Solution Photochemistry of 4-Alkylidene-3,3,5,5-tetramethyl-Δ^1-pyrazolines

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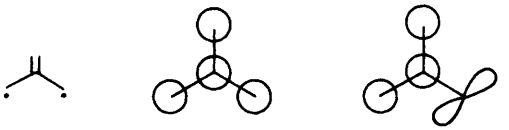
Direct photolysis of 4-([$^2H_6$]isopropylidene)-3,3,5,5-tetramethyl-1-pyrazoline (11) is believed to proceed *via* a singlet trimethylene-methane (TMM). It gives mainly the ' least motions ' product ([$^2H_6$]isopropylidene)-2,2,3,3-tetramethylcyclopropane (12). This implies that the *singlet* TMM adopts a bis-orthogonal geometry (21) rather than the mono-orthogonal geometry (20) expected. Direct photolysis of 13 different α-methylated 4-alkylidene-pyrazolines (5) shows that, in this series, formation of the ' least motions ' product (22) is normally preferred. In the initially formed bis-orthogonal biradicals, the ability of C–$\dot{C}Me_2$ rotation to compete with ring closure seems to be determined by steric factors. Generally, the tendency to form the ' least motions ' product (22) is greatest in those cases where the alkylidene group bears two substituents (X, Y ≠ H), less where there is one (X = H, Y ≠ H), and least of all where there is none at all (X, Y = H). The two main exceptions to this least motions rule are for 4-(2',2',3',3'-tetramethylcyclopropylidene)-3,3,5,5-tetramethyl-1-pyrazoline (27) and for 3,3,5,5-tetramethyl-1-pyrazolin-4-ylidenemalononitrile (32). In both of these cases there may be special factors which destabilise the ' least-motions ' product. By way of contrast to the direct photolysis, triplet sensitised photolysis of 4-([$^2H_6$]isopropylidene)-3,3,5,5-tetramethyl-1-pyrazoline (11) gives a statistical mixture of the deuteriated methylenecyclopropanes (12) and (13). This is consistent with the expected planar geometry (19 or the kinetic equivalent thereof) of the *triplet* TMM biradical. Some examples of the photochemical interconversion of methylenecyclopropanes and one example of a photochemical reduction of a pyrazoline are also reported.

TRIMETHYLENEMETHANE (TMM) (1) is one of the most interesting and intensely studied members of the family of π biradicals.[1] Theory and experiment agree that it has a triplet ground state with a three-fold axis of symmetry;[2] almost certainly the symmetrical, planar geometry shown in formula (2). The singlet state is less well understood. Theory predicts[3] that it will adopt a mono-orthogonal geometry (3) (with one methylene twisted through 90°) although the energy difference between the planar and mono-orthogonal singlets is not thought to be very great. For some derivatives of TMM



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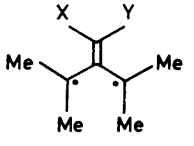
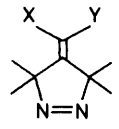


(4)

there is experimental evidence to support this geometry[4] but it is interesting to note that some results which were initially interpreted in terms of a mono-orthogonal singlet have since been reassessed.[5,6] It is also disturbing to note that there is very poor agreement between the best theoretical and experimental estimates of the energy difference between the singlet and triplet states.[3,7,8] Some of the results presented in this and in the following paper suggest that in the singlet state the tetramethylated derivatives of TMM (4) react through neither a planar nor a mono-orthogonal geometry.

Perhaps the best precursors to TMM biradicals are 4-methylene-1-pyrazolines and in a previous paper we reported an efficient, flexible synthesis of the α-methylated pyrazolines (5) in which the 4-alkylidene group was introduced *via* a thioketone/diazo-compound reaction.[9] Before discussing the solution photochemistry of these compounds it is worth mentioning two improvements on our original synthetic route. Firstly, we have found that oxidation of the pyrazolidone (6) to the pyrazolone (7a) can be carried out to give an equally good yield of product at considerably less expense using chlorine rather than mercury(II) oxide. Secondly, we have found that the thioketone (7c) is best made by the hydrazone–disulphur dichloride reaction, recently described by Okazaki *et al.*,[10] rather than by the ketone phosphorus pentasulphide reaction which we had used previously.[9] Although the overall yield of product by the ketone→hydrazone→thioketone route is little better than that obtained before, the thioketone obtained is essentially pure and the need for extensive chromatographic purification is obviated.

The photochemistry of 4-alkylidene-1-pyrazolines has been the subject of several detailed mechanistic studies.[11–15] The available evidence seems to point to a TMM intermediate and shows that direct photolysis proceeds *via* the singlet state whereas triplet sensitisation with ketone sensitisers, $E_T > ca.$ 65 kcal mol^{-1}, allows direct access to the triplet TMM manifold.[11,12] In the case of the specifically deuteriated pyrazoline (8) Gajewski has shown that the singlet-state reaction gives rise to a statistical 2 : 1 mixture of the methylenecyclopropanes (9) and (10) suggesting that, in the singlet TMM intermediate, rotation about the CH_2–C and CD_2–C bonds is rapid relative to ring closure[13] (or, less probably, that the intermediate is planar). By way of contrast we have found that the specifically deuteriated pyrazoline (11) gives mainly the 'least motions' product (12) on direct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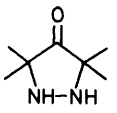
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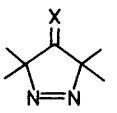
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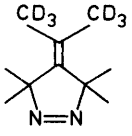
a; X = O
b; X = N—NH_2
c; X = S


(8)


(9)


(10)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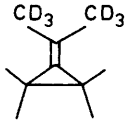
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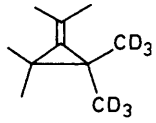
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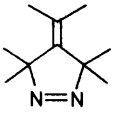
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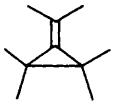
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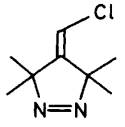
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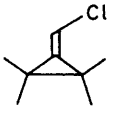
photolysis and only gives a fully scrambled, 1 : 2 mixture, of (12) and (13) in photosensitised, triplet TMM, reactions.

These reactions are most conveniently followed by ^{1}H n.m.r. spectroscopy. A solution of the undeuteriated pyrazoline (14) in benzene shows signals at δ 1.38 (12 H) and 1.47 (6H). As the photolysis proceeds these are cleanly replaced by signals for the corresponding cyclopropane (15), at δ 1.19 (12H) and 1.73 (6H). This appears (g.l.c.) to be the only reaction product. The photokinetics of this nitrogen elimination have previously been investigated by Engel [14] and by Turro [15] who concluded that it proceeds *via* the singlet state and that, in the singlet excited state of the pyrazoline, there is a 6.5—10 kcal/mol barrier to nitrogen loss. In the photolysis of the deuteriated analogue (11) we have found that the signal at δ 1.38 is replaced by one at δ 1.19 but very little vinyl methyl signal is observed. The actual integrated spectra correspond to a 93 ± 3 to 7 ± 3 mixture of the cyclopropanes (12) and (13). When a large excess of benzophenone is added to the reaction mixture (sufficient to absorb >96% of the incident light), however, the product vinyl (δ 1.73) and non-vinyl (δ 1.19) methyl resonances appear in a 1 : 2 ratio corresponding to a statistical 1 : 2 mixture of products (12) and (13). It was clear from the n.m.r. spectra that there was no significant scrambling of the deuterium label in (11) prior to nitrogen loss and, in a separate experiment, it was shown that the cyclopropanes (12) and (13) were not interconverted under the reaction conditions. The preference for a 'least motions' product in the direct photolysis is similar to that noted by Andrews and Day in their detailed studies of the photolysis of pyrazoline (16). They showed that the photolyses proceeding *via* the singlet TMM (*i.e.* direct photolyses) gave a *ca.* 3 : 1 ratio of the cyclopropanes (17) and (18) but those *via* the triplet TMM (*i.e.* photolysis in the presence of an excess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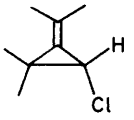
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of high-energy triplet sensitiser) a *ca.* 1 : 3 ratio of the cyclopropanes (17) and (18). They also studied the effect of sensitiser triplet excitation energy, E_T, on the product ratio and produced a 'Saltiel' plot (product ratio *vs.* E_T) which showed a changeover from singlet to triplet behaviour roughly in the region E_T (sensitiser) = 65 kcal mol^{-1}. Some of their results together with our findings for pyrazoline (11) are summarised in Table 1.

TABLE 1

Effect of photosensitisers on the product ratios obtained by pyrazoline photolysis

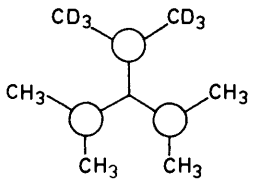
Photosensitiser (PS)	Triplet energy (kcal mol^{-1})	Mol ratio PS/ substrate	%(12) from (11) (±3) [c]	Mol ratio PS/ substrate	(17)% from (16) (±1) [d]
None	—	—	93	—	77
Anthracene [a]	42	1.0 [e]	94	1.0 [e]	75
Phenanthrene [b]	62	5.3 [e]	92	5.0 [e]	71
Fluorenone	53	3.2 [e]	60	3.0 [e]	76
2-Naphthaldehyde	60	2.3 [e]	50	2.2 [e]	43
Benzophenone	69	5.0 [f]	39	4.8 [f]	32
	69	10.0 [e]	35	9.5 [e]	25
	69	—	—	4.8	24

[a] Photodimerises which may effectively remove the photosensitiser from the reaction mixture. [b] May act as a singlet sensitiser (P. S. Engel, *Chem. Rev.* 1980, **80**, 99). [c] From n.m.r. integrals. Photolysis in benzene at room temperature. [d] Results of Andrews and Day (ref. 11). G.l.c. determination. Photolysis in refluxing pentane. [e] Sufficient to absorb >96% of the incident light. [f] Sufficient to absorb *ca.* 93% of the incident light.

Unfortunately, for the pyrazoline (11), the use of an n.m.r. method of product analysis required relatively concentrated solutions and so only a limited range of sensitisers could be employed (because most sensitisers were not sufficiently soluble). However, there is a reasonably good parallel between the two sets of results.

The fact that the photolysis of the pyrazoline (11) in the presence of 10 mol equiv. of benzophenone gives (within experimental error) a statistical ratio of products is consistent with the idea that the triplet hexamethyl-TMM is planar (19) and/or that intersystem crossing is sufficiently slow so that rotation about the C–CMe_2 bonds is fast relative to ring closure. The fact that direct photolysis gives >90% of the cyclopropane (12) shows that the singlet-state reaction cannot be passing through a TMM which is planar (19) (which would give a 1 : 2

ratio in the absence of secondary isotope effects) or one which is mono-orthogonal (20) (which would give a 1 : 1 product ratio provided it forms and closes in a ' least motions ' sense,[6] otherwise a >1 : 1 ratio). The most reasonable alternative seems to be the bis-orthogonal TMM (21) for which it is supposed that the rate of ring closure is faster than that for rotation about the C–$\dot{C}Me_2$ bonds. Relative to the pyrazoline (8) studied by Gajewski the effect of the methyl substituents is seen to be one of slowing the rate of C–C bond rotation relative to ring closure. This has analogies in other biradical reactions.[8b] The effect may be enhanced in this particular instance by the increase in steric hindrance in passing to the biradical in either geometry (19) or geometry (20). Further support for this ' steric effect ' argument has been obtained by studying the direct photolysis of a range of 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines (5) the results for which are summarised in



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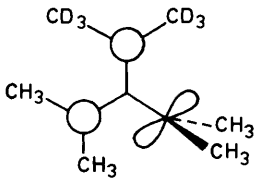

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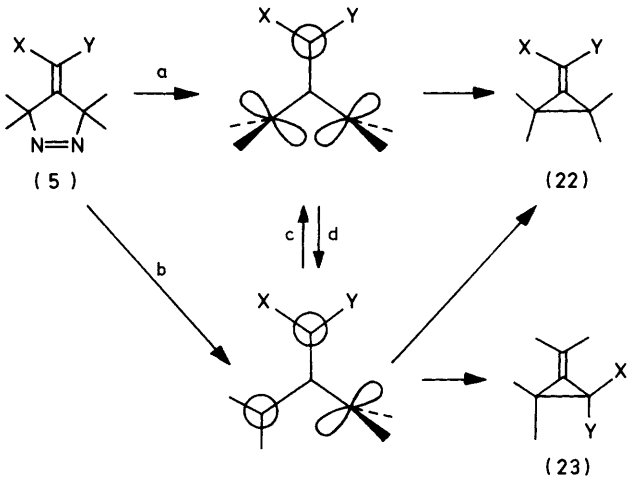

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(1) Probably the best simple explanation is that these biradicals are always generated in a bisorthogonal geometry (arrow a) and that the steric bulk of the substituents X and Y determines the extent to which this bis-orthogonal biradical can equilibrate with other geometries (arrows c and d) before ring closure. The main objection to this interpretation is the implied energy barrier to closure of a ' face-to-face ' 1,3-biradical. However, although calculations suggest that there is no barrier to the closure of ' face-to-face ' trimethylene itself, this result cannot necessarily be extrapolated to the present system.

(2) A second possible explanation is that the steric bulk of the substituents determines the initial ' split ' between the bis-orthogonal and other biradical geometries (for example, arrows a and b in the Scheme). Weak support for this idea comes from studies of the related thermal elimination of nitrogen [16] where there is some evidence for a greater increase in conjugation in the transition state for the less sterically hindered systems. The The main objection to this interpretation is that, in such cases, the conformation of the pyrazoline itself is nor-

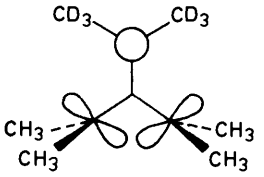
TABLE 2

Product ratios from the direct photolysis of 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines (5) in benzene

Substituents X, Y		Unrearranged cyclopropane (22)	Rearranged cyclopropane (23)	Method of analysis
CMe_2–SO_2–CMe_2		100	0	N.m.r.
CMe_2–N=N–CMe_2		100	0	Product isolation
Cl	Cl	100	0	N.m.r., g.l.c.
CD_3	CD_3	93	7	N.m.r.
Ph	Ph	*ca.* 90 [a]	*ca.* 10 [a]	N.m.r.
CO_2Et	CO_2Et	85 [a]	15 [a,b]	N.m.r.
Bu^t	H	100	0	N.m.r., g.l.c.
Me	H	100	0	N.m.r.
Cl	H	77	23	G.l.c.[c]
CO_2Et	H	70	30 [b]	N.m.r.
OCOEt	H	64	36	G.l.c.[c]
Ph	H	*ca.* 54 [a]	*ca.* 46 [a]	N.m.r., g.l.c.
H	H	52	48	N.m.r.
CMe_2	CMe_2	45 [b]	55	N.m.r.
CN	CN	0	100	N.m.r., g.l.c.

[a] Estimate of the initial product ratio. Products interconvert under the reaction conditions. [b] Minor product not fully characterised. Identification rests on spectroscopic data only. [c] Results of Andrews and Day (ref. 11) for photolysis in pentane solution.

mally thought to determine the ' split '.[17] In the present case this is contrary to what we know concerning the conformations of the pyrazolines.[18] 3,3,3',3',5,5,5',5'-Octamethyl-bi-(1-pyrazolinylidene) (5; X = CMe_2N=$NCMe_2$), in which the pyrazoline ring is folded by 16°, gives only the ' least motions ' product (27) but the pyrazoline (11), in which the ring is nearly planar, gives some of the ' non-least motions ' product.



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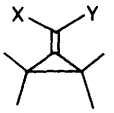

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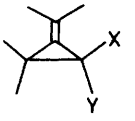

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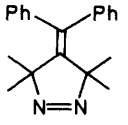

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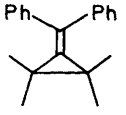

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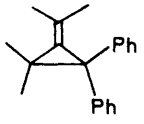

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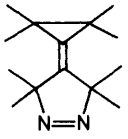

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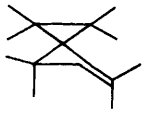

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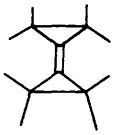

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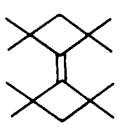

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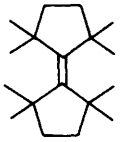


(31)

We therefore favour the first of these explanations as the simplest working hypothesis although the second cannot be wholly discounted and other more elaborate pictures of the energy surface invoking, for example, differences in the rate of biradical ring closure are, of course, quite tenable.

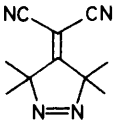
No evidence was obtained to suggest that isomerisation of the pyrazoline occurred prior to deazetation in any of these reactions and in most of the cases studied the products appeared to be stable to irradiation. In three cases, however, there was evidence of a photochemical interconversion of the products (22) and (23). For example photolysis of the diphenylpyrazoline (24) initially gave a 9 : 1 mixture of the cyclopropanes (25) and (26) and, at the stage where deazetation was complete ($8\frac{1}{2}$ h), the cyclopropane (25) was still the major product (77%). If the photolysis was continued, however, a slow conversion of the cyclopropane (25) into its isomer (26) was observed and after 3 days compound (26) was the only detectable product. Similar behaviour was noted for the diester (5; X = Y = CO_2Et) and the mono-phenyl substituted system (5; X = H, Y = Ph) except that, in the latter case, the rates of deazetation and product interconversion were comparable. This type of photochemical interconversion of methylenecyclopropanes has previously been reported in related systems.[19]

The last two entries in Table 2 appear to represent exceptions to the general trend and deserve separate comment.

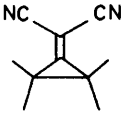
Once again, the photolysis of the pyrazoline (27) in benzene is conveniently monitored by n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum of the starting pyrazoline in benzene shows singlets at δ 1.0 (12 H) and 1.31 (12 H). The photolysis product shows peaks attributable to the spiro-compound (28) (which was available in pure form from our pyrolysis studies), most notably the vinyl methyl signals at δ 1.73 and 1.78, but the spectrum was overlaid by an intense singlet at δ 1.22. Similarly in the ^{13}C n.m.r. spectrum, besides the signals attributable to the spiro-compound (28) there were a number of other signals, most notably a strong signal at δ 21.4. The most reasonable explanation of the data is that the signals at δ 1.22 (^{1}H n.m.r.) and 21.4 (^{13}C n.m.r.) are due to the ' direct ' nitrogen elimination product (29). This is an interesting compound both in its own right (being yet another example of an alkene bearing four quaternary carbon substituents) and also because the homologues (30) and (31) [20] have recently been reported. Although integration of the ^{1}H n.m.r. spectrum of the mixture of isomers (28) and (29) suggests that they are produced in a 55 : 45 ratio, all attempts to isolate the latter compound by column chromatography have failed. It also appears that compound (29) is quite readily rearranged since attempted preparative g.l.c. gave only a single fraction which was the pure spiro-compound. The instability of compound (29) which is related to the fact that it bears four quaternary carbons on the double bond, is probably greater than in compounds (30) and (31) (and in related compounds which we have prepared) since the eclipsing interaction of the methyl groups cannot be relieved by envelope-type ' folding ' of the rings.[18] Some of these eclipsing interactions are, however, relieved in passing to the isomer (28) and this difference in product stabilities may be the reason that the photochemical elimination of nitrogen from pyrazoline (27) does not follow the ' normal ' least-motions route.

The other photochemical elimination of nitrogen which does not follow a ' least motions ' route is that of the dicyanopyrazoline (32). In this case the only product is the cyclopropane (34). It is just possible that compound (33) is formed as an intermediate which then undergoes a photochemical isomerisation analogous to the conversion of the cyclopropane (25) into its isomer (26). This, however, seems unlikely. All attempts (spectroscopic and g.l.c.) to detect an intermediate in this reaction have failed. It is also noteworthy that thermal elimination of nitrogen from the pyrazoline (32) only

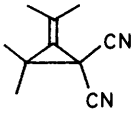
gives the cyclopropane (34).[16] Once again it seems that product stabilities may be a significant factor. In this context, it is worth noting that although the cyclopropane (34) is non-conjugated it carries its electron-withdrawing substituents on the cyclopropane ring; also an analogy between the chemistry of C=O and C=$C(CN)_2$[21] suggests an instability associated with the isomer (33) analogous to the instability of cyclopropanone.[22] This may be why the cyclopropane (33) is not formed in the present reaction and why, to the best of our knowledge, dicyanomethylenecyclopropanes have not so far been made.



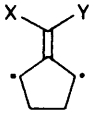
(32)



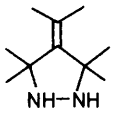
(33)



(34)



(35)



(36)

In our previous paper [9] we reported how the dicyanopyrazoline (32) could be prepared by the reaction of the thioketone (7c) with dicyanodiazomethane. Since the yield of this reaction is low and dicyanodiazomethane is a highly explosive material, an alternative preparation has been developed. The most obvious method seemed to be a Knoevenagel reaction except that such reactions are known to be difficult for sterically hindered ketones. Initial attempts with the normal range of Knoevenagel bases were unsuccessful but it was eventually found that the *thioketone* and malononitrile could be condensed by using potassium hydroxide–methanol.

So far, the only products isolated in these reactions have been methylenecyclopropanes derived by simple ring closure of the TMM biradical intermediate. Although it is known that the five-membered-ring derivatives of TMM (35) can be efficiently trapped by olefins,[23] attempts to trap the corresponding tetramethylated derivatives (4) with olefins have so far proved unsuccessful.[11] In this context it is also interesting to note that attempts to trap the parent TMM (1) have never given very high yields.[24] Similar attempts to trap a TMM with a hydrogen atom source, by photolysing the pyrazoline (14) in triphenytin hydride, resulted only in isolation of the pyrazoline photoreduction product (36).[25]

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were recorded in $CHCl_3$ and n.m.r. spectra in $CDCl_3$ solution.

Oxidation of 3,3,5,5-*Tetramethyl*-4-*pyrazolidone* (6) *with Chlorine*.—Chlorine was bubbled for 1.5 h through a solution of the pyrazolidone (50 g) in water (500 cm^3) containing cetyltrimethylammonium chloride (0.5 g) cooled in a water-bath. The solid, which precipitated out was filtered off, and additional material isolated from the aqueous phase by ether extraction to give the pyrazolone (total 43 g, 88%), m.p. 83—86 °C (lit.,[9] 83.5—85 °C), spectroscopic data identical with that previously reported.[9]

Improved Method for the Preparation of 3,3,5,5-*Tetramethyl*-1-*pyrazoline*-4-*thione* (7c).—From two dropping funnels and during a period of 30 min solutions of disulphur dichloride (2.2 g, 16 mmol) in dry ether (20 cm^3) and 3,3,5,5-tetramethyl-4-pyrazolidone hydrazone (2.31 g, 15 mmol) in dry ether (40 cm^3) were added simultaneously to a stirred solution of triethylamine (21 cm^3, 0.15 mol) in dry ether (40 cm^3) at 0 °C under an atmosphere of dry nitrogen. The mixture was stirred at room temperature for 2 h, filtered, and the residue washed with ether. The combined filtrate and washings were washed thrice with ice-cold water, dried, and evaporated. Chromatography on a short silica column (to remove sulphur) with methylene chloride–ether (19 : 1) as eluant gave the thione (1.92 g, 82%) as red crystals whose spectroscopic and physical characteristics were identical with the material previously prepared.[9]

[$^2H_6$]*Acetone Hydrazone and* 4-([$^2H_6$]*Isopropylidene*)-3,3,5,5-*tetramethyl*-1-*pyrazoline* (11).—[$^2H_6$]Acetone (10 ml, 7.9 g) was cooled in ice and stirred. 100% Hydrazine hydrate (3.6 g) was added dropwise during 10 min to the mixture which was then stirred at 0 °C for 30 min. Subsequently, solid potassium hydroxide (2.7 g) was added to the mixture which was then stirred at 0 °C for a further 20 min. The upper layer was then removed, dried with solid potassium hydroxide (1.4 g), and filtered. Anhydrous hydrazine (2.25 ml) was added to the filtrate (7.2 g) and the mixture heated at 100 °C for 18 h. Distillation gave the [$^2H_6$]-hydrazone (9.3 g, 95%) which was used to prepare 2-diazo[$^2H_6$]propane and thence 4-[$^2H_6$]isopropylidene)-3,3,-5,5-tetramethyl-1-pyrazoline (11) in the usual manner.[9] It was expected that this synthesis could result in some loss of deuterium from the α-position, particularly in the first two steps. However, since comparison of the mass spectra of deuteriated and undeuteriated materials at each stage showed that they were $\geqslant 96\%$ deuteriated (from $>99\%$ deuteriated acetone), deuterium loss was quite small.

Photolysis of 4-([$^2H_6$]*Isopropylidene*)-3,3,5,5-*tetramethyl*-1-*pyrazoline* (11).—The pyrazoline (50 mg) in benzene was photolysed in a sealed n.m.r. tube fixed to the outside wall of a water-cooled Hanovia medium-pressure u.v. lamp and the n.m.r. spectrum observed at various periods throughout the photolysis. Product ratios reported in Table 1 are the average of several n.m.r. integrations and are corrected to allow for *ca.* 4% non-deuteriated vinyl methyl in the substrate; they are probably accurate to ±3%. In the photosensitised reactions the following weights of photosensitiser were added: benzophenone (529 and 265 mg; 10 : 1 and 5 : 1 molar ratios respectively), 2-naphthaldehyde (105 mg), phenanthrene (272 mg), fluorenone (165 mg in $CDCl_3$), and anthracene (50 mg). In a separate experiment the pyrazoline (11) was photolysed to give (mainly) the cyclopropane (12). Benzophenone (500 mg) was then added and the photolysis continued. Even after many hours no conversion of the cyclopropane (12) into its isomer (13) could be detected.

Photolysis of 3,3,5,5-*Tetramethyl*-4-(2,2,4,4-*tetramethylthietan*-3-*ylidene*)-1-*pyrazoline* S,S-*Dioxide* (5; X, Y = $CMe_2SO_2CMe_2$).—The pyrazoline (30 mg) was photolysed in benzene (0.5 ml) for 30 min. The n.m.r. spectrum indi-

cated a single product, 2,2,4,4-*tetramethyl*-3-(2,2,3,3-*tetramethylcyclopropylidene*)*thietan* S,S-*dioxide*, which was purified by recrystallisation from light petroleum (b.p. 40—60 °C), m.p. 105—109 °C (Found: C, 65.3; H, 9.3; S, 12.9%; M^+, 256.149 7. $C_{14}H_{24}O_2S$ requires C, 65.6; H, 9.4; S, 12.5%; M^+, 256.149 7), $\nu_{max.}$ ($CHCl_3$) 1 110 and 1 295 cm^{-1} (SO_2); δ_H 1.19 (cyclopropyl CMe_2) and 1.60 (thietan CMe_2); *m/e* 192 (M^+, 24%), 177 ($M^+ - 15$, 17), and 149 ($M^+ - C_3H_7$, 100).

Photolysis of 3,3,3′,3′,5,5,5′,5′-*Octamethylbi*-(1-*pyrazolin*-4-*ylidene*).—A solution of the pyrazoline (300 mg) in chloroform was photolysed in the customary manner and the reaction monitored by n.m.r. spectroscopy. After 12 h most of the starting material had reacted. The solvent was removed and the residue chromatographed on Kieselgel with chloroform as eluant to give recovered starting material (30 mg) and 3,3,5,5-*tetramethyl*-4-(2,2,3,3-*tetramethylcyclopropylidene*)-1-*pyrazoline* (27) (160 mg, 67%) as a white crystalline solid, m.p. 102—103.5° (Found: C, 76.3; H, 11.0; N, 12.8. $C_{14}H_{24}N_2$ requires C, 76.3; H, 11.0; N, 12.7%), δ_H 1.18 (12 H, s, cyclopropyl Me) and 1.40 (12 H, s, pyrazoline Me); δ_C 20.7 (cyclopropyl CMe_2), 22.0 (cyclopropyl CMe_2), 27.0 (pyrazoline CMe_3), 89.3 (pyrazoline CMe_2), and 133.2 (vinyl C); *m/z* 192 ($M^+ - N_2$, 31%), 177 ($M^+ - N_2Me$, 30), and 149 ($M^+ - C_3H_7$, 100%).

Photolysis of 3,3,5,5-*Tetramethyl*-4-(2,2,3,3-*tetramethylcyclopropylidene*)-1-*pyrazoline* (27)—.The pyrazoline (100 mg) was photolysed in benzene in the customary manner. Besides product peaks attributed to the spiro-compound (28) and ^1H n.m.r. spectrum showed a strong singlet at δ 1.22 and the ^{13}C n.m.r. spectrum of strong singlet at δ 21.4. These signals were attributed to 2,2,2′,2′,3,3,3′,3′-octamethylbicyclopropylidene (29). Integration of the ^1H n.m.r spectrum indicated a product ratio of *ca.* 55 : 45.

Photolysis of 4-*Dichloromethylene*-3,3,5,5-*tetramethyl*-1-*pyrazoline* (5; X=Y=Cl).—A solution of the pyrazoline (100 mg) in benzene [δ_H 1.33; δ_C 22.92 (CH_3), 92.96 (CMe_2), 114.15 (Cl_2C), and 146.10 (C-4)] was photolysed in the customary manner for 3 h. The singlet δ_H 1.33 of the starting material was cleanly replaced by a singlet at δ_H 1.01 due to 1-*dichloromethylene*-2,2,3,3-*tetramethylcyclopropane* which was isolated as a clear liquid by preparative g.l.c. (PEG at 110 °C) (20 mg, 23%) (Found: C, 54.0; H, 6.9. $C_8H_{12}Cl_2$ requires C, 53.6; H, 6.8%), δ_H ($CDCl_3$) 1.16 (12 H, s); δ_C (C_6D_6) 19.18 (CH_3), 29.85 (CMe_2), 107.86 (very weak, ? Cl_2C), and 141.45 (C-1).

Photolysis of 4-*Diphenylmethylene*-3,3,5,5-*tetramethyl*-1-*pyrazoline* (5; X=Y=Ph.—The pyrazoline (0.5 g) was photolysed in benzene in the customary manner for 14 h. After removal of solvent the residue was chromatographed on Kieselgel (elution with petroleum–ether (5 : 1)) to give first *diphenylmethylene*-2,2,3,3-*tetramethylcyclopropane* (285 mg, 63%), m.p. 36—38 °C (Found: C, 91.4; H, 8.5. $C_{20}H_{22}$ requires C, 91.6; H, 8.4%), δ_H 1.14 (12 H, s, CMe_2) and 7.2 (10 H, broad s, ArH); *m/e* 262 (M^+, 84%), 247 ($M^+ - CH_3$, 74%), and 219 ($M^+ - C_3H_7$, 100%). The second fraction from the column was 1-*isopropylidene*-3,3-*dimethyl*-2,2-*diphenylcyclopropane* (95 mg, 21%), m.p. 50—53 °C (Found: C, 91.2; H, 8.7%; M^+, 262.172 6. $C_{20}H_{22}$ requires C, 91.5; H, 8.5%; M^+, 262.172 1), δ_H 1.01 (6 H, s, cyclopropyl CMe_2), 1.87 2.17 (each 3 H, s, vinyl CMe_2), and 7.1—7.5 (10 H, m, ArH); *m/e* (M^+, 35%), 247 ($M^+ - CH_3$, 40%), 219 ($M^+ - C_3H_7$, 87%), and 91 ($C_7H_7^+$, 100%). The product ratio was time dependent. In the first 20% of reaction the product contained *ca.* 90% of the unrearranged material (22; X=Y=Ph) but by 90% deazetisation (8½ h) this had fallen to 77%; when photolysis was continued beyond this point the proportion of product (23; X=Y=Ph) increased until it was the only product which could be detected. Similar results were obtained for photolysis in chloroform solution but overlap of signals in this solvent made it difficult to estimate product ratios.

Photolysis of Diethyl 3,3,5,5-*Tetramethyl*-1-*pyrazolin*-4-*ylidenemalonate* (5; X=Y=CO_2Et).—A solution of the pyrazoline (150 mg) in benzene was photolysed until all of the starting material had disappeared (2¼ h). The major product, *diethyl* 2,2,3,3-*tetramethylcyclopropylidenemalonate* was isolated by column chromatography on Kieselgel [elution with petroleum–ether (4 : 1)] and bulb distillation (170—180 °C/25 mmHg) as a clear liquid (110 mg, 83%) (Found: C, 66.1; H, 8.4%; M^+, 264.150 3. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.7%; M^+, 254.151 8), $\nu_{max.}$ (film) 1 720 cm^{-1}; δ_H 1.27 (12 H, s, CMe_2), 1.35 (3 H, t, *J* 7 Hz, CH_3CH_2), and 4.26 (2 H, q, *J* 7 Hz, CH_3CH_2); δ_H (benzene) 1.02 (3 H, t), 1.14 (12 H, s), and 4.08 (2 H, q); *m/z* 254 (M^+, 15%), 165 (38), and 162 (100%). A minor product was also detected in the n.m.r. spectrum δ_H (benzene) 0.99 (3 H, t, *J* 7 Hz), 1.42 (6 H, s), 1.66 (3 H, s), 1.92 (3 H, s), and 4.03 (2 H, q, *J* 7 Hz). This product was almost certainly 2,2-dicarboxyethyl-1-isopropylidene-3,3-dimethylcyclopropane. The initial proportion of the product was quite small (*ca.* 15%) but if the photolysis was continued for 9 h the proportion of this product increased to *ca.* 33%.

Photolysis of 4-(2,2-*Dimethylpropylidene*)-3,3,5,5-*tetramethyl*-1-*pyrazoline* (5; X=H, Y=Bu^t).—A solution of the pyrazoline (0.35 g) in benzene in an n.m.r. tube was photolysed until the reaction was complete (10½ h). N.m.r. spectroscopy and g.l.c. (10% PEG, 45 °C) indicated essentially a single product, 1-(2,2-*dimethylpropylidene*)-2,2,3,3-*tetramethylcyclopropane*, which was isolated by bulb distillation (70 °C/25 mmHg) as a clear liquid (0.26 g, 90%) (Found: C, 86.8; H, 13.3%; M^+, 166.172 8. $C_{12}H_{22}$ requires C, 86.7; H, 13.3%; M^+, 166.172 1), δ_H 1.04 (9 H, s Bu^t), 1.07, 1.12 (each 6 H, s, CMe_2), and 5.63 (1 H, s, vinyl H). Very similar results were obtained on photolysis in $CDCl_3$. On photolysis of the pyrazoline (20 mg) with acetophenone sensitiser (120 mg) in benzene 1-(2,2-dimethylpropylidene)-2,2,3,3-tetramethylcyclopropane was once again the major product.

Photolysis of 4-*Ethylidene*-3,3,5,5-*tetramethyl*-1-*pyrazoline* (5); X=H, Y=Me).— A solution of the pyrazoline (20 mg) in benzene in an n.m.r. tube was photolysed until the reaction was complete (5 h). The n.m.r. spectrum indicated a single product, 1-*ethylidene*-2,2,3,3-*tetramethylcyclopropane* (Found: M^+, 124.124 5. C_9H_{16} requires M^+, 124.125 2), δ_H (benzene) 1.15, and 1.19 (each 6 H, singlets, CMe_2), 1.74 (3 H, d, *J* 7.5 Hz, CH_3CH), and 5.66 (1 H, q, *J* 7.5 Hz, $CH_3CH{=}C$); *m/z* 124 (M^+, 27%), 109 ($M^+ - CH_3$, 42), 81 ($M^+ - C_3H_9$, 56), and 67 (100). Very similar results were obtained on photolysis in $CDCl_3$.

Photolysis of Ethyl 3,3,5,5-*Tetramethyl*-1-*pyrazolin*-4-*ylideneacetate* (5; X=H, Y=CO_2Et).—A solution of the pyrazoline (250 mg) in benzene was photolysed in the customary manner (2½ h). The major product was isolated by chromatography on Kieselgel [elution petroleum–ether (4 : 1)] and bulb distillation (92 °C/25 mmHg) to give *ethyl* 2,2,3,3-*tetramethylcyclopropylideneacetate* as a clear liquid (110 mg, 51%) (Found: C, 72.4; H, 10.2%; M^+, 182.131 9. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%; M^+ 182.130 7), $\nu_{max.}$ (film) 1 720 cm^{-1} (C=O); δ_H (benzene) 1.0 (9 H, overlapping

s and t, CMe_2 and CH_3CH_2), 1.2 (6 H, s, CMe_2), 4.06 (2 H, q, CH_3CH_2), and 6.12 (1 H, s, C=CH).

As well as this major product a minor product was also detected in the n.m.r. spectrum δ_H (benzene) 1.13 and 1.40 (each 3 H, s), 1.70 (6 H, m), 2.10 (1 H, m), and 4.04 (2 H, q). This product was almost certainly 2-carboxyethyl-3,3-dimethyl-1-isopropylidenecyclopropane, the signal for the CH_3 of the ethyl group being obscured by the signals of the major isomer. It made up *ca.* 30% of the product mixture. This proportion was not increased on prolonged photolysis.

Photolysis of 4-*Benzylidene*-3,3,5,5-*tetramethyl*-1-*pyrazoline* (5; X=H, Y=Ph).—A solution of the pyrazoline (0.4 g) in benzene was photolysed in the customary manner (48 h) and the mixture of products separated by preparative g.l.c. (30% PDEAS at 160 °C) to give first 1-*isopropylidene*-3,3-*dimethyl*-2-*phenylcyclopropane* (Found: C, 90.5; H, 9.7%; M^+, 186.140 1. $C_{14}H_{18}$ requires C, 90.3; H, 9.7%; M^+, 186.140 8), δ_H 0.82 and 1.30 (each 3 H, s, cyclopropyl CMe_2), 1.82 (6 H, broad s, C=CMe_2), 2.41 (1 H, broad s, CH), and 7.1—7.4 (5 H, m, ArH); *m/e* 186 (M^+, 26%), 171 ($M^+ - CH_3$, 100%), and 143 ($M^+ - C_3H_7$, 46%). The second fraction from preparative g.l.c. was 1-*benzylidene*-2,2,3,3-*tetramethylcyclopropane* (Found: C, 89.9; H, 9.8%; M^+, 186.140 1. $C_{14}H_{18}$ requires C, 90.3; H, 9.7%; M^+, 186.140 8), δ_H 1.19, 1.28 (each 6 H, s, CMe_2), 6.58 (1 H, s, vinyl H), and 7.33 (5 H, broad, s, ArH); *m/e* 186 (M^+, 27%) and 171 ($M^+ - CH_3$, 100). The first 10—20% of product mixture contained *ca.* 54% of the cyclopropane (22; X=H, Y=Ph) and 46% of the cyclopropane (23; X=H, Y=Ph). As the reaction proceeded the proportion of (23) increased so that it was *ca.* 70% of the mixture by the time deazetation was complete; continued photolysis beyond this point gave eventually 100% (23).

Photolysis of 3,3,5,5-*Tetramethyl*-4-*methylene*-1-*pyrazoline* (5; X=Y=H).—Photolysis in the customary manner gave a 52 : 48 mixture of 2,2,3,3-tetramethyl-1-methylenecyclopropane [26] [δ_H (benzene) 1.12 (12 H, s, CMe_2) and 5.39 (2 H, s, $C=CH_2$)] and 2,2-dimethyl-1-(2-methylethylidene)cyclopropane [26] [δ_H (benzene) 0.85 (2 H, m, CH_2), 1.19 (6 H, s, CMe_2), and 1.61 and 1.81 (each 3 H, m, C=CMe_2)].

3,3,5,5-*Tetramethyl*-1-*pyrazolin*-4-*ylidenemalononitrile* (32).—Potassium hydroxide (560 mg, 10 mmol) in dry methanol (10 cm³) was added to a stirred solution of 3,3,5,5-tetramethyl-1-pyrazoline-4-thione (780 mg, 5 mmol) and malononitrile (660 mg, 10 mmol) in dry methanol (20 cm³) under an atmosphere of nitrogen. After 30 min the mixture was poured into chloroform and the chloroform solution washed twice with water, dried with sodium sulphate, filtered, and the solvent removed under reduced pressure. The residue was chromatographed on silica gel [elution with petroleum–ether (4 : 1)] to give a small amount of the thione and the title compound as a white solid (534 mg, 56%), m.p. 107—108 °C (from light petroleum) (Found: C, 64.1; H, 6.6; N, 29.8. $C_{10}H_{12}N_4$ requires C, 63.8; H, 6.4; N, 29.8%), $\nu_{max.}$ ($CHCl_3$) 2 242 (CN) and 1 622 (C=C) cm^{-1}; δ_H 1.72 (12 H, s).

Repetition of the above reaction with 3,3,5,5-tetramethyl-1-pyrazolin-4-one (280 mg), after a reaction time of 3 h and similar work up gave the same product (114 mg, 30%).

Photolysis of 3,3,5,5-*Tetramethyl*-1-*pyrazolin*-4-*ylidene-malonitrile* (32).—A solution of the pyrazoline (40 mg) in benzene (0.5 cm³) was photolysed in the customary manner until reaction was complete. The solvent was removed under reduced pressure and the residue recrystallised from light petroleum (b.p. 30—40 °C) to give a quantitative yield of 2,2-*dicyano*-1-*isopropylidene*-3,3-*dimethylcyclopropane* (34), m.p. 54—55 °C (Found: C, 74.7; H, 7.6%; M^+, 160.100 1. $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.6%; M^+, 160.100 0), $\nu_{max.}$ ($CHCl_3$) 2 242 (CN) cm^{-1}; δ_H 1.55 (6 H, s, cyclopropyl CMe_2), and 1.90 and 1.98 (each 3 H, s, vinyl CMe_2); *m/e* 160 (M^+, 9%), 159 ($M^+ - 1$, 19%), and 145 ($M^+ - CH_3$, 46%).

Photolysis of 4-*Isopropylidene*-3,3,5,5-*tetramethyl*-1-*pyrazoline in Triphenyltin Hydride.*—A solution of the pyrazoline (25 mg) in triphenyltin hydride (1.0 g) and benzene (0.2 cm³) was photolysed for 2 h and the reaction monitored by n.m.r. spectroscopy. The signals attributable to the starting material δ_H 1.4 (12 H) and 1.5 (6 H) were replaced by signals at 1.3 (12 H), 1.52 (6 H), and 4.8 (2 H). The reaction mixture was poured into ether and extracted with dilute hydrochloric acid; the acid extract was then basified with sodium hydrogen carbonate and extracted with ether. The extract was washed with water, dried with sodium sulphate, and the solvent removed under reduced pressure to give 4-*isopropylidene*-3,3,5,5-*tetramethylpyrazolidine* (36) as a white crystalline solid (20 mg, 79%) (Found: M^+, 168.168 5. $C_{10}H_{20}N_2$ requires M^+, 168.162 6) δ_H 1.30 (12 H, s, pyrazoline CMe_2), 1.73 (6 H, s, CMe_2), and 3.20 (2 H, broad s, NH); *m/e* 168 (M^+, 1%), 167 ($M^+ - 1$, 5), and 81 ($C_6H_9^+$, 100%).

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