The Introduction of Alkylidene Substituents into the 4-Position of the 3,3,5,5-Tetramethyl-Δ^1-pyrazoline Nucleus by the Thioketone plus Diazoalkane Reaction: [1] Synthesis of Tetrasubstituted Episulphides and Alkenes

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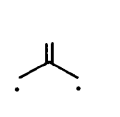
A wide range of 4-alkylidene-3,3,5,5-tetramethyl-Δ^1-pyrazolines (2), potential precursors of unsymmetrical trimethylenemethane biradicals, can be made through the reaction of thioketone (3b) with various diazo compounds (9) or the reaction of diazo compound (3e) with thioketones. In some cases, depending on the nature of the substituents X and Y, thiadiazoline and/or episulphide intermediates can be isolated but in others the alkene is obtained directly. Reaction of the thioketone (3b) with the diazo compound (3e) gives the thiadiazoline (13) which, when heated in the solid state and then treated with trimethyl phosphite gives the unusual, highly crowded olefin (12). A byproduct of the reaction of thioketone (3b) with diazodicyanomethane is the novel azomethine imine (11).

E.S.R. studies of trimethylenemethane (TMM) (1) [2] suggest that it has a three-fold axis of symmetry and a triplet ground state. Processes which lower this symmetry and remove the degeneracy of the singly occupied molecular orbitals ψ_2 and ψ_3 could, if sufficiently strong, bring the energy of the singlet state close to or below that



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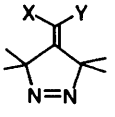

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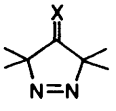
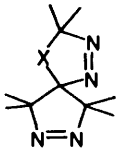
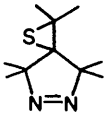


(3) a; X = O
b: X = S
c; X = S = O
d; X = N–NH_2
e; X = N_2



(4) a; X = S
b; X = SO



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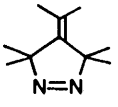

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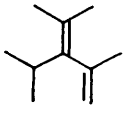

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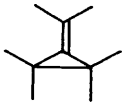

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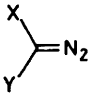

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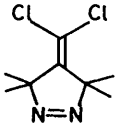

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of the triplet state. The most obvious ways of perturbing the system are (1) by unsymmetrical substitution,[3,4] (2) by rotation of one or more of the methylenes (which could be induced by replacing the hydrogens with bulky alkyl substituents), or (3) by angular distortion within the plane (which can be induced by incorporation into a cyclic structure [5]). As part of a program of work aimed at testing these possibilities we required a synthesis of the pyrazolines (2) in which the substituents X and Y may be bulky alkyl groups or of the donor, acceptor, or conjugating type. The pyrazolines were chosen since they appear to be the most efficient precursors for TMM [2,5,6] and the α-methyl groups are present to prevent the $-N{=}N{-}CH_2- \longrightarrow -NH{-}N{=}CH-$ tautomerism which has proved a problem in related studies.[2,7]

Other workers have already devised synthesis for some of these compounds. Hence Day and Whiting have prepared the pyrazoline (2; X = H, Y = OCOEt) [8] and Andrews and Day [3] the compound (2; X = H, Y = Cl) using routes analogous to the synthesis of 4-methylene-Δ^1-pyrazoline itself; [9] that is addition of 2-diazopropane to the appropriate trisubstituted allene. However this method is not general since with many allenes addition to the 'wrong' double bond and/or a reverse orientation of addition occurs.[10] Alternatively the pyrazolone (3a) originally made by Corey and Mock [11] has been used by Crawford and Tokunaga [12] to prepare the pyrazoline (2; X = Y = H) *via* a Wittig reaction, and by Engel and Shen [13] to prepare the pyrazoline (2; X = Y = CH_3) by reaction with isopropyllithium followed by dehydration. These methods, based on the ketone, are also difficult to generalise, however, partly because of the steric crowding around the carbonyl group. The problem can be overcome if the alternative 'thiadiazoline' method developed particularly by the groups of Barton [14] and Kellog [15] is employed, since this is especially suited to the creation of double bonds in sterically crowded environments. We have previously proved its usefulness in related work on 3-alkylidene-2,2,4,4-tetramethylthietan 1,1-dioxides [16] and in the present instance we have found that using this method enables all the required types of pyrazoline to be prepared in good yield.

Corey and Mock's synthesis of the pyrazolone (3a) [11] involved bromination of di-isopropyl ketone, reaction with sodium azide, reduction of the diazide with hydrogen sulphide, and finally oxidation with sodium hypobromite. We have employed a modification of this

route in which ammonium sulphide replaces hydrogen sulphide in the reduction step but better results were obtained by a modification of the route of Crawford and Tokunaga.[12] These workers reacted the dibromide of the ketone with hydrazine and oxidised the resultant pyrazolidone with manganese dioxide. By modifying their procedures, in particular by using yellow mercury(II) oxide as the oxidant, the yields can be improved and 20—50 gram quantities of the pyrazolone readily obtained.

Treatment of this ketone with phosphorous pentasulphide in refluxing pyridine for several days gives the bright red thioketone (3b). The fact that these pyrazolines survive such vigorous reaction conditions is perhaps surprising and a reflection of their unusually high thermal stability.[13] However, attempts to reduce the reaction time by employing higher boiling solvents were not successful and resulted in extensive formation of tarry products.

Reaction of the thioketone (3b) with 2-diazopropane gave the thiadiazoline (4a). In $CDCl_3$ this showed singlets at δ 1.30 (12 H) and 1.75 (6 H). If the solution is gently warmed this spectrum is replaced by that of the episulphide (5) (three equal singlets at δ 1.44, 1.47, and 1.70). If the n.m.r. tube is then sealed and heated for three days at 130 °C this is further transformed to the alkene (6) [δ 1.48 (12 H) and 1.77 (6 H)]. These steps appear to occur in a nearly quantitative manner. Further heating at *ca.* 200 °C results in elimination of nitrogen. In contrast to the results of flash vacuum pyrolysis, when mixtures of the diene (7) and cyclopropane (8) are cleanly formed,[1] pyrolysis in solution gives a complex mixture in which some of the diene (7) could be detected, but in which other, possibly intermolecular, products were present.

Summary of percentage yields

Compound (9) X	Compound (9) Y	Thiadiazoline	Episulphide	Alkene
Me	Me	86 [a]	*ca.* 100 [b]	98 [c]
Me	H		86 [a]	100 [c]
H	H		99 [a]	70 [c]
Bu^t	Bu^t	49 [a]		
Bu^t	H		74 [a]	78 [c]
CO_2Et	H		82 [a]	90 [c]
CO_2Et	CO_2Et			58 [a]
CN	CN			13 [a]
C_6H_5	H		82 [a]	98 [c]
C_6H_5	C_6H_5		75 [a]	94 [c]
Compound (3e)		70 [a]	*ca.* 100 [b]	*ca.* 100 [c]

[a] Product isolated directly from the reaction of the diazo compound with the thioketone (3b). [b] Yield from heating the thiadiazoline. [c] Yield from heating the thiadiazoline or episulphide with trimethyl phosphite.

Whilst it was shown that some of the episulphides obtained in this work would eliminate sulphur thermally, better yields and cleaner reactions usually resulted when triphenylphosphine or trimethyl phosphite was used to remove the sulphur. Of these two the latter has proved the more useful since excess of reagent and side-products are easier to remove at the end of the reaction.

The Table summarises yields and products obtained in the reactions of thioketone (3b) with a range of diazo compounds (9). In most cases reaction was clean and rapid, even at temperatures below 0 °C and the highly coloured nature of the reactants enabled the reactions to be carried out almost as 'titrations'. Except in the unsubstituted (X = Y = H) and monomethylated (X = H, Y = CH_3) series, products and intermediates were highly crystalline and most very readily sublimed. It may be seen that the thiadiazoline was only isolated in those cases where the diazo compound was relatively sterically hindered. More often the episulphide was the initial product and, in the cases of dicyano- and bisethoxycarbonyl-diazomethanes, the alkene was obtained directly. Presumably, in the last two cases, the conjugated nature of the product provides an extra driving force for the thermal elimination of sulphur.* It was found that the number of methyl resonances in the ^1H n.m.r. spectra could be reliably used to distinguish the alkene from the other two possible products but ^1H n.m.r. or mass spectroscopic distinction between the episulphide and thiadiazoline was difficult. In fact the simplest method of differentiation was u.v. spectroscopy since the episulphides showed a single N=N, $n \longrightarrow \pi^*$ band at *ca.* 325 nm, but the thiadiazolines two bands at *ca.* 295 and 325 nm. The first of these appears to be characteristic of the thiadiazoline chromophore.[15b] ^{13}C N.m.r. spectroscopy was also of some use since C-4 of the pyrazoline nucleus resonated at δ *ca.* 117 for the thiadiazolines, δ *ca.* 63 for the episulphides, and below δ 140 for the alkenes, but the weakness of the signals for these quaternary carbons sometimes made them difficult to detect with certainty. Almost none of the mass spectra obtained showed a parent ion, the first fragments observed being almost always those for $M^+ - N_2$ ($M^+ - N_4$ for the thiadiazolines) and $M^+ - CH_3N_2$. $M^+ - N_2C_3H_7$ was also a common fragment. The mass spectra of the episulphides and thiadiazolines always showed strong peaks at *m/e* 96 and 81 (tetramethylallene and tetramethylallene $- CH_3$) and for all compounds a strong peak was observed at *m/e* 41 for the allyl cation. For the alkenes, besides tetramethylallene the fragments corresponding to the alternative allene $XYC{=}C{=}CMe_2$ and loss of CH_3, from this, could normally be detected.

As a possible alternative to the thioketone (3b) the sulphine (3c) was also investigated.[17] This may be prepared from the thioketone by oxidation with permaleic acid. It forms an adduct (4b) with 2-diazopropane in 55% yield and, on heating with triphenylphosphine, this is converted into the alkene (6). Yields obtained by this route were, however, inferior to those obtained *via* the thioketone.

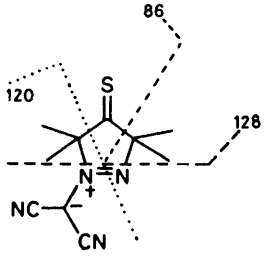
Whereas the reaction of thioketone (3b) with diazo compounds could be used to prepare most of the required pyrazolines it is not suitable for those in which the substituents X and Y are of the donor type since the

* In the case of reaction with diazobisethoxycarbonylmethane, copper was added to the reaction mixture and this may also have affected the elimination of sulphur.

required diazo compounds are either unknown or highly unstable. To overcome this problem we employed the thioketone and diazo compound in reverse, i.e. the reaction of thioketones with the diazo compound (3e). This can be prepared from the pyrazolone (3a) by reaction with hydrazine and oxidation of the resultant hydrazone (3d) with nickel peroxide.[11] It was shown that reaction of the diazo compound (3e) with thiobenzophenone gave the same episulphide and subsequently the same alkene as the reaction of thioketone (3b) and diazodiphenyl methane. Overall yields were very similar. Furthermore, reaction of diazo compound (3e) with thiophosgene gave the alkene (10), unobtainable by the earlier route, in 71% yield. An intermediate episulphide or thiadiazoline was detected spectroscopically but proved too unstable to isolate.

Most of the thioketone–diazo compound reactions occurred cleanly in the absence of significant by-products.[17] However, the reaction of thioketone (3b) with diazodicyanomethane gave a low yield (13%) of the required olefin together with a product which crystallised as slender bright orange needles and which is assigned the azomethine imine structure (11).[18] Analysis showed it to have the formula $C_{10}H_{12}N_4S$ and the u.v. and ^{13}C n.m.r. spectra showed the C=S grouping to be still present. The ^1H and ^{13}C n.m.r. spectra showed there to be two distinct types of methyl group. The mass spectrum showed a strong parent ion M^+ and an $M^+ - 15$ peak but no $M^+ - 28$ which suggests that it is not a simple pyrazoline. Instead there are large peaks at 86, 120, and 128 corresponding to the fragmentations shown (elemental compositions confirmed by accurate mass determination).

The formation of olefin (12) is also worthy of separate comment since it created special problems and it represents one of the few alkenes with four quaternary



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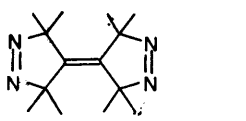
carbons attached to the double bond.[16] It also represents a possible entry into the tetramethylene-ethylene series of biradicals.[19] When the thioketone (3b) and diazo compound (3e) are mixed in ether at 0 °C and the mixture cooled to −70 °C the thiadiazoline (13) precipitates out as a powdery solid. If this is heated in solution a bright red colour develops and an almost quantitative recovery of the thioketone (3b) results. Clearly the reverse of the diazo compound plus thioketone reaction competes with the desired elimination of the central nitrogen. To try to suppress this reverse cycloaddition, an attempt was made to oxidise the central sulphur atom. However, treatment of the thiadiazoline (13) with *m*-chloroperbenzoic acid gave a product, $C_{14}H_{24}N_6SO$, which showed six methyl resonances in the ^1H n.m.r. spectrum and must therefore be assigned the structure (14) rather than either of the alternative oxidation products (15) and (16). Eventually it was found that the problem of reversibility could be overcome if the thiadiazoline was heated in the solid



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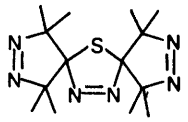

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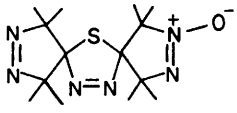

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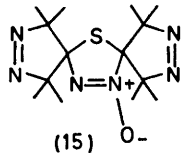

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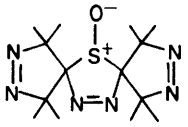

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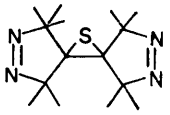

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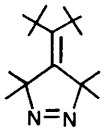

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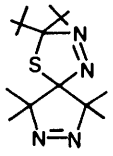

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state rather than in solution. Under these circumstances almost no red colour develops and an almost quantitative yield of the episulphide (17) results. Presumably if (13) reverts to (3b and e) in the solid state they are held close together and recombine before the diazo compound has a chance to decompose and eventually the thiadiazoline (13) persists long enough for the central nitrogen to be eliminated. Treatment of the episulphide (17) with trimethyl phosphite gives the alkene (12) whose structure was confirmed by *X*-ray crystallography.[1b] Contrary to expectations no twisting was found about the central double bond.[20]

In an attempt to prepare the even more sterically crowded olefin (18) the thioketone (3b) was reacted with diazodi-t-butylmethane. The thiadiazoline (19) thus obtained gave the thioketone (3b) when heated in solution and when heated in the solid phase (3b) and the episulphide (17) were formed. The latter product presumably arises by combination of (3b and e) arising from a retrocycloaddition reaction of (19) in both possible senses. It was found that diazodi-t-butyl

methane could be more conveniently prepared by nickel peroxide oxidation of the hydrazone than by sodium hydride treatment of the tosylhydrazone used by Barton.[14]

EXPERIMENTAL

Unless otherwise specified the light petroleum used for chromatography was refractionated AnalaR grade, b.p. 30—40 °C, and for recrystallisations the fraction, b.p. 40—60 °C. Column chromatography on Kieselgel refers to ' short column ' chromatography [21] using Merck Kieselgel G. Silica gel chromatography employed Sorbsil M60 supplied by Crossfield. ^1H and ^{13}C n.m.r. spectra were obtained in deuteriochloroform solution and shifts are relative to Me_4Si. In most cases where elemental compositions are given for ions observed by mass spectroscopy these have been checked by accurate mass determination or, in the case of commonly occurring ions such as $C_6H_9^+$, checked in at least one case. Most solids prepared in this work were readily sublimed and some were so volatile that microanalyses using an automatic analyser gave totally unreliable results and more traditional micro methods were employed.

3,3,5,5-Tetramethyl-4-pyrazolidone.— 2,4-Dibromo-2,4-dimethylpentan-3-one [22] and hydrazine hydrate gave [12] the pyrazolidone as crystals, m.p., after vacuum sublimation, 117—117.5 °C (lit.,[12] 115—117 °C) (Found: M^+, 142.110 5, $C_7H_{14}N_2O$ requires M, 142.110 6), δ_H 1.15 (12 H, s, Me) and 3.61br (2 H, s, NH), δ_C 23.02 (CH_3), 61.63 (CMe_2), and 224.25 (CO), *m/e* 142 (M^+, 11%) and 58 (100).

Higher and more reproducible yields (*ca.* 60% after recrystallisation from pentane) than those reported in the literature [12] (20—50% crude) were obtained if care was taken to regulate the rate of hydrazine addition such that no colour developed and the temperature of the mixture was maintained at 30—40 °C until all the hydrazine had been added.

3,3,5,5-Tetramethyl-Δ¹-pyrazol-4-one (3a).[12]—3,3,5,5-Tetramethyl-4-pyrazolidone (25 g, 0.17 mol) in ether (100 cm³) was added over 10 min to a stirred suspension of yellow mercury(II) oxide (50 g, 0.23 mol) in ether (250 cm³). The mixture was stirred and refluxed for 1 h. The solid was removed by filtration and washed with ether. The combined filtrate and washings were evaporated under reduced pressure and the resultant yellow solid recrystallised from pentane to give the pyrazolone as crystals (23 g, 93%; lit.,[12] 55% by manganese dioxide oxidation), m.p. 84—85 °C (lit.,[12] 83.5—85 °C) (Found: M^+, 140.094 6. $C_7H_{12}N_2O$ requires M, 140.094 9), $\nu_{max.}$ (Nujol) 1 755 cm^{-1} (C=O), δ_H 1.33 (s, Me), δ_C 22.3 (CH_3), 82.31 (CMe_2), and 221.2 (C = O), *m/e* 140 (M^+, 7%), 112 ($M^+ - N_2$, 2), 69 (32), 58 (87), and 44 (100).

Alternatively this compound was prepared *via* the diazide.[11] A stirred mixture of 2,4-dibromo-2,4-dimethylpentan-3-one (1 g) and sodium azide (0.52 g) in ethanol (8 cm³) and water (2 cm³) was refluxed for 18 h, poured into water, and extracted with chloroform. The chloroform extracts were washed, dried ($MgSO_4$), and evaporated under reduced pressure to give the crude diazide as a yellow oil (0.75 g, 100%), $\nu_{max.}$ (film) 2 110 (N_3) and 1 720 cm^{-1} (CO), δ_H 1.55. Aqueous ammonium sulphide (8%; 10 cm³) was added to a stirred solution of the crude diazide (1 g) in ethanol. The mixture went brown and gas was evolved. After 18 h the mixture was extracted with methylene chloride and the extract dried ($MgSO_4$) and evaporated under reduced pressure to give the crude diamine as a brown oil (0.7 g, 96%), $\nu_{max.}$ (film) 3 350 (NH_2) and 1 600 cm^{-1} (CO), δ_H 1.38 (12 H, s, CH_3) and 2.15br (4 H, s, removed by D_2O, NH_2). The crude diamine (0.5 g) in water was added dropwise to two equivalents of aqueous sodium hydrobromite [from bromine (1 g) and sodium hydroxide (1.3 g)]. The resultant yellow suspension was extracted with methylene chloride to give the pyrazolone (0.4 g, 82%) whose spectroscopic and other properties were identical to those of the material obtained previously.

3,3,5,5-Tetramethyl-Δ¹-pyrazole-4-thione.— 3,3,5,5-Tetramethyl-Δ¹-pyrazol-4-one (26 g) was added to a stirred solution of phosphorous pentasulphide (40 g) in pyridine (300 cm³; dried by distillation from calcium hydride) at 100 °C. The mixture was stirred and refluxed under an atmosphere of dry nitrogen for 3 days and the hot mixture poured into ether (1.5 l). The ethereal solution was washed repeatedly with iced water and iced 5M-hydrochloric acid to remove pyridine, dried ($MgSO_4$), evaporated without heat under reduced pressure, and the residue chromatographed on Kieselgel (elution with methylene chloride–ether (10 : 1) to yield some recovered starting material (7 g) and the *thione* (10 g, 47% based on ketone consumed) as highly volatile deep pink flakes, m.p. (sealed capillary) 44—45.5 °C (Found: C, 53.4; H, 7.8; S, 20.2%; M^+, 156.071 7. $C_7H_{12}N_2S$ requires C, 53.8; H, 7.7; S, 20.5%; M, 156.072 1), $\lambda_{max.}$ (EtOH) 530 and 550 nm (ε 8.4, C=S $n \longrightarrow \pi^*$), δ_H 1.48 (CH_3), δ_C 26.8 (CH_3), 99.1 (C-3, -5), and 269.0 (C-4), *m/e* 156 (M^+, 54%), 128 ($M^+ - N_2$, 99), 113 (128 — CH_3, 100), 95 (70), and 85 ($M^+ - C_3H_7N_2$, 84).

3,3,5,5-Tetramethyl-Δ¹-pyrazole-4-thione S-Oxide.— The thione (153 mg, 0.98 mmol) in methylene chloride (2 cm³) was added dropwise to a refluxing solution of permaleic acid [from maleic anhydride (1 g) and 100 vol hydrogen peroxide (0.2 g)] in methylene chloride (7 cm³). When the mixture had become colourless (5 min) it was diluted with methylene chloride (20 cm³), washed with water and aqueous sodium carbonate, dried, and evaporated under reduced pressure. The residue was chromatographed on Kieselgel (elution with 2 : 1 ether–methylene chloride) to yield the S-*oxide* as crystals (128 mg, 76%), m.p. after recrystallisation from light petroleum and sublimation 41—43 °C [Found: C, 48.2; H, 6.7; N, 15.8%; M (ebullioscopic), 179; M^+, 172.066 8. $C_7H_{12}N_2OS$ requires C, 48.8; H, 7.0; N, 16.3%; M, 172; M, 172.067 0], $\nu_{max.}$ (Nujol) 1 070 cm^{-1} (C=S=O), δ_H 1.63 and 1.80 (each 6 H, s, Me), δ_C 23.9, 29.1 (CH_3), 91.4, 97.9 (C-3 and -5), and 199.7 (C=S=O), *m/e* 172 (M^+, 4%) 144 ($M^+ - N_2$, 7), 140 (40), 96 (C_7H_{12}*, 94), and 81 ($C_6H_9^+$, 100).

4-Diazo-3,3,5,5-tetramethyl-Δ¹-pyrazoline.[11]— 3,3,5,5-Tetramethyl-Δ¹-pyrazol-4-one (2.0 g) and hydrazine hydrate (100%, 1.5 g) in absolute ethanol (40 cm³) were refluxed for 11 h in an apparatus fitted with a Soxhlet extractor containing activated molecular sieve. Work-up in the usual manner and recrystallisation from light petroleum gave the hydrazone as prisms (1.38 g, 63%), m.p. 120.5—121.5 °C, $\nu_{max.}$ (Nujol) 3 380, 3 280, and 3 200 (NH_2) and 1 610 cm^{-1} (C=N), δ_H 1.42 (6 H, s, Me), 1.62 (6 H, s, Me), and 5.2br (2 H exchanged by D_2O, s, NH_2). The hydrazone (0.2 g) in ether under an atmosphere of nitrogen was stirred with nickel peroxide [23] (1 g) for 30 min at 0 °C. This gave a yellow solution of the diazo compound which was used immediately.

Reaction of Thioketone (3b) *with 2-Diazopropane.*—2-Diazopropane in ether [from acetone hydrazone (2 g) and

yellow mercury(II) oxide (15 g) [24]] at −78 °C was added dropwise to a stirred ice-cooled solution of the thioketone (1 g) in ether (25 cm³) until a slight excess was present, *i.e.* the initially red solution became first colourless and then pale pink. The reaction mixture was allowed to warm to room temperature and after 18 h, dried with ($MgSO_4$), evaporated under reduced pressure, and the residue chromatographed on silica gel (elution with 4 : 1 light petroleum–ether) to give 3,3,5,5,5′,5′-*hexamethyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-(1′,3′,4′-Δ³′-*thiadiazoline*) as needles (1.1 g, 86%), m.p. 78—80 °C (decomp.) (Found: C, 53.4; H, 7.8; N, 25.0%; $M^+ - N_2$, 198.119 2. $C_{10}H_{18}N_4S$ requires C, 53.1; H, 8.0; N, 24.8%; $M - N_2$, 198.119 0), $\lambda_{max.}$ (EtOH) 290 and 275 nm (ε 640 and 536, thiadiazoline and N=N $n \longrightarrow \pi^*$), δ_H 1.3 (12 H, s, pyrazoline CH_3) and 1.75 (6 H, s, thiadiazole CH_3), δ_C 20.8, 26.3, and 30.5 (CH_3), 93.0 (C-3 and -5) and 105.3 (C-5′), *m/e* 170 ($M^+ - N_4$, 4.7%), 155 ($M^+ - C_3H_7N_2$, 52), 138 ($M^+ - N_4S$, 5.3), 123 ($M^+ - C_3H_7N_2S$, 11.7), 96 ($C_7H_{12}^+$, 38), and 81 ($C_6H_9^+$, 100). When this product was warmed in solution or allowed to stand at room temperature it was converted into 3,3,3′,3′,5,5-*hexamethyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-*thiiran*, m.p. 75—80 °C (decomp.) [Found: C, 60.6; H, 9.1; N, 13.8; S, 16.3%; *M* (ebullioscopic) 217. $C_{10}H_{18}N_2S$ requires C, 60.6; H, 9.2; N, 14.1; S, 16.2%; *M*, 198], $\lambda_{max.}$ (EtOH) 320 nm (ε 152, N=N $n \longrightarrow \pi^*$), δ_H 1.44 and 1.47 (each 6 H, s, pyrazoline Me), and 1.70 (s, 6 H, thiiran Me), δ_C 24.9, 28.5, and 29.4 (Me), 45.4 (C-3′), 69.8 (ring fusion carbon), and 89.6 (C-3 and -5). The mass spectrum was almost identical with that of the thiadiazoline.

Reaction of the Thioketone S-*Oxide with* 2-*Diazopropane*.—Excess 2-diazopropane [24] at −78 °C was added to the thioketone *S*-oxide (128 mg) in ether (10 cm³) at 0 °C and the mixture allowed to warm to room temperature over 18 h. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on Kieselgel (elution with 2 : 1 light petroleum–ether) to give 3,3,5,5,-5′,5′-*hexamethyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-(1′,3′,4′-Δ³′-*thiadiazoline*) S-*oxide* as a solid (100 mg, 55%), m.p. 95—96 °C (decomp.) (Found: $M^+ - N_2$, 214.114 7. $C_{10}H_{18}N_4SO$ requires $M - N_2$, 214.114 0), δ_H 1.17 (3 H, s), 1.45 (6 H, s), 1.65 (3 H, s), 1.8 (3 H, s), and 1.9 (3 H, s), δ_C 18.9, 20.2, 22.2, 24.7, and 26.0 (6 × Me, signal at 22.2 of double intensity), 92.1, 97.6 (C-3 and -5), and 112.1 (C-5′), *m/e* 166 ($M^+ - SON_2$, 11%), 96 ($C_7H_{12}^+$, 67), 90 (? $C_3H_6SO^+$, 37), and 81 ($C_6H_9^+$, 100).

4-*Isopropylidene*-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline*.— 3,3,-5,5,5′,5′-hexamethyl-Δ¹-pyrazoline-4-spiro-2′-(1′,3′,4′-Δ³′-thiadiazoline) (1 g) and trimethyl phosphite (2 cm³) in chloroform were refluxed for 18 h. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on silica to give the *alkene* as needles (0.72 g, 98%), m.p. 83—84 °C (from light petroleum) (Found: C, 72.4; H, 10.8; N, 16.8%; $M^+ - N_2$, 138.141 0. $C_{10}H_8N_2$ requires C, 72.2; H, 10.9; N, 16.9%; $M^+ - N_2$, 138.140 8), $\lambda_{max.}$ (hexadecane) 328 nm (ε 227, N=N $n \longrightarrow \pi^*$), δ_H 1.48 (12 H, s, ring Me) and 1.77 (6 H, s, vinyl Me), δ_C 22.2 (vinyl Me), 25.5 (ring Me), 89.9 (C-3 and -5), 123.2 (C=*C*Me₂), and 140.1 (C-4), *m/e* 138 ($M^+ - N_2$, 21%), 123 ($M^+ - CH_3N_2$, 58), 96 ($C_7H_{12}^+$, 20), and 81 ($C_6H_9^+$, 100).

This compound could also be prepared from the corresponding *S*-oxide in a similar manner but in rather poorer yield.

Reaction of Thioketone (3b) *with Diazoethane*.—Diazoethane [25] [from *N*-ethyl-*N*-nitrosourea (1.5 g)] in ether (20 cm³) at −10 °C was added to the thione (0.5 g). After 18 h the solvent was removed under reduced pressure and the resultant orange oil (0.66 g) chromatographed on silica gel (elution with 5 : 1 light petroleum–ether) to give 3,3,3′,5,5-*pentamethyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-*thiiran* (0.51 g, 86%) as an oil which could be recrystallised at low temperatures from light petroleum, m.p. *ca.* 0 °C (Found: C, 58.3; H, 9.1; N, 15.3%; $M^+ - N_2$, 156.097 3. $C_9H_{16}N_2S$ requires C, 58.7; H, 8.8; N, 15.2%; $M^+ - N_2$, 156.097 3), δ_H ($CDCl_3$) 1.30, 1.38, 1.48, 1.52 (each 3 H, s, pyrazoline Me), 1.66 (3 H, d, C*H*$_3$CH, *J* 7 Hz), and 3.04 (1 H, q, CH$_3$C*H*, *J* 7 Hz), *m/e* 156 ($M^+ - N_2$, 12%), 141 ($M^+ - CH_3N_2$, 27), 96 ($C_7H_{12}^+$, 27), and 81 ($C_6H_9^+$, 100).

4-*Ethylidene*-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline*.— 3,3,3′,-5,5-pentamethyl-Δ¹-pyrazoline-4-spiro-2′-thiiran (0.57 g) and trimethyl phosphite (2 cm³) in chloroform (10 cm³) were refluxed for 3 days. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on silica (elution with 2 : 1, light petroleum–ether) to give the *alkene* as an oil (0.49 g, 100%) (Found: C, 70.9; H, 10.4. $C_9H_6N_2$ requires C, 71.0; H, 10.6%) δ_H ($CDCl_3$) 1.28, 1.41 (each 6 H, s, ring Me), 1.70 (6 H, d, vinyl Me, *J* 7 Hz), and 5.3 (1 H, q, vinyl H, *J* 7 Hz), *m/e* 124 ($M^+ - 28$, 34%), 109 ($M^+ - CH_3N_2$, 44), 96 ($C_7H_{12}^+$, 5.7), 82 ($C_6H_{10}^+$, 6), 81 ($C_6H_9^+$, 31), and 67 ($C_5H_7^+$, 100).

2,2,4,4-*Tetramethyl*-3-*diazopentane*.—Preparation of this compound from the tosylhydrazone by the method of Barton *et al.*[14] was found to give rather variable yields when employed on a small scale. More reliable was the following preparation. Nickel peroxide [23] (2.5 g) was added in portions over 5 min to a stirred, ice–salt-cooled solution of the hydrazone of 2,2,4,4-tetramethylpentan-3-one [26] (500 mg) in light petroleum (b.p. 30—40 °C) (20 cm³). After a further 15 min the mixture was filtered and the filtrate evaporated under reduced pressure to give the diazo compound as an orange oil (480 mg) which showed no significant impurities in the n.m.r. spectrum.

Reaction of Thioketone (3b) *with* 2,2,4,4-*Tetramethyl*-3-*diazopentane*.—The thioketone (3b) (0.25 g) and 2,2,4,4-tetramethyl-3-diazopentane (0.25 g) were mixed in pentane at −78 °C. The mixture was stored at 0 °C for 18 h, the solvent removed under reduced pressure at 0 °C, and the residue chromatographed on silica (elution with 9 : 1 light petroleum–ether) to give 3,3,5,5-*tetramethyl*-5′,5′-*di*-*t*-*butyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-(1′,3′,4′-Δ³′-*thiadiazoline*) as needles (245 mg, 49%), which rapidly turned pink on warming and decomposed (Found: C, 62.2; H, 9.8; N, 17.8; S, 10.6. $C_{16}H_{30}N_4S$ requires C, 61.9; H, 9.8; N, 18.1; S, 10.3%), δ_H 1.22 (18 H, s, Bu^t), 1.42 and 1.52 (each 6 H, s, Me), δ_C 22.5, 26.9 (Me), 31.6 [(*C*H$_3$)$_3$C], 43.2 [(CH$_3$)$_3$*C*], 97.4 (C-3, and -5), 116.4 (spiro-C), and 130.9 (C-5′).

Reaction of Thioketone (3b) *with* 2,2-*Dimethyldiazopropane*.—A solution of 2,2-dimethyldiazopropane (from *N*-t-butyl-*N*-nitrosourea (2 g)] in ether at 0 °C was added to a solution of the thioketone (1.2 g) in ether (20 cm³) also at 0 °C. The resulting pale yellow solution was allowed to stand at room temperature for 18 h, the solvent removed by evaporation under reduced pressure and the residue purified by chromatography on Kieselgel (elution with 4 : 1 light petroleum–ether) and recrystallisation from petrol to give 3,3,5,5-*tetramethyl*-3′-*t*-*butyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-*thiiran* as crystals (1.27 g, 74%), m.p. 48—50 °C (Found: C, 63.6; H, 9.6; N, 12.2; S, 14.4%; $M^+ - N_2$, 198.144 5. $C_{12}H_{22}N_2S$ requires C, 63.7; H, 9.8; N, 12.4; S, 14.29%; $M - N_2$, 198.144 2), δ_H 1.15 (9 H, s, Bu^t), 1.26, 1.38, 1.53,

1.59 (each 3 H, s, Me), and 2.72 (1 H, s, CH), δ_C 26.1, 26.5, 26.5, 33.8 (Me), 29.3 [$(CH_3)_3C$], 40.8 [$(CH_3)_3C$], 53.7 (C-3'), 66.0 (spiro-C), 87.0, and 91.9 (C-3 and -5), *m/e* 198 ($M^+ - N_2$, 7%), 141 ($M^+ - C_4H_9N_2$, 13), 96 ($C_7H_{12}^+$, 43), and 81 ($C_6H_9^+$, 100).

4-(2,2-*Dimethylpropylidene*)-3,3,5,5-*tetramethyl*-Δ^1-*pyrazoline*.— 3,3,5,5-tetramethyl-3'-t-butyl-Δ^1-pyrazoline-4-spiro-2'-thiiran (1.51 g) and trimethyl phosphite (2 cm³) in chloroform (25 cm³) were refluxed for 4 days. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on silica (elution with 1 : 10 ether–light petroleum) gave the *alkene* (1.02 g, 79%) as a pale yellow oil which gave crystals on low-temperature recrystallisation from pentane, m.p. *ca.* 0 °C (Found: C, 73.9; H, 11.1%; $M^+ - N_2$, 166.172 3. $C_{12}H_{22}N_2$ requires C, 74.2; H, 11.4%; $M - N_2$, 166.172 1), δ_H ($CDCl_3$) 1.13 (9 H, s, Bu^t), 1.34 and 1.54 (each 6 H, s, Me), and 5.27 (1 H, s, vinyl H), *m/e* 166 ($M^+ - N_2$, 5%), 151 ($M^+ - CH_3N_2$, 7), 123 ($C_9H_{15}^+$, 24), 96 ($C_7H_{12}^+$, 43), and 81 ($C_6H_9^+$, 100).

Reaction of Thioketone (3b) *with Diazomethane*.—A solution of diazomethane in ether [from Diazald (4.3 g)] at −78 °C was added to the thioketone (1.0 g) in ether (10 cm³) at 0 °C. After 18 h the excess of diazomethane was destroyed with acetic acid, the ethereal solution washed with aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on silica (elution with 4 : 1 light petroleum–ether) to give 3,3,5,5-*tetramethyl*-Δ^1-*pyrazoline*-4-*spiro*-2'-*thiiran* as a volatile yellow oil (1.08 g, 99%) which on low-temperature recrystallisation from light petroleum and vacuum sublimation gave yellow crystals, m.p. 23—25 °C (Found: C, 56.3; H, 8.4; S, 18.6%; $M^+ - N_2$, 142.081 8. $C_8H_{14}N_2S$ requires C, 56.4; H, 8.3; S, 18.8%; $M - N_2$, 142.081 6), δ_H 1.33br (12 H, s, Me) and 2.46 (2 H, s, CH_2), δ_C 24.8, 28.3 (Me), 25.5 (CH_2), 59.2 (C-4), and 88.9 (C-3 and -5), *m/e* 142 ($M^+ - N_2$, 8%), 127 ($M^+ - CH_3N_2$, 42), 81 ($C_6H_9^+$, 42), and 67 ($C_5H_7^+$, 100).

3,3,5,5-*Tetramethyl*-4-*methylene*-Δ^1-*pyrazoline*.— 3,3,5,5-Tetramethyl-Δ^1-pyrazoline-4-spiro-2'-thiiran (0.53 g) and trimethyl phosphite (1 cm³) in chloroform (10 cm³) was refluxed for three days. The solvent was removed under reduced pressure and the residue chromatographed on silica (elution with 4 : 1 light petroleum–ether) to give the alkene as a volatile oil (0.30 g, 70%) whose spectroscopic and other properties were identical to those of material prepared by the method of Crawford *et al.*[12]

Reaction of Thioketone (3b) *with Ethyl Diazoacetate*.— Ethyl diazoacetate (1.02 g, 0.008 8 mol) in ether (5 cm³) was added to the thioketone (0.7 g, 0.004 4 mol) in ether (10 cm³). After 18 h at room temperature the initially pink solution had become yellow. It was washed with 2M-hydrochloric acid, saturated sodium hydrogencarbonate solution, and water, and dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to give *ethyl* 2,2,5,5-*tetramethyl*-Δ^1-*pyrazoline*-4-*spiro*-2'-*thiiran*-3'-*carboxylate* (0.9 g, 82%) as a crystalline solid which was recrystallised from light petroleum, m.p. 41.5—43 °C (Found: C, 54.5; H, 7.4; N, 11.9; S, 13.7%; $M^+ - N_2$, 214.103 4. $C_{11}H_{18}N_2SO_2$ requires C, 54.5; H, 7.5; N, 11.6; S, 13.2%; $M^+ - N_2$, 214.102 7), $\lambda_{max.}$ (EtOH) 330 nm (ε 131, N=N $n \longrightarrow \pi^*$), $\nu_{max.}$ (Nujol) 1 753 cm^{-1} (CO), δ_H 1.31, 1.47, 1.60 (6 H, 3 H, and 3 H, respectively, s, ring Me), 1.31 (3 H, t, *J* 7 Hz, CH_3CH_2), 3.41 (1 H, s, CH), and 4.27 (2 H, q, *J* 7 Hz, CH_3CH_2), *m/e* 214 ($M^+ - N_2$, 4.5%), 182 ($M^+ - N_2S$, 27), 154 (45), 141 ($M^+ - N_2CO_2Et$, 58), 139 (29), 136 (39), 107 (45), 99 (35), 93 (69), and 81 (77, $C_6H_9^+$).

Ethyl 3,3,5,5-*Tetramethyl*-Δ^1-*pyrazolin*-4-*ylideneacetate*.— Ethyl 2,2,5,5-tetramethyl-Δ^1-pyrazoline-4-spiro-2'-thiiran-3'-carboxylate (0.7 g) and trimethyl phosphite (3 cm³) were heated together for 1 h at 100 °C. The excess of trimethyl phosphite was removed under reduced pressure and the residual cream solid chromatographed on silica gel (elution with 4 : 1 light petroleum–ether) and recrystallisation from pentane to yield the *alkene* as crystals (0.7 g, 90%), m.p. 121—122 °C (Found: C, 62.9; H, 8.6%; $M^+ - N_2$, 182.130 1. $C_{11}H_{18}N_2O_2$ requires C, 62.8; H, 8.6%; $M^+ - N_2$, 182.130 7), $\nu_{max.}$ (Nujol) 1 712 cm^{-1} (C=O), δ_H 1.3 (3 H, t, *J* 7 Hz, CH_3CH_2), 1.45, 1.65 (each 6 H, s, ring Me), 4.2 (2 H, q, *J* 7 Hz, CH_3CH_2), and 5.75 (1 H, s, vinyl H), δ_C 14.26 (CH_3CH_2), 23.3, 27.3 (ring Me), 60.2 (CH_3CH_2), 90.3, 92.4 (C-3 and -5), 111.5 (C=CCO_2Et), 165.1, and 167.9 (other vinyl and C=O carbons), *m/e* 182 ($M^+ - N_2$, 58%), 165 ($M^+ - OEt$, 26), 154 ($M^+ - N_2C_2H_4$, 84), 139 (59), 136 (72), 93 (97), 81 ($C_6H_9^+$, 21), 67 (99), and 41 (100).

Reaction of Thioketone (3b) *with Diethyl Diazomalonate*.— Diethyl diazomalonate[27] (0.6 g), the thioketone (0.5 g), and copper[28] (0.2 g) in acetonitrile (10 cm³) were refluxed for 6 days by which time all the diazo compound and most of the thioketone had been consumed (t.l.c.). The mixture was filtered and the residue washed with chloroform. The combined filtrate and washings were evaporated under reduced pressure and the residue chromatographed on silica gel (elution with 2 : 1 light petroleum–ether) to give recovered thioketone (50 mg), and *diethyl* 3,3,5,5-*tetramethyl*-Δ^1-*pyrazolin*-4-*ylidenemalonate* as a low-melting crystalline solid (0.477 g, 58% based on thioketone consumed), m.p. 39—41 °C after low-temperature recrystallisation from light petroleum (Found: C, 59.5; H, 7.7; N, 9.8%; $M^+ - N_2$, 254.151 0. $C_{14}H_{22}N_2O_4$ requires C, 59.5; H, 7.9; N, 9.9%, $M^+ - N_2$, 154.151 8), $\nu_{max.}$ (Nujol) 1 732 cm^{-1} (C=O), δ_H 1.30 (6 H, t, *J* 7 Hz, CH_3CH_2), 1.60 (12 H, s, ring Me), and 4.25 (4 H, q, *J* 7 Hz, CH_3CH_2), δ_C 14.0 (CH_3CH_2), 24.3 (ring Me), 61.4 (CH_3CH_2), 92.2 (C-3 and -5), 121.0 [$C(CO_2Et)$], 163.8, and 164.1 (C=O and C-4).

Reaction of Thioketone (3b) *with Diazomalononitrile*.— Diazomalononitrile[29] [from precursor (0.9 g)] in a minimum volume of chloroform was added to the thioketone (3 g) also dissolved in a minimum volume of chloroform and the mixture refluxed for 1 h. Silica gel (15 g) was added and the solvent removed under reduced pressure. Chromatography on silica gel (elution with 4 : 1 light petroleum–ether) gave first recovered thioketone (2 g), then 3,3,5,5-*tetramethyl*-Δ^1-*pyrazolin*-4-*ylidenemalonitrile* as crystals (150 mg, 13% based on thioketone consumed), m.p. (from light petroleum) 107.5—109 °C (Found: $M^+ - N_2$, 160.099 5. $C_{10}H_{12}N_2$ requires $M^+ - N_2$, 160.100 0), $\lambda_{max.}$ (EtOH) 242 [ε 10 000, C=C(CN)$_2$] and 322 nm (437, N=N $n \longrightarrow \pi^*$), $\nu_{max.}$ (Nujol) 2 220 (CN) and 1 640 (C=C) cm^{-1}, δ_H 1.70 (12 H, s), δ_C 23.5 (Me), 80.8 [$C(CN)_2$)$_2$], 93.4 (C-3 and -5), 110.3 (CN), and 188.3 (C-4), *m/e* 160 ($M^+ - N_2$, 19%), 159 (38), 145 ($C_9H_9N_2$, $M^+ - CH_3N_2$, 100), 118 ($M^+ - CH_3N_2HCN$, 66), and 92 ($M^+ - CH_3N_2$ and 2 × HCN, 31).

Chromatography also produced N-*dicyanomethylene*-3,3,-5,5-*tetramethyl*-Δ^1-*pyrazoline*-4-*thione* which was further purified by rechromatography on silica gel (elution with benzene) and recrystallisation from light petroleum–chloroform (180 mg, 13% based on thioketone consumed) as slender bright orange needles, m.p. 147—150 °C [Found: C, 54.3; H, 5.4; N, 25.7; S, 14.6%; *M* (ebullioscopic)

213; M^+, 220.078 1. $C_{10}H_{12}N_4S$ requires C, 54.5; H, 5.5; N, 25.4; S, 14.6%; M, 220; M, 220.078 1], $\lambda_{max.}$ (EtOH), 235 (ε 6 100), 347 (10 800), and 508 nm (12.8, C=S $n \longrightarrow \pi^*$), $\nu_{max.}$ (Nujol) 2 200 and 1 990 cm^{-1} (CN), δ_H 1.6 and 1.95 (each 6 H, s), δ_C 28.5, 29.2 (Me) 87.8, 95.4 (C-3 and -5), 112.8, 113.3 (very weak ? CN), 254.4 (C=S), *m/e* 220 (68%, M^+), 205 (30, $M^+ - CH_3$), 128 (81, $C_7H_{12}S^+$), 120 (34), 113 (36), 95 (41), and 86 (100).

Reaction of Thioketone (3b) *with Diazophenylmethane.*— Excess diazophenylmethane [30] [from benzylidenehydrazine (2 g) and mercuric(II) oxide] in ether (50 cm^3) was added to a stirred solution of the thioketone (1 g) in ether (10 cm^3) at −5 °C. The mixture was allowed to warm to room temperature and after 18 h had changed from deep red to pale pink. It was washed with 2M aqueous acetic acid, saturated sodium hydrogencarbonate, and water, dried ($MgSO_4$), and filtered. The ether was removed by evaporation under reduced pressure and the residue chromatographed on silica gel (elution with 3 : 1 light petroleum–ether) to give 3′-*phenyl*-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-*thiiran* which was recrystallised from light petroleum to give crystals (1.37 g, 82%), m.p. 82—84 °C (Found: C, 68.4; H, 7.4; N, 11.4; S, 13.0%; $M^+ - N_2$, 218.113 2. $C_{14}H_{18}N_2S$ requires C, 68.3; H, 7.4; N, 11.4; S, 13.0%; $M - N_2$, 218.112 9), δ_H 0.65 (3 H, s, ring Me shifted upfield by an adjacent phenyl), 1.40, 1.52 (6 H, and 3 H, s, ring Me), 4.1 (1 H, s, CH), and 7.3 (5 H, s, ArH), δ_C 24.4, 26.5, 27.4, 29.9 (ring Me), 42.4 (*C*-Ph), 65.6 (spiro-C), 88.7, 90.7 (C-3 and -5), 127.8, 128.3, 128.7, and 135.2 (aromatic ring C), *m/e* 218 ($M^+ - 28$, 20%), 171 (12), 134 (22), 129 (19), 96 ($C_7H_{12}^+$, 57), 91 (11), and 81 ($C_6H_9^+$, 100).

4-*Benzylidene*-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline.*— 3′-Phenyl-3,3,5,5-tetramethyl-Δ¹-pyrazoline-4-spiro-2′-thiiran (0.693 g), trimethyl phosphite (1.5 cm^3), and chloroform (10 cm^3) were refluxed for 6 days. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on silica gel (elution with 4 : 1 light petroleum–ether) to yield the *alkene* (0.59 g, 98%) which was recrystallised from light petroleum as plates, m.p. 59—60 °C (Found: C, 78.7; H, 8.3; N, 13.2%; $M^+ - N_2$, 186.140 8. $C_{14}H_{18}N_2$ requires C, 78.5; H, 8.5; N, 13.1%; $M - N_2$, 186.140 8), δ_H 1.35, 1.50 (each 6 H, s, ring Me), 6.45 (1 H, s, vinyl H), and 7.25br (5 H, s, ArH), δ_C 26.2, 27.9 (Me), 88.4, 91.5 (C-3 and -5), 121.3 (C-4), 127.0, 128.0, 128.7, 136.9 (phenyl ring C), and 150.1 (*C*HPh), *m/e* 186 ($M^+ - N_2$, 25%), 171 ($M^+ - CH_3N_2$, 100), 128 (42), 91 (28), and 77 (24).

Reaction of Thioketone (3b) *with Diazodiphenylmethane.*— Diazodiphenylmethane [31] [from benzophenone hydrazone (1.8 g), and mercury(II) oxide] in ether was added to the thioketone (1 g) in ether (10 cm^3) at −10 °C. After 18 h at room temperature the solution was washed with 2M-HCl to destroy the excess of diazo compound (vigorous shaking required), saturated sodium hydrogencarbonate, and water, dried ($MgSO_4$), filtered, and the ether removed by evaporation under reduced pressure. The yellow residue was chromatographed on Kieselgel (elution with 4 : 1 light petroleum–ether) to give 3,3,5,5-*tetramethyl*-3′,3′-*diphenyl*-Δ¹-*pyrazoline*-4-*spiro*-2′-*thiiran* as needles (1.52 g, 75%) after recrystallisation from light petroleum, m.p. 165.5—166 °C (Found: C, 74.0; H, 6.8; N, 8.6; S, 10.1%; $M^+ - N_2$, 294.144 1. $C_{20}H_{22}N_2S$ requires C, 74.5; H, 6.9; N, 8.7; S, 9.9%; $M^+ - N_2$, 294.144 2) δ_H 1.08, 1.35 (each 6 H, s, Me), 7.1—7.4, and 7.6—7.9 (10 H, m, ArH), δ_C 25.6, 28.7 (Me), 62.4 (C-4), 72.0 (C-3′), 88.9 (C-3 and -5), 127.6, 127.8, 130.8, and 139.8 (phenyl ring C), *m/e* 294 ($M^+ - 28$, 13%), 262 ($M^+ - N_2S$, 1.4), 198 (Ph_2CS^+, 100), 165 (76), 121 ($PhCS^+$, 46), 96 ($C_7H_{12}^+$, 25), and 81 ($C_6H_9^+$, 75).

4-(*Diphenylmethylene*)-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline.*— 3,3,5,5-Tetramethyl-3′,3′-diphenyl-Δ¹-pyrazoline-4-spiro-2′-thiiran (1.3 g) and trimethyl phosphite (1.5 cm^3) in chloroform were refluxed for 18 h. The solvent was removed by evaporation under reduced pressure and the residue chromatographed on silica (elution with 1 : 4 ether–light petroleum) to give the *alkene* as white crystals (1.14 g, 94%), m.p. (after vacuum sublimation) 163 °C (Found: C, 82.4; H, 7.3; N, 9.5%; $M^+ - N_2$, 262.172 4. $C_{20}H_{22}N_2$ requires C, 82.7; H, 7.6; N, 9.6%; $M^+ - N_2$, 262.172 1), δ_H 1.30 (12 H, s, Me) and 7.25 (10 H, s, ArH), δ_C 27.0 (Me), 90.6 (C-3 and -5), 126.9, 127.9, 128.5, 136.5 (phenyl ring C), 141.9, and 145.2 (C=C), *m/e* 262 ($M^+ - N_2$, 37%), 247 ($M^+ - CH_3N_2$, 64), 232 ($M^+ - C_2H_6N_2$, 20), 219 ($M^+ - C_3H_7N_2$, 100).

Reaction of Thiobenzophenone with Diazo Compound (3e).— A stirred solution of 4-diazo-3,3,5,5-tetramethyl-Δ¹-pyrazoline [from the hydrazone (0.13 g) and nickel peroxide (0.5 g)] in ether at 0 °C was treated with an ice-cooled solution of thiobenzophenone [32] (0.10 g) in ether. The blue colour of the thioketone was immediately discharged. The solvent was removed by evaporation under reduced pressure to give the episulphide (0.20 g, 87% crude) as a yellow crystalline solid which appeared to be essentially pure as assessed by t.l.c. and n.m.r. spectroscopy. Further purification by chromatography gave material with identical physical and spectroscopic properties to those obtained previously.

Reaction of Thiophosgene with Diazo Compound (3e).— Thiophosgene (0.74 g) and 4-diazo-3,3,5,5-tetramethyl-Δ¹-pyrazoline [from hydrazone (1 g) and nickel peroxide (5 g)] in ether were mixed at 0 °C, when rapid evolution of gas was observed, and the solvent removed by evaporation under reduced pressure at 0 °C. Trimethyl phosphite (2 cm^3) was added and the whole left at 0° for 18 h. After 3 days at room temperature n.m.r. spectroscopic examination showed that reaction was *ca.* 80% complete and after a further day at 40 °C no starting material remained. 4-*Dichloromethylene*-3,3,5,5-*tetramethyl*-Δ¹-*pyrazoline* was isolated in the normal way (0.95 g, 71%), m.p. (from light petroleum and vacuum sublimation) 75.5—76 °C (Found: C, 46.2; H, 5.9; Cl, 33.9%; M^+, 206.037 5. $C_8H_{12}Cl_2N_2$ requires C, 46.4; H, 5.8; Cl, 34.2%; M, 206.037 7), δ_H 1.59 (s), *m/e* 180, 178 ($M^+ - N_2$, 10, 18%), and 81 (24, $C_6H_9^+$).

Reaction of Thioketone (3b) *with Diazo Compound* (3e).— An ice-cooled solution of 4-diazo-3,3,5,5-tetramethyl-Δ¹-pyrazoline [from 3,3,5,5-tetramethyl-Δ¹-pyrazolone hydrazone (0.5 g) and nickel peroxide (2.5 g)] in ether was added to an ice-cooled solution of 3,3,5,5-tetramethyl-Δ¹-pyrazole-4-thione (0.5 g) in ether. After 18 h at 0 °C the solution was cooled in dry ice–acetone when 1,3,4-Δ³-*thiadiazoline*-2,5-*di*(*spiro*-4′-3′,3′,5′,5′-*tetramethyl*-Δ¹-*pyrazoline*) precipitated as a powder (0.7 g, 70%) and was isolated by filtration, m.p. 210—212 °C (decomp.) (Found: C, 54.6; H, 7.7; N, 27.6; S, 10.3%; M^+, 308.178 9. $C_{14}H_{24}N_6S$ requires C, 54.5; H, 7.8; N, 27.2; S, 10.4%; M, 308.178 3), $\lambda_{max.}$ (EtOH) 303 and 334 nm (ε 1 570 and 1 310), δ_H 1.38 (24 H, s), δ_C 21.4, 27.0 (Me), 94.2 (C-3′ and -5′), and 117.1 (C-4′), *m/e* 308 (M^+, 1%), 237 ($C_{13}H_{21}SN_2^+$, 2), 224 ($C_{14}H_{24}S^+$, 2), 210 ($C_{11}H_{18}N_2S^+$, 7), 168 ($C_8H_{12}N_2S^+$, 18), 128 ($C_7H_{12}S^+$, 100), 113 (100), 96 (100), and 81 (100).

The thiadiazoline (100 mg) in methylene chloride was treated with *m*-chloroperbenzoic acid (112 mg; 2 equiv.) at room temperature for 2 h. The mixture was poured into water which was extracted with ether. The ether extracts were washed with aqueous sodium carbonate, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residue was chromatographed on silica (elution with 4 : 6 light petroleum–ether) and recrystallised from chloroform–light petroleum to give the N-*oxide* (14) (70 mg, 69%) as needles, m.p. *ca.* 218 °C (decomp.) (Found: C, 52.0; H, 7.7; N, 25.5; S, 10.1. $C_{14}H_{24}N_6SO$ requires C, 51.8; H, 7.5; N, 25.9; S, 9.9%), $\lambda_{max.}$ (EtOH) 301 and 331 nm (ε 1 390 and 955), δ_H 1.23, 1.32, 1.38, 1.42, 1.52 1.64 (s, 3 H, 3 H, 6 H, 6 H, 3 H, and 3 H, respectively), *m/e* 210 (32%), 172 (15, $C_7H_{12}N_2SO^+$), 168 (34, $C_8H_{12}N_2S^+$), 128 (46, $C_7H_{12}S^+$), 96 (100, $C_7H_{12}^+$), 86 (100, $C_4H_6S^+$), 81 (100, $C_6H_9^+$), and 41 (100, $C_3H_5^+$).

Thiiran-2,3-di(spiro-4′-3′,3′,5′,5′-tetramethyl-Δ^1*-pyrazoline*) (17).—The thiadiazoline (50.6 mg) was heated at 120 °C for 1 h. The fairly pure *thiiran* thus obtained (44.5 mg, 100% crude) was further purified by chromatography on silica gel (elution with 1 : 1 light petroleum–ether) and recrystallisation from 95 : 5 light petroleum–ether, m.p. 210 °C (decomp.) (Found: C, 60.1; H, 8.8; N, 20.1. $C_{14}H_{24}N_4S$ requires C, 60.0; H, 8.6; N, 20.0%), $\lambda_{max.}$ (EtOH) 323 nm (ε 283, N=N $n \longrightarrow \pi^*$), δ_H 1.57 and 1.66 (s, each 12 H), δ_C 27.4, 28.8 (Me), 67.4 (C-4′), and 90.4 (C-3′ and -5′), *m/e* 224 ($M^+ - N_4$, 1%), 209 ($M^+ - CH_3N_4$, 11), 181 ($C_{11}H_{17}S^+$, 6), 167 ($C_{10}H_{15}S^+$, 9), 153 ($C_9H_{13}S^+$, 4), 149 ($C_{11}H_{17}^+$, 52), 128 ($C_7H_{12}S^+$, 44), 113 ($C_6H_9S^+$, 43), 96 ($C_7H_{12}^+$, 56), and 81 ($C_6H_9^+$, 100).

3,3,5,5,3′,3′,5′,5′-Octamethyl-di-(Δ^1*-pyrazolinylidene*) (12).—A mixture of the thiiran (65 mg) and trimethyl phosphite (50 mg) was heated at 110 °C for 30 min, cooled and filtered, and the crude product washed with cold light petroleum and recrystallised from 1 : 1 ether–light petroleum to give the *alkene* as crystals, m.p. (sealed capillary) 214—215 °C (decomp.) (Found: C, 67.3; H, 10.0; N, 22.6%; $M^+ - N_4$, 192.187 7. $C_{14}H_{24}N_4$ requires C, 67.7; H, 9.7; N, 22.6%; $M - N_4$, 192.187 8), δ_H 1.65 (s, 24 H), δ_C 27.5 (Me), 91.3 (C-3 and -5), and 141.3 (C-4), *m/e* 192 ($M^+ - N_4$, 2%), 177 ($C_{13}H_{21}^+$, 22), and 149 ($C_{11}H_{17}^+$, 100).

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