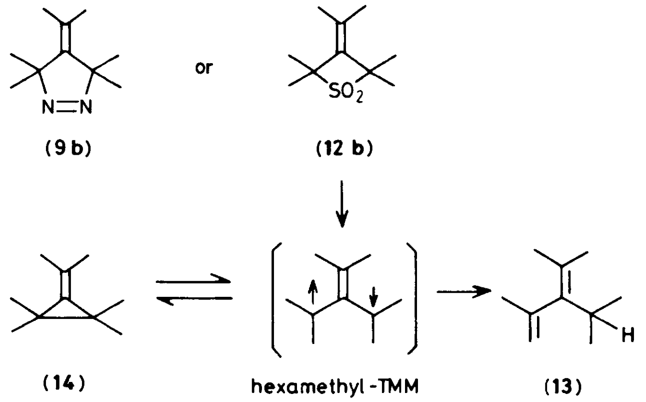


(12)

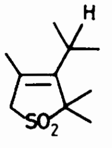
a; $X = Y = CD_3$
b; $X = Y = CH_3$

the thermal dediazenations of these pyrazolines and the related thermal elimination of sulphur dioxide from the thietanes (**12**) show a tendency to give least-motions products; a more demanding problem since the methylenecyclopropanes formed thermally interconvert making it difficult to obtain kinetic product ratios.

We initially investigated the flash vacuum pyrolysis (f.v.p.) of the thietanes (**12a** and **b**). Previous studies had shown that f.v.p. of the thietane (**12b**) at and above 770 °C gave a quantitative yield of the diene (**13**).[2] At lower temperatures some cyclopropane (**14**) could be detected,[13] but at these lower temperatures mainly starting material was recovered. The lowest practicable operating temperature was *ca.* 650 °C, which gave a mixture of *ca.* 90% unchanged thietane, 5% diene (**13**), and 5% methylenecyclopropane (**14**). These reactions are most simply rationalised in terms of a common hexamethyl-TMM intermediate as shown in the Scheme. F.v.p. of the hexadeuteriated thietane (**12a**) at 800 °C gave a product which, as assessed directly by ^1H n.m.r. spectroscopy or (more easily) *via* the ^1H n.m.r. spectrum of its crystalline sulphur dioxide adduct (**15**), had an almost statistical distribution of deuterium. This is not necessarily evidence for a symmetrical TMM intermediate. The result is more likely to reflect scrambling of the label *via* the methylenecyclopropane (**14**) and possibly also *via* 1,5-hydrogen shifts in the product. Since usable yields of hydrocarbon could not be obtained at lower temperatures, attention was switched to the pyrazolines (**9a** and **b**). The f.v.p. of the pyrazoline (**9b**) follows a similar course to that of thietane. At *ca.* 800 °C only



Scheme. Probable mechanistic course of the f.v.p. of compounds (**9a**), (**12a**), and (**14**)



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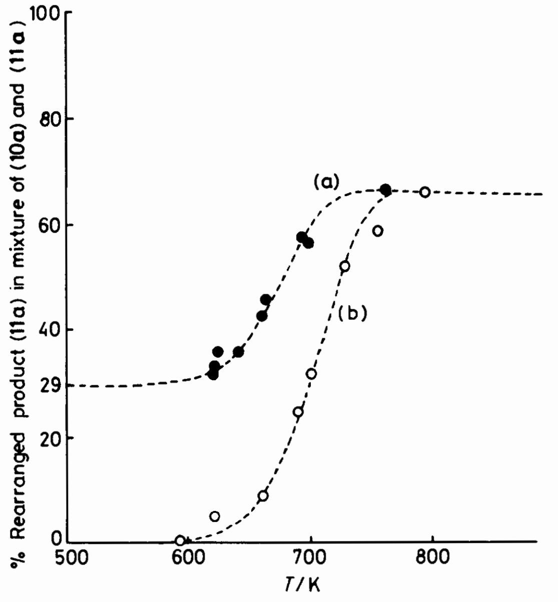

Figure 3. Composition of the mixture of cyclopropanes produced by the flash vacuum pyrolysis of (a) 4-([$^2H_6$]-isopropylidene)-3,3,5,5-tetramethyl-4,5-dihydro-3*H*-pyrazole (**9a**) and (b) 3-([$^2H_6$]isopropylidene)-1,1,2,2-tetramethylcyclopropane (**10a**) at various column temperatures; the dotted lines are the result of a computer-generated best fit to the experimental data (see text)

the diene was obtained and below 500 °C essentially only the cyclopropane. The main difference was that, since thermal dediazenation is easier than elimination of SO_2 even at temperatures as low as 350 °C, detectable amounts of hydrocarbon were obtained. When the hexadeuteriated pyrazoline (**9a**) was subjected to f.v.p. at *ca.* 800 °C and the diene obtained converted into its sulphur dioxide adduct (**15**), once again, a near-statistical scrambling of the label was observed. However, when pyrazoline (**9a**) was subjected to pyrolysis at 400 °C and below, the cyclopropanes (**10a**) and (**11a**) were obtained and the mixture always contained more than the statistical amount of the least-motions product (**10a**). The actual compositions of the mixtures of hydrocarbon products are shown in Figure 3 together with the results of an independent study of the thermal isomerisation of the methylenecyclopropane (**10a**) to its isomer (**11a**) under identical f.v.p. conditions. From this it is clear that, at the lower end of the temperature range employed for the f.v.p. of the pyrazoline (**9a**), there would have been very little thermal interconversion of the products. The curves fitted to the data points in Figure 3 are the result of a computer simulation. In making this simulation it was assumed that the contact times were constant (0.001 s) over the temperature range and that the reactions followed the Arrhenius rate law. The best fit to the experimental data for the pyrazoline was obtained using a kinetic product ratio [(**10a**):(**11a**)] of 71:29. Attempted fits to the data using an assumed initial % of (**11a**) outside the range 28—30% were unsuccessful. At the lower end of the temperature range employed (*ca.* 350 °C) the actual yields of dediazenation products were very low and there was a high recovery of unchanged pyrazoline. In all cases the ^1H n.m.r. spectrum of this recovered pyrazoline showed no evidence for scrambling of the deuterium label.

The f.v.p. results obtained here suggest that, if these reactions indeed pass through a singlet hexamethyl-TMM intermediate,[17,28—30] this is generated principally in a bis-orthogonal geometry. They are in agreement with our previous studies of hexamethyl-TMM and with the simple model for the effect of methyl substituents on the geometry of TMM described at the beginning of this paper.

Experimental

The syntheses of the pyrazolines (**9a**)[16] and (**9b**)[14] and the thietane (**12b**)[12] have been described in previous papers in this series. The synthesis of the specifically deuteriated thietane (**12a**) was essentially the same as that of its non-deuteriated analogue except that [$^2H_6$]acetone was used to prepare the 2-diazopropane.[16]

3-([$^2H_6$]*Isopropylidene*)-1,1,2,2-*tetramethylcyclopropane* (**10a**).—Newmann's isopropylidenecarbene precursor (5,5-dimethyl-3-nitroso-oxazolidin-2-one) was prepared in a manner analogous to that for the non-deuteriated material,[31] except that [$^2H_6$]acetone was used for the initial Reformatsky reaction.[32] A stirred mixture of the pure, recrystallised nitroso compound (4.0 g; dried over P_2O_5) and 2,3-dimethylbut-2-ene (21 g) in a 250 cm^3 flask equipped with a double-surface condenser was treated with the lithium salt of 2-ethoxyethanol[31] (rapid addition of two portions of 2 g each, dried over P_2O_5). A vigorous reaction ensued and a froth developed which filled the flask. Ice-cold water was added, and the organic layer was washed with further portions of ice-cold water (5 × 100 cm^3), and dried ($MgSO_4$). Most of the 2,3-dimethylbut-2-ene was removed by distillation. Analytical g.l.c. showed that the residue (3.5 g) consisted of *ca.* 1:3 cyclopropane:starting material (g.l.c. yield *ca.* 33%). It was subjected in small portions to preparative g.l.c. on a 9 ft column packed with 10% polyethylene glycol succinate at 45 °C. The product was trapped on firebrick coated with Apiezon. It was removed from the Apiezon and concentrated into a small trap by vacuum-line distillation, to give the cyclopropane (150 mg; isolated yield 4%) which was pure according to analytical g.l.c. and ^1H n.m.r. spectroscopy.

Although the yield obtained was very low, this route, based on Newmann's isopropylidenecarbene precursor, was preferable to that based on Seyferth's method.[33] 3-([$^2H_6$]Isopropylidene)-1,1,2,2-tetramethylcyclopropane prepared by a suitable modification of Seyferth's route contained impurities which could not be removed by preparative g.l.c.

Flash Vacuum Pyrolysis of 3-([$^2H_6$]*Isopropylidene*)-2,2,4,4-*tetramethylthietane* 1,1-*Dioxide* (**12a**), 4-([$^2H_6$]*Isopropylidene*)-3,3,5,5-*tetramethyl*-4,5-*dihydro*-3H-*pyrazole* (**9a**), *and* 3-([$^2H_6$]-*Isopropylidene*)-1,1,2,2-*tetramethylcyclopropane* (**10a**).—The thietane (**12a**) (200 mg) was subjected to f.v.p. at 800 °C using the apparatus previously described.[12,17,29] The volatile products were collected in a large, liquid nitrogen-cooled, trap and then concentrated into a smaller trap by vacuum-line distillation. Sulphur dioxide (3 vols) was also distilled into this trap, which was sealed and heated at 100 °C for 2 days. The 2,5-dihydro-3-isopropyl-2,2,4-trimethylthiole 1,1-dioxide (**15**) obtained by this reaction showed physical data in agreement with those reported previously.[12] The ^1H n.m.r. spectrum was integrated six times; the average results were: $\delta_H(CDCl_3)$ 3.64 (1.46 ± 0.08 H, CH_2), 2.54 (0.67 ± 0.03 H, $CHMe_2$), 1.88 (2.10 ± 0.22 H, vinyl Me), 1.43 (3.99 ± 0.11 H, CMe_2), and 1.23 (3.79 ± 0.12 H, $CHMe_2$). A statistical distribution of deuterium would have given δ_H 3.64 (1.33 H), 2.54 (0.67 H), 1.88 (2.0 H), 1.43 (4.0 H), and 1.23 (4.0 H).

A similar f.v.p. of the pyrazoline (**9a**) at 800 °C followed by reaction with sulphur dioxide gave the thiole (**15**) with an average ^{1}H n.m.r. spectrum (five integrations) δ_H($CDCl_3$) 3.64 (1.27 ± 0.04 H), 2.54 (0.63 ± 0.04 H), 1.88 (2.09 ± 0.10 H), 1.43 (3.88 ± 0.15 H), and 1.23 (4.12 ± 0.22 H). In lower-temperature pyrolyses of this compound, for example those runs used to produce the data displayed in Figure 3, mixtures of starting material and deuteriated 3-isopropylidene-1,1,2,2-tetramethylcyclopropanes were obtained. These were readily separated by vacuum-line distillation. Most of the unchanged pyrazoline condensed in the neck of the f.v.p. apparatus and the rest was left behind on a simple trap-to-trap distillation. In assessing mixtures of cyclopropanes (**10a**) and (**11a**) produced by f.v.p. of either (**9a**) or (**10a**) the ^{1}H n.m.r. spectrum was integrated at least five times and an average taken. It was found that solutions of this methylenecyclopropane in deuteriochloroform decomposed over 1—2 days; hence it was necessary to obtain n.m.r. spectra immediately after the f.v.p. was performed.

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