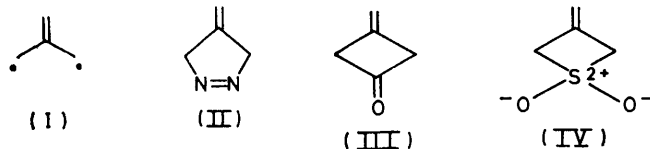


Synthesis of 3-Alkylidene-2,2,4,4-tetramethylthietan 1,1-Dioxides, Possible Precursors of 2-Methylenetrimethylene †

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The title compounds (Va—c) may be synthesised by the reaction of 2,2,4,4-tetramethylthietan-3-thione 1,1-dioxide (VIIb) with diazoalkanes and treatment of the resultant spirothiirans (Xa—c) with triphenylphosphine. Flash vacuum pyrolysis (770 °C) of the isopropylidene compound (Va) gives almost exclusively 3-isopropyl-2,4-dimethylpenta-1,3-diene (XI). This is consistent with the formation of an intermediate 2-methylenetrimethylene diradical (XIII), although other intermediates cannot be excluded.

DESPITE continuing theoretical interest in the 2-methylenetrimethylene diradical (I),¹ there are still relatively few reports of its generation. Most of these are variations



on the original routes,²⁻⁴ involving elimination of nitrogen from a pyrazoline (II)^{2,4} or carbon monoxide from a cyclobutanone (III).³ The published routes are, how-

† Also known as trimethylenemethyl.

¹ F. Weiss, *Quart. Rev.*, 1970, **24**, 278; P. Dowd, *Accounts Chem. Res.*, 1972, **5**, 242; D. R. Yarkony and H. Schaefer, *tert.*, *J. Amer. Chem. Soc.*, 1974, **96**, 3754.

² P. Dowd, *J. Amer. Chem. Soc.*, 1966, **88**, 2587.

ever, rather specific and difficult to modify for the generation of 2-methylenetrimethylene diradicals with particular substitution patterns or which have particular geometrical constraints.⁵ This paper examines the possibility of generating 2-methylenetrimethylene by elimination of sulphur dioxide from a thietan dioxide [parent system (IV)]. In structures (II) and (III) the hydrogen atoms α to the 'leaving group' are highly labile. It was anticipated that this would also be true of the thietan system (IV) and that double bond migration would create difficulties in the synthesis and could even compete with the desired elimination reaction. In the pyrazoline and cyclobutanone series

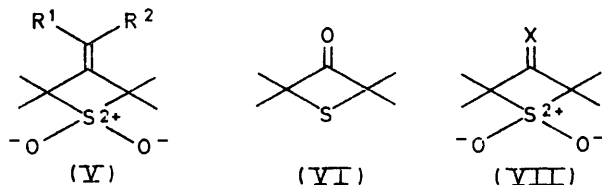
³ P. Dowd and K. Sachdev, *J. Amer. Chem. Soc.*, 1967, **89**, 715.

⁴ R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, 1966, **88**, 2589.

⁵ J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, 1971, **93**, 1544.

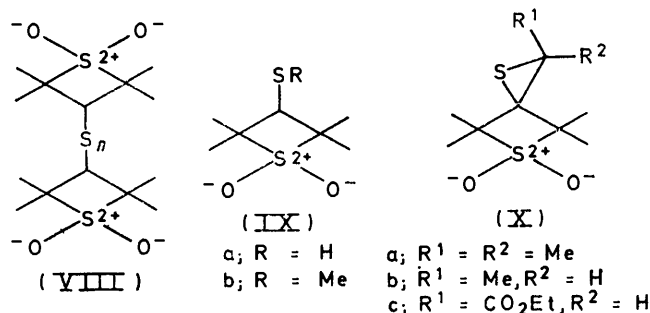
this has been overcome in two ways; either by replacing the α hydrogen atoms with alkyl groups⁶ or by working in bicyclic systems in which these α -positions are bridgeheads.⁵ For the thietans it was decided to aim for the α -methylated systems (V).

2,2,4,4-Tetramethylthietan-3-one (VI)⁷ is readily available in quantity from the reaction of 2,4-dibromo-2,4-dimethylpentan-3-one⁸ with sodium sulphide. Initial attempts to oxidise this thietanone (VI) with hydrogen peroxide-acetic acid gave complex mixtures of starting material, sulphone, sulphoxide, and sulphoxide rearrangement products.⁹ Oxidation to the sulphone (VIIa) could, however, be cleanly accomplished



a; R¹ = R² = Me
b; R¹ = Me, R² = H
c; R¹ = CO₂Et, R² = H

a; X = O
b; X = S



a; R = H
b; R = Me

a; R¹ = R² = Me
b; R¹ = Me, R² = H
c; R¹ = CO₂Et, R² = H

by using either perphthalic acid in benzene (yield 83%) or peracetic acid in benzene (97%). Once again, problems were encountered in attempting the Wittig reaction on either of the thietanones [(VI) and (VIIa)],¹⁰ but replacement of the carbonyl by an alkylidene group, could be achieved in good yield by a manner analogous to that employed by Diebert in a related system.¹¹ This involves treating the ketone (VIIa) with phosphorus pentasulphide in pyridine to give the thioketone (VIIb), adding a diazoalkane to give a thiiran (X), and finally heating with triphenylphosphine to give the alkene (V). The only problems encountered were in the first step, and arose from a side reaction which apparently converts the thioketone, in the presence of pyridine and phosphorus pentasulphide, into a mixture of polysulphides

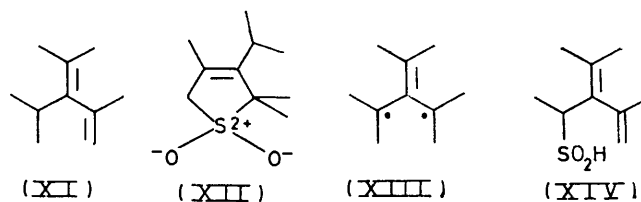
* A similar sequence of reactions has been carried out with Diebert's thioketone¹¹ (2,2,4,4-tetramethyl-3-thioxocyclobutanone) and diazomethane, diazoethane, 2-diazopropane, 2-diazol-1,1,1-trifluoroethane, and ethyl diazoacetate. The overall yields are all good except in the case of the diazotrifluoroethane.

⁶ S. D. Andrews and A. C. Day, *J. Chem. Soc. (B)*, 1968, 1271.

⁷ G. Claeson and A. Thalen, *Acta Chem. Scand.*, 1963, **17**, 1172; G. Claeson, A. Thalen, and L. Schotte, *Arkiv Kemi*, 1966, **21**, 295.

(VIII; $n \geq 2$). This side reaction could be virtually eliminated under strictly anhydrous conditions. The structure of the stable, red crystalline thioketone followed unambiguously from spectral and analytical data. The structure of the polysulphide was more difficult to establish. However, when treated with triphenylphosphine it gave the pure disulphide (VIII; $n = 2$) whose spectra were more informative (the ¹³C n.m.r. spectrum was particularly simple) and which was independently synthesised by reduction of (VIIb) with sodium borohydride followed by aerial oxidation. Similar reduction of (VIIb) followed by treatment with methyl iodide gave the thioether (IXb), but the thiol (IXa) was never isolated.

The reaction sequence (VIIb) \rightarrow (X) \rightarrow (V) was carried through with three diazo-compounds (diazoethane, 2-diazopropane,¹² and ethyl diazoacetate) and in all cases satisfactory yields were obtained.* Initial studies of the flash vacuum pyrolysis of the three alkylidene thietans (Va-c) indicated very similar behaviour; that is, formation of conjugated dienes. Only the product from (Va) was examined in detail. (The other products would both be expected to be mixtures of isomers.) Pyrolysis of (Va) under vacuum at 770 °C gave a product whose n.m.r. spectrum showed only peaks attributable to the diene (XI) (100% yield of crude material). T.l.c. showed that the product also contained a trace of starting material but that the reaction was essentially quantitative. The yield of diene isolated after chromatography and bulb distillation was only 64%, mainly because of the difficulty of separating such volatile and low-boiling material from solvent. The diene did not form an adduct with *N*-phenylmaleimide and although there was a rapid reaction with *N*-phenyltriazolinedione a mixture resulted and no simple [$\pi_2 + \pi_4$] adduct could be isolated. It did, however, form a crystalline adduct (XII) when heated in a sealed tube with liquid sulphur dioxide.¹³



The formation of the diene (XI) is consistent with a 2-methylenetrimethylene intermediate (XIII), but other possibilities such as (XIV) [suggested by analogy to the thermal rearrangement of (VI) *S*-oxide⁹] are difficult to exclude, particularly as, at the high temperature of the

⁸ A. Faworski, *J. prakt. Chem.*, 1913, **88**, 641.

⁹ R. J. Bushby, unpublished work.

¹⁰ D. P. G. Hamon, *Chem. Comm.*, 1969, 164; A. P. Krapcho, M. P. Silvon, and S. D. Flanders, *Tetrahedron Letters*, 1974, 3817.

¹¹ C. E. Diebert, *J. Org. Chem.*, 1970, **35**, 1501.

¹² S. D. Andrews, A. C. Day, P. Raymond, and M. C. Whiting, *Org. Synth.*, 1970, **50**, 27.

¹³ S. D. Turk and R. L. Cobb, '1,4-Cycloaddition Reactions,' ed. J. Harner, Academic Press, New York, 1967, pp. 13 *et seq.*

reaction, the possibilities of degenerate 1,5-hydrogen shifts are likely to invalidate any attempt to use normal 'product ratio' or 'isotopic labelling' methods.

EXPERIMENTAL

2,4-Dibromo-2,4-dimethylpentan-3-one.⁸—Prepared by the reaction of bromine (100 cm³) with 2,4-dimethylpentan-3-one (98 g) in carbon tetrachloride (400 cm³), this was obtained as a yellow oil (213 g, 91%), b.p. 116—118° at 40 mmHg (lit.,⁸ 84—85° at 9 mmHg), τ (CDCl₃) 7.87 (s, CH₃).

2,2,4,4-Tetramethylthietan-3-one (VI).⁷—Prepared by the reaction of 2,4-dibromo-2,4-dimethylpentan-3-one (213 g) with sodium sulphide [from sodium (36 g)] in methanol (800 cm³) and recrystallised from methanol, this was obtained as large white needles (79.6 g, 70%) (lit.,⁷ 70% after sublimation and on a much smaller scale). It sublimed rapidly above 90°; m.p. 102—107° (sealed capillary) (lit.,⁷ 106—108°), ν_{\max} (CHCl₃) 1 767 cm⁻¹ (C=O), τ (CDCl₃) 8.33 (s, CH₃).

2,2,4,4-Tetramethylthietan-3-one 1,1-Dioxide (VIIa).¹⁴—Peracetic acid (40% w/v; 13.3 cm³, 70 mmol) was added over 2 min to a stirred, cooled solution of the ketone (VI) (5.0 g, 35 mmol) in benzene (90 cm³). After 7 days at room temperature the mixture was poured into chloroform (400 cm³). The solution was washed with aqueous sodium carbonate (2 × 400 cm³), dried, and evaporated under reduced pressure to give the *sulphone* (5.91 g, 97%) as white needles which sublimed at ca. 100°. A sample recrystallised from petroleum had m.p. 167.5—170° (sealed capillary) (Found: C, 47.6; H, 6.9; S, 18.6. C₇H₁₂SO₃ requires C, 47.7; H, 6.9; S, 18.2%), ν_{\max} (CHCl₃) 1 128 (SO₂ sym.), 1 327 (SO₂ asym.), and 1 786 cm⁻¹ (C=O), τ (CDCl₃) 8.33 (s, CH₃).

2,2,4,4-Tetramethylthietan-3-thione 1,1-Dioxide (VIIb).—A stirred mixture of phosphorus pentasulphide (6.0 g) and pyridine (60 cm³; freshly distilled from calcium hydride) under dry nitrogen was heated to boiling and the ketone (VIIa) (4.4 g) was added. After refluxing for 30 min the mixture was poured into ether (1 l). The solution was rapidly washed twice with ice-water, dried, and evaporated, and the residue was chromatographed on silica (elution with chloroform) to yield the *thioketone* (3.33 g, 69%) as clusters of red crystals which sublimed above 120°; m.p. 142—145° (sealed capillary), unchanged after recrystallisation from methanol (Found: C, 43.6; H, 6.3; S, 33.0. C₇H₁₂S₂O₂ requires C, 43.7; H, 6.3; S, 33.4%), λ_{\max} (CHCl₃) 526 nm (ϵ , 11, C=S $n-\pi^*$), ν_{\max} (Nujol) 1 100 and 1 313 cm⁻¹ (SO₂), τ (CDCl₃) 8.30 (s, CH₃). Chromatography also gave a white solid which was a mixture of polysulphides (VIII) (0.55 g, ca. 12%). The composition of this mixture seemed very dependent on the reaction conditions. A sample recrystallised twice from ethanol afforded white needles, m.p. 152—164° (Found: C, 39.9; H, 6.3; S, 38.4. Calc. for C₁₄H₂₆S₅O₄: C, 40.2; H, 6.3; S, 38.3%), ν_{\max} (Nujol) 1 112 and 1 300 cm⁻¹ (SO₂), τ (CDCl₃) 6.48, 6.54, and 6.80 (total 2 H, 3 s, CH; relative intensities varied from sample to sample; the signal at 6.80 is almost certainly due to the disulphide), 8.37, and 8.43 (each 12 H, broad s, CH₃), δ_{C} (from Me₄Si) 20.4, 20.8, 24.4, and 24.7 (4 CH₃), 59.7, 60.3, and 60.7 (C-S_n-C), and 79.8 and 80.0 (C-SO₂-C).

The use of a longer reaction time reduced the yield of thioketone and a shorter reaction time gave mixtures of

ketone and thioketone which were difficult to separate. The use of insufficiently dried pyridine or addition of traces of water to calcium hydride-dried pyridine resulted in less thioketone and more polysulphide. For example, the reaction of the ketone (VIIa) (4.5 g) with phosphorous pentasulphide (11 g) in refluxing pyridine (70 cm³; 'dried' over KOH) for 1 h followed by the same work-up procedure gave the thioketone (0.85 g, 17%) and polysulphide (2.47 g, ca. 48%).

Reaction of the Polysulphide (VIII) with Triphenylphosphine.—The polysulphide (450 mg; m.p. 162—164°) and triphenylphosphine (1.0 g) in benzene (30 cm³) were refluxed for 3 days. The solution was evaporated and the residue chromatographed on silica (elution with chloroform) to yield the crude disulphide (427 mg; m.p. 222—223°). Recrystallisation from ethanol gave 2,2,2',2',4,4,4',4'-*octamethyl-3,3'-dithiodi(thietan) 1,1,1',1'-tetraoxide* (VIII; $n = 2$) as long white needles, m.p. 226—227° [Found: C, 43.4; H, 7.0; S, 33.0%; M (ebullioscopic), 386. C₁₄H₂₆S₄O₄ requires C, 43.5; H, 6.8; S, 33.2%; M , 386], ν_{\max} (Nujol) 1 110 and 1 298 cm⁻¹ (SO₂), τ (CDCl₃) 6.80 (2 H, s, CH), and 8.37 and 8.42 (each 12 H, s, CH₃), δ_{C} (from Me₄Si) 20.3 and 24.6 (CH₃), 59.6 (C-S₂-C), and 79.8 (C-SO₂-C).

Reduction of the Thioketone (VIIb) with Sodium Borohydride.—Sodium borohydride (130 mg) was added to a stirred solution of the thioketone (VIIb) (200 mg) in ethanol (10 cm³). After 16 h ether and water were added and the ethereal extract was washed with dilute acid, dried, and evaporated. The residue was chromatographed on silica (elution with chloroform) to yield the disulphide (VIII; $n = 2$) (157 mg, 78%), identical (m.p., mixed m.p., and i.r. data) with the material described above.

2,2,4,4-Tetramethyl-3-(methylthio)thietan 1,1-Dioxide (IXb).—Sodium borohydride (200 mg) was added to a stirred solution of the thioketone (VIIb) (200 mg) in ethanol (15 cm³) under nitrogen. Within 2 min the red solution had become yellow. Methyl iodide (2 cm³) was added and the solution became colourless. After 16 h, work-up as before and recrystallisation from methanol-petroleum gave the *thioether* (170 mg, 79%) as small white needles, m.p. 95—99° (Found: C, 46.0; H, 7.7; S, 30.4. C₈H₁₆S₂O₂ requires C, 46.1; H, 7.7; S, 30.8%), ν_{\max} (Nujol) 1 110 and 1 280 cm⁻¹ (SO₂), τ (CDCl₃) 7.0 (1 H, s, CH), 7.87 (3 H, s, SCH₃), and 8.46 (12 H, s, ring CH₃).

2,2,3',3',4,4-Hexamethylthietan-3-spiro-2'-thiiran 1,1-Dioxide (Xa).—2-Diazopropane¹² [from acetone hydrazone (20 g)] in ether (100 cm³) at -78°C was added to a solution of the thioketone (VIIb) (2.5 g) in chloroform (100 cm³) and the mixture was allowed to warm to room temperature. After 24 h the colourless solution was evaporated and the residue chromatographed on silica (elution with chloroform) to yield the *thiiran* as fine white needles (2.42 g, 79%). A sample recrystallised from petroleum had m.p. 174—178° (subl.) (Found: C, 51.5; H, 7.6; S, 27.3. C₁₀H₁₈S₂O₂ requires C, 51.3; H, 7.8; S, 27.3%), ν_{\max} (Nujol) 1 120 and 1 290 cm⁻¹ (SO₂), τ (CDCl₃) 8.16 and 8.59 (2 × 6 H, s, thietan CH₃), and 8.35 (6 H, s, thiiran CH₃).

2,2,3',4,4-Pentamethylthietan-3-spiro-2'-thiiran 1,1-Dioxide (Xb).—Diazoethane (from *N*-ethyl-*N*-nitrosourea¹⁵) in ether was added dropwise to a stirred suspension of the thioketone (VIIb) (1.0 g) in ether (50 cm³) until a permanent pale yellow colour was obtained. Work-up as before gave the *thiiran* as white crystals (0.7 g, 61%). A sample

¹⁴ This reaction has been reported before but details have not been published; see W. L. Mock as quoted by R. Kalish and W. H. Prikle, *J. Amer. Chem. Soc.*, 1967, **89**, 2781.

¹⁵ W. W. Hartman and L. J. Roll, *Org. Synth.*, Coll. Vol. 2, 1943, p. 460.

recrystallised from ethanol had m.p. 185—187° (decomp.) (Found: C, 48.6; H, 7.2. $C_9H_{16}S_2O_2$ requires C, 49.0; H, 7.3%), ν_{\max} (Nujol) 1 110 and 1 295 cm^{-1} (SO_2), τ ($CDCl_3$) 6.93 (1 H, q, J 6 Hz, CH), 8.39 (3 H, d, J 6 Hz, thiiran CH_3), and 8.24, 8.39, 8.49, and 8.69 (4×3 H, s, thietan CH_3).

Ethyl 2,2,4,4-Tetramethylthietan-3-spiro-2'-thiiran-3'-carboxylate 1,1-Dioxide (Xc).—Ethyl diazoacetate (0.4 g) was added to a stirred solution of the thioketone (VIIb) (0.5 g) in chloroform (25 cm^3). After 2 h the mixture was worked up as before to give the thiiran as an oil (706 mg, 97%). A sample was purified by bulb distillation (140° and 0.5 mmHg), after which it crystallised; m.p. 75—78° (Found: C, 47.1; H, 6.3; S, 23.2. $C_{11}H_{18}S_2O_4$ requires C, 47.5; H, 6.5; S, 23.0%), ν_{\max} (Nujol) 1 093, 1 290 (SO_2), and 1 738 cm^{-1} (C=O), τ ($CDCl_3$) 5.72 (2 H, q, J 7 Hz, $O\cdot CH_2\cdot CH_3$), 6.58 (1 H, s, CH), 8.30, 8.37, 8.42, and 8.67 (4×3 H, s, thietan Me), and 8.67 (3 H, t, J 7 Hz, $O\cdot CH_2\cdot CH_3$).

3-Isopropylidene-2,2,4,4-tetramethylthietan 1,1-Dioxide (Va).—A mixture of the thiiran (Xa) (2.31 g) and triphenylphosphine (3.4 g) in benzene (50 cm^3) was refluxed for 40 h and evaporated, and the residue was chromatographed twice on silica (elution with chloroform) to yield the alkene as white needles, m.p. 101—102.5° (2.03 g, 100%). A sample purified by sublimation (water pump; 120 °C) and recrystallisation from petroleum had m.p. 100—102° (Found: C, 59.3; H, 8.7; S, 15.7. $C_{10}H_{18}SO_2$ requires C, 59.4; H, 9.0; S, 15.8%), ν_{\max} (Nujol) 1 128, 1 290 (SO_2), and 1 680 cm^{-1} (C=C), τ ($CDCl_3$) 8.26 (6 H, s, vinyl CH_3) and 8.34 (12 H, s, thietan CH_3).

3-Ethylidene-2,2,4,4-tetramethylthietan 1,1-Dioxide (Vb).—A mixture of the thiiran (Xb) (0.5 g) and triphenylphosphine (0.7 g) in benzene (10 cm^3) was refluxed for 46 h and evaporated, and the residue was chromatographed twice on silica (elution with chloroform) to yield the alkene as white crystals (0.38 g, 89%). A sample recrystallised from petroleum had m.p. 82—83° (Found: C, 57.1; H, 8.4; S, 16.6. $C_9H_{16}SO_2$ requires C, 57.4; H, 8.6; S, 17.0%), ν_{\max} (Nujol) 1 100, 1 290 (SO_2), and 1 690 cm^{-1} (C=C), τ ($CDCl_3$) 4.49 (1 H, q, J 7 Hz, vinyl H), 8.28 (3 H, d, J 7 Hz, vinyl CH_3), and 8.33 and 8.45 (2×6 H, s, thietan CH_3).

Ethyl 2,2,4,4-Tetramethylthietan-3-ylideneacetate SS-Dioxide (Vc).—A mixture of the thiiran (Xc) (0.65 g) and triphenylphosphine (1 g) in benzene (20 cm^3) was refluxed for 48 h and evaporated, and the residue was chromatographed on silica (elution with 2 : 1 chloroform-petroleum) to yield the alkene as white crystals (0.31 g, 54%), m.p. 130—132° (some sublimation over 120°), unchanged on recrystallisation from petroleum (Found: C, 53.6; H, 7.2; S, 13.2. $C_{11}H_{18}O_4S$ requires C, 53.6; H, 7.4; S, 13.0%), ν_{\max} (Nujol) 1 100, 1 300 (SO_2), 1 655 (C=C), and 1 715 cm^{-1} (C=O), τ ($CDCl_3$) 4.13 (1 H, s, vinyl H), 5.78 (2 H, q, J 7 Hz, $O\cdot CH_2\cdot CH_3$), 8.20 and 8.36 (2×6 H, s, thietan CH_3), and 6.89 (3 H, t, J 7 Hz, $O\cdot CH_2\cdot CH_3$).

Pyrolysis of the Alkylidenethietan Dioxide (Va).—The

alkene (Va) (150 mg) was sublimed (at ca. 0.1 mmHg) through a silica tube (1.1 \times 20 cm) maintained at 770 °C. The volatile products were collected in a trap cooled in liquid nitrogen and then concentrated into a small trap by distillation on a vacuum line (10^{-3} — 10^{-4} mmHg) to yield the crude 3-isopropyl-2,4-dimethylpenta-1,3-diene (XI) (109 mg, 100%). The n.m.r. spectrum of the total product showed no peaks other than those attributable to (XI) but t.l.c. (silica eluting with chloroform or methylene chloride) showed that it still contained a trace of starting material.

In a separate experiment the product from pyrolysis of (Va) (140 mg) was chromatographed on a short kieselgel column [elution with re-fractionated reagent grade petroleum (b.p. 30—40°)]. The solvent was distilled off on a water-bath and the residue distilled (b.p. 100—110°) to yield the fairly pure diene (61 mg, 64%) (Found: C, 85.9; H, 12.9%; M^+ , 138.1411. $C_{10}H_{18}$ requires C, 86.9; H, 13.1; M , 138.1408), ν_{\max} (film) 890 (=CH₂), 1 628 (C=C), and 3 075 cm^{-1} (vinyl H), τ ($CDCl_3$) 5.05 and 5.50 (2×1 H, m, C=CH₂), 7.3 (1 H, sept, J 6 Hz, $CHMe_2$), 8.23 [3 H, s with some fine structure, $CH_2=C(CH_3)_2$], 8.33 and 8.40 [2×3 H, s, C=C(CH_3)₂], and 9.05 [6 H, d, J 6 Hz, $CH(CH_3)_2$], m/e 138 (M^+ , 30%), 123 ($M^+ - CH_3$, 100%), and 82 (123 - C_3H_5 , 100%). The diene became yellow and viscous after a few days.

3-Isopropyl-2,2,4-trimethyl- Δ^3 -thiolen 1,1-Dioxide (XII).—The product from a similar pyrolysis of (Va) (100 mg) was concentrated into a small trap (on the vacuum line) in the normal manner. Sulphur dioxide (ca. 400 mg) was condensed into the trap, which was sealed off and heated on a steam-bath for 2 days. The mixture was poured into ether and the solution dried and evaporated. The crude product (72 mg) was chromatographed on silica (elution with chloroform) to yield the thiolen (56 mg, 56%) as an oil which after bulb distillation (150° and 15 mmHg) slowly crystallised; m.p. 36—38° (Found: C, 59.7; H, 8.6. $C_{10}H_{18}SO_2$ requires C, 59.4; H, 9.0%), ν_{\max} (film) 1 120 and 1305 cm^{-1} (SO_2), τ ($CDCl_3$) 6.34 (2 H, m, splitting very small, CH_2), 7.46 [1 H, sept, J 7 Hz, (CH_3)₂CH], 8.12 (3 H, m, splitting very small, vinyl CH_3), 8.57 [6 H, s, C(CH_3)₂], and 8.77 [6 H, d, J 7 Hz, (CH_3)₂CH].

Trial Pyrolysis of the Ethylidenethietan Dioxide (Vb).—The product from a pyrolysis of (Vb) under similar conditions appeared to be a mixture of (*E*)- and (*Z*)-3-isopropyl-2-methylpenta-1,3-diene, τ ($CDCl_3$) 4.78 (q, $CH_3\cdot CH=C$), 5.25 and 5.41 (2 m, C=CH₂), 7.4 [m, $CH(CH_3)_2$], 8.1—8.5 (vinylic CH_3), and 8.8—9.1 (CH_3).

Trial Pyrolysis of the Ester (Vc).—Compound (Vc) likewise gave what appeared to be a mixture of (*E*)- and (*Z*)-ethyl 3-isopropyl-4-methylpenta-2,4-dienoate, τ ($CDCl_3$) 4.40 and 4.44 (2 s, C=CH \cdot CO₂Et), 5.09 and 5.40 (2 m, C=CH₂), 5.88 and 5.90 (2 q, $O\cdot CH_2\cdot CH_3$), 7.4 [m, $CH(CH_3)_2$], 8.0—8.3 (vinylic CH_3), 8.72 and 8.74 (2 t, $O\cdot CH_2\cdot CH_3$), and 8.88 and 8.92 [2 d, $CH(CH_3)_2$].

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