The Pyrolysis of 4-Alkylidene-3,3,5,5-tetramethyl-1-pyrazolines [1]

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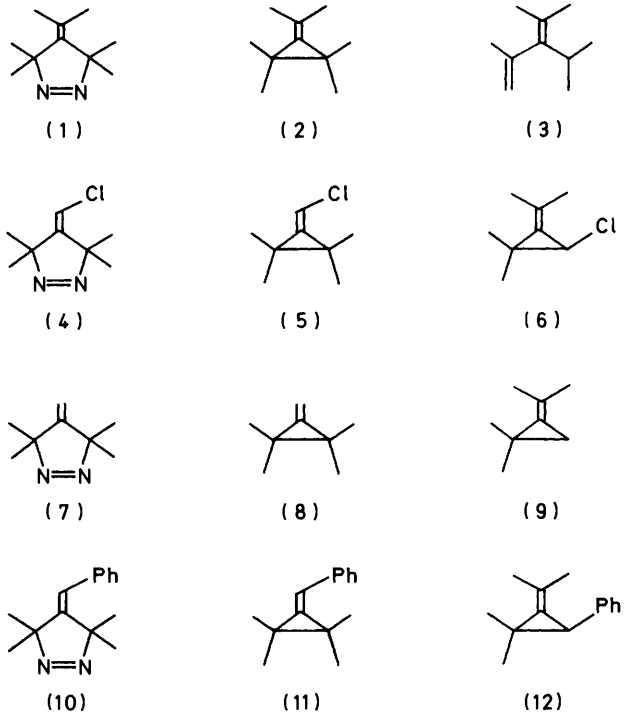
The pyrolysis of 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines [*e.g.* compound (1)] normally gives alkylidene-2,2,3,3-tetramethylcyclopropanes [*e.g.* compound (2)] and at higher temperatures or longer reaction times conjugated dienes [*e.g.* compound (3)]. In some cases interesting variations occur. For example 3,3,5,5-tetramethyl-1-pyrazolin-4-ylidenemalonitrile (22) gives (eventually) 3-cyano-4-isopropenyl-5-methylpyridine (27) and in the dichloro-substituted series a rearrangement from 2,2-dichloro-3,3-dimethylisopropylidenecyclopropane (30) to 3,4-dichloro-3,5-dimethylhexa-2,4-diene (31) and a double HCl elimination to give 2,5-dimethylhexa-1,5-dien-3-yne (32) are observed. The kinetics of nitrogen elimination have been determined for ten differently substituted pyrazolines (33). The reactions have positive entropies of activation and hence seem to pass through a singlet rather than (as suggested in analogous systems) a triplet intermediate but it is difficult to be sure whether this is a TMM biradical (simultaneous cleavage of both C–N bonds) or a diazenyl biradical (sequential cleavage of the C–N bonds). It is, however, interesting to note that there is no correlation between the reaction rate and the radical-stabilising ability of the substituents X and Y on the alkylidene group. This, in turn, suggests little or no rotation of the CMe_2 groups at the transition state and possibly the formation of a bis-orthogonal TMM (47) or a mono-orthogonal diazenyl biradical (48).

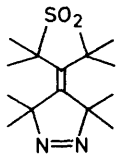
FLASH VACUUM PYROLYSIS (f.v.p.) of 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (1) at 500 °C (contact time in the region 10^{-3} s) gives the cyclopropane (2) but at temperatures above 750 °C the diene (3) is the only product.[2] In the intermediate temperature range mixtures of compounds (2) and (3) result. Pyrolysis in solution at *ca.* 200 °C gives a complex mixture (g.l.c./t.l.c.) in which some of the diene (3) could be detected. This general pattern of a cyclopropane as the first product and a diene at higher temperatures (or at longer reaction times) seems common to most of the 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines which we have investigated, as does the general observation that f.v.p. gives 'cleaner' products than does pyrolysis in solution.

The formation of cyclopropanes from these pyrazolines has been noted before. Hence Andrews and Day [3] reported that when the chloromethylene derivative (4) was heated at 210 °C a mixture of the cyclopropanes (5) and (6) results and Crawford and Tokunaga [7] reported that the methylene derivative (7) gives a mixture of the cyclopropanes (8) and (9). Similarly we have shown that the benzylidenepyrazoline (10), heated in benzene at *ca.* 200 °C, gives a 1 : 6 mixture (n.m.r.) of the cyclopropanes (11) and (12). In none of these cases can any great significance be attached to the product ratios which are obtained since the temperatures required for nitrogen elimination from (4), (7), and (10) are also sufficient to cause the methylenecyclopropane products to interconvert. As was mentioned in the introduction further heating normally results in formation of dienes. In solution this is usually accompanied by the formation of side-products but one exception is the pyrazoline sulphone (13). When this is heated in benzene or in diphenyl ether at *ca.* 200 °C the cyclopropane (14) is formed first and this is then cleanly converted into the diene (15). In a similar manner when a solution of the t-butylmethylenepyrazoline (16) in benzene is heated at 196 °C the first product observed is the cyclopropane (17) and when this is further heated a mixture of three



(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12)

hydrocarbons (mass spectrum/g.l.c.) results. These are probably (n.m.r.) the dienes (18), (19), and (20). Reaction of this crude mixture with sulphur dioxide and chromatography of the product gave the crystalline adduct (21) [from the dienes (18) and (19)]. In some cases the diene gave rise to further products. One interesting example is the dicyanopyrazoline (22). When this pyrazoline is heated in solution (195 °C) or subjected to f.v.p. (450 °C) the initial product is the cyclopropane (23) and this then gives rise to the diene (24). However f.v.p., at 550 °C gives a white crystalline product (26) which on exposure to the air rapidly oxidises to the pyridine (27). This was characterised as its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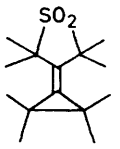
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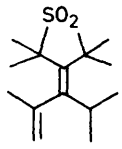
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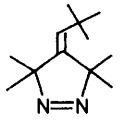
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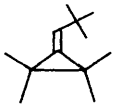
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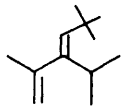
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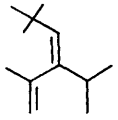
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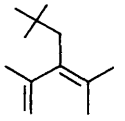
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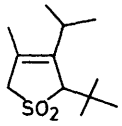
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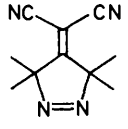
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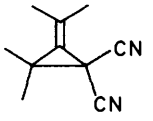
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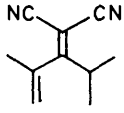
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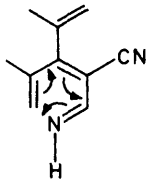
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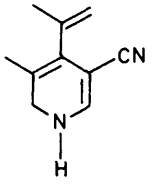
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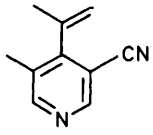
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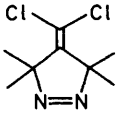
picrate. The reaction mechanism may be formulated in several ways but one possibility is that two 1,5-hydrogen shifts give rise to the intermediate (25) which undergoes an electrocyclic reaction to give the dihydropyridine (26). Another interesting sequence of transformations was found in the case of the dichloromethylenepyrazoline (28). We were particularly interested in this compound since it was expected that the presence of the chlorine substituents would aid intersystem crossing of the initially formed singlet TMM to its triplet ground state and that instead of a methylenecyclopropane (the normal product from singlet TMM's) a dimethylenecyclohexane (characteristic of the triplet TMM [5]) might result. In the event no dimers were obtained. F.v.p. at *ca.* 400 °C gives mixtures of starting material and the cyclopropane (29). At *ca.* 450 °C the major product is the rearranged cyclopropane (30). At *ca.* 550 °C the rearrangement product (31) results and at *ca.* 650 °C the double HCl elimination product (32) whose structure was confirmed by independent synthesis. A similar sequence, at least as far as product (31), can be also observed by heating a solution of the pyrazoline (28) at *ca.* 200 °C in benzene but the solution pyrolysis is accompanied by tarry by-products.

The solution pyrolyses of the diphenylpyrazoline (33; X = Y = Ph), the diester (33; X = Y = CO_2Et)* and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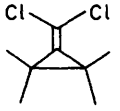
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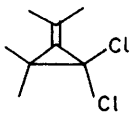
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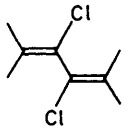
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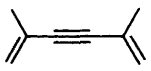
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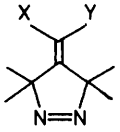
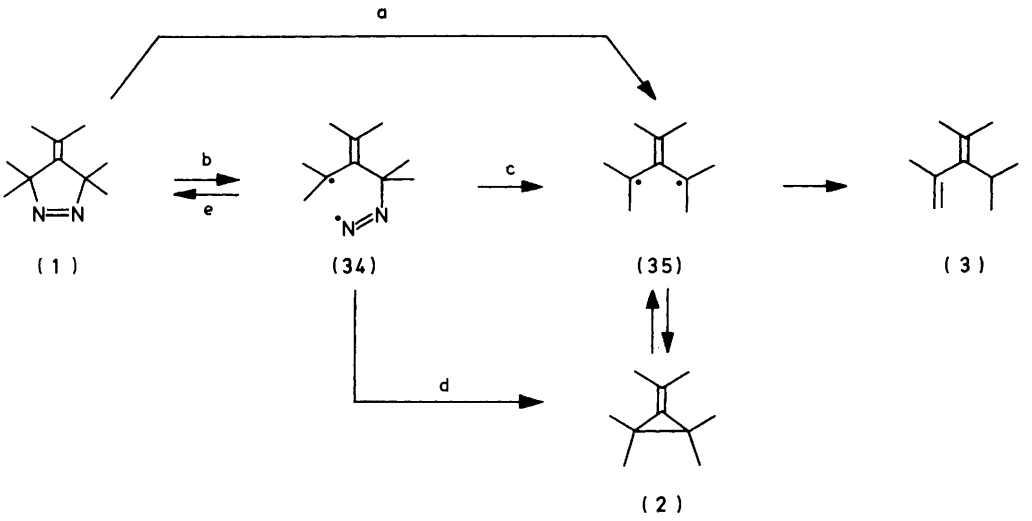

(33)

the monoester (33; X = H, Y = CO_2Et)* were also investigated in a preliminary manner but, although there was (n.m.r.) evidence for the formation of some cyclopropane and/or diene products, mixtures resulted and the products were not fully characterised.

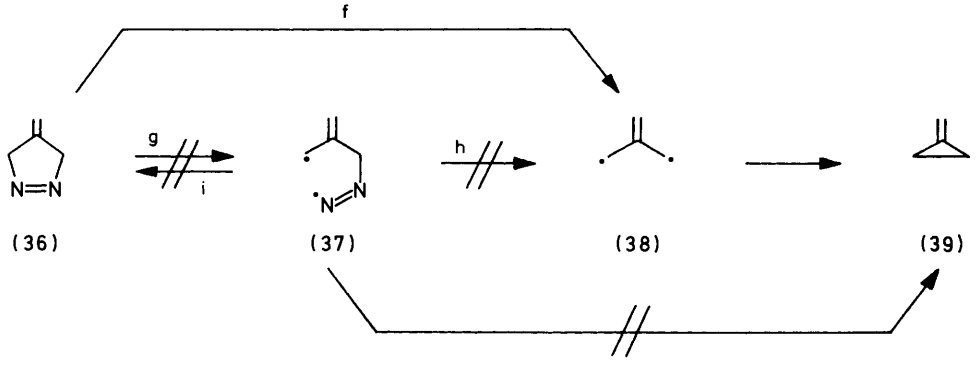
The mechanism of these and related 4-methylene-1-pyrazoline pyrolyses will be discussed by reference to Schemes 1—3. Certainly the simplest mechanism for the pyrolysis of the pyrazoline (1) (and of related compounds) would be to postulate a common TMM intermediate (35) which can either close directly to the cyclopropane (2) or undergo a 1,4-hydrogen shift to give the diene (3) (Scheme 1). If, however, a TMM intermediate is involved it is pertinent to ask whether this is formed in the singlet state or in its triplet (ground) state. It is also unclear whether such an intermediate would be formed directly (arrow a) or *via* the diazine (34) (arrows b and c) and it is also possible that the cyclopropane (2) arises from the diazine (34) (arrows b and d) rather than from the TMM.[6] The first of these questions was raised by the original work in this area by Crawford.[7] He studied the mechanism of thermolysis of the 'parent' compound (36) (Scheme 2). On the basis of isotope distribution studies he was able to eliminate the possibility that the cyclopropane originated directly from the diazine (37) and implicated rather the TMM intermediate (38). On the basis of secondary kinetic isotope effects he concluded that both C–N bonds were broken at once (arrow f) rather than in a stepwise sequence (arrows g and h). Furthermore, he measured the kinetics of the reaction and obtained a negative entropy of activation $\Delta S^{\ddagger}$ −1.1 cal K^{-1} mol^{-1}. This is unusual for a pyrazoline pyrolysis and Crawford explained it by postulating that nitrogen elimination was accompanied by intersystem crossing and that the TMM intermediate was generated in its triplet state. An elaborate justification for this mechanism has been propounded by Trindle *et al.*[8] The

* T. Sakai, T. Katayama, and A. Takeda, *J. Org. Chem.*, 1981, **46**, 2924, have recently reported the thermal conversion of a related ester to a furanone derivative.



SCHEME 1

initial result may, however, be somewhat suspect. Firstly, it is known that reactions that generate the triplet state of TMM (38) usually give rise to at least some 1,4-dimethylenecyclohexane [9] whereas Crawford only reports the formation of methylenecyclopropane.[7,10] Secondly, it is known that $-N{=}N{-}CH_2{-}/{-}NH{-}N{=}CH-$ tautomerism in compound (36) can compete with nitrogen elimination which may have complicated the kinetics,[10,11] and thirdly Crawford has thrown doubt on some of his interpretations in this paper.[10,12] In order to throw light on this and related mechanistic problems we have studied the kinetics of nitrogen elimination from ten different α-methylated alkylidene-1-pyrazoline (33), compounds in which complications from $-N{=}N{-}CH_2{-}/{-}NH{-}N{=}CH$ tautomerism cannot arise. The kinetics of nitrogen elimination in hexadecane solution were conveniently followed by monitoring the disappearance of the N=N $n\rightarrow\pi^*$ band at *ca.* 325 nm in the u.v. spectrum. Typical spectroscopic data is shown in Figure 1. Good first-order kinetics were obtained and the rate data together with related literature data [13,14] are collected together in Table 1. The data for two of the systems (33; X = Y = Ph) and (33; X = Y = CO_2Et) need to be treated with some caution since products were produced which themselves gave rise to u.v. absorptions in the region of interest and the baseline continued to drift upwards even when nitrogen elimination was complete. The resultant uncertainty in baseline position means that the data must be considerably less accurate. It should be noted that for the α-methylated 4-alkylidenepyrazolines positive entropies of activation were obtained in each case; they were in the normal range for pyrazoline pyrolysis and this suggests, therefore, a singlet rather than a triplet intermediate. Similar positive entropies of activation had been previously reported and interpreted, similarly, by Berson for bicyclic 4-alkylidene-1-pyrazolines [*e.g.* compound (42)].[13] Trindle,[8] however, had attributed the lack of intersystem crossing here to the fact that the bicyclic compounds are bound to open in a manner which involves disrotation of the developing radical centres rather than (what he believes to be) the favoured conrotatory manner. This restriction does not apply to the compounds investigated in the present study. Although it, therefore, seems that these reactions involve a singlet intermediate, the problem which remains is whether the first formed intermediate is a TMM or a diazyl biradical.[6] In his more recent papers Crawford [12] has argued in favour of a diazenyl biradical but the only



SCHEME 2

clear evidence of a diazenyl biradical intermediate is that which has been obtained by Berson [14] in his studies of the pyrolysis of pyrazoline (42) (Scheme 3). Here deazetation is accompanied by formation of the rearrangement product (43) showing that at least some of the pyrolysis is proceeding *via* the biradical (45). It may, however, be significant that this is the only example of its kind. It

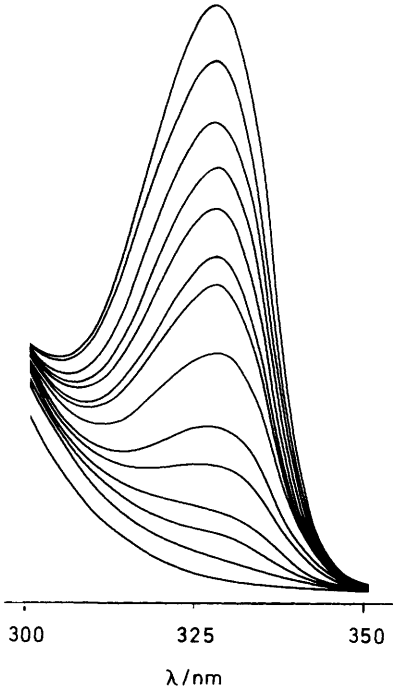
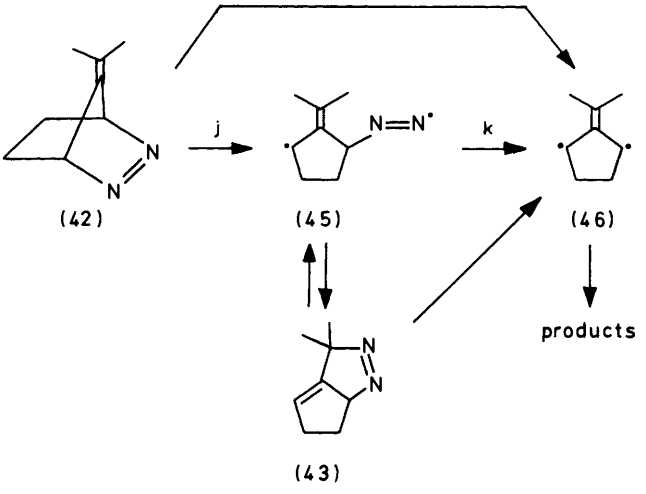


FIGURE 1 Pyrolysis of 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (1) in hexadecane at 216.4 °C. Portion of the u.v. spectrum showing the disappearance of the N=N n→π* bond at *ca.* 325 nm

seems reasonable to expect that if this mechanism were general other examples of rearrangement before nitrogen elimination would be noted but neither in Crawford's studies nor in the case of any of the compounds that we have investigated could such a rearrangement be found. Furthermore the stereospecificity of certain singlet TMM + olefin (2π) cycloaddition reactions [5,15] suggests that they are concerted and, by inference, that the virtual reverse of this process, fragmentation of a 4-alkylidenepyrazoline into a singlet TMM and nitrogen (2π), can also be concerted. Berson has suggested that the balance between stepwise and synchronous C–N bond breaking is determined by orbital symmetry factors relating to the ordering of the energies of ψ_2 and ψ_3 in the singlet TMM generated, which, in turn, is determined by the substituents on the system.[14] If this is the case then the mechanism will be expected to vary from system to system. Whether the intermediate is a diazenyl biradical or a TMM, however, it seems reasonable to expect that substituents X and Y on the double bond of the pyrazoline (33) which are capable of stabilising a developing radical centre should increase the rate of the reaction. Indeed it is known that the rate of nitrogen elimination from other diazines correlates well with the stability of the radical produced.[16] Reference to Table 1, however, shows that the pyrazolines (33) do *not* fulfil this expectation. For example, comparison of the last two entries in the Table shows that replacement of one of the hydrogens in the methylene group by a radical-stabilizing phenyl substituent increases the reaction rate but a second phenyl slows it down again. It is also interesting to note that whereas a 4-alkylidene group itself normally lowers the barrier to nitrogen loss by *ca.* 10 kcal mol^{-1} [compare compounds (40) with (36) and compounds (41) with (42) and (43)], in the α-methylated series, this is not the case [compare compounds (44) with (33)]. The ' anomolous ' behaviour of the α-methylated pyrazolines may be attributed to two factors. Firstly, the presence of the α-methyl groups seems to flatten the pyrazoline ring; [17] a normal envelope-like folding of the ring resulting in a clash of the methyl substituents on C-3 and C-5. In the case of compound (1) an *X*-ray crystallographic structure determination has shown (in the solid state) an angle of only 2° between the plane defined by atoms C(3)–C(4)–C(5) and that defined by atoms N(1)–N(2)–C(3)–C(5).[17b] In 'normal' pyrazolines this fold angle is 24 ± 9° [18] and in compound (42) it is 51°.[19] A result of this flattening is that in compound (33) [unlike (36) and (42)] the π-bond of the 4-alkylidene substituent and the breaking C–N α bonds are nearly orthogonal. The other factor which is probably important is the geometry of the intermediate

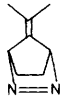


SCHEME 3

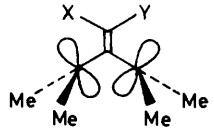
produced. For the α-methylated 4-alkylidene-1-pyrazolines our photochemical studies suggested that the singlet TMM is generated in a bis-orthogonal geometry (47) and that rotation of the CMe_2 groups is slow relative to ring closure.[20] If the same state of affairs applies to the thermal reactions it seems likely that, not only are the π bond of the alkylidene group and the breaking C–N bonds almost orthogonal to start with, but that this orthogonality is preserved in the intermediate so that there is little chance of increased conjugation in the transition state. However, this may not be equally

TABLE 1

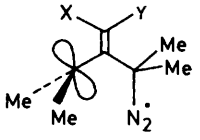
Rate data for the pyrolysis of 4-alkylidene-1-pyrazolines

Pyrazoline	X	Y	Medium	$k_{rel.}$ (200 °C)	E_a/kcal mol^{-1} (error)	$\Delta H^{\ddagger}$/kcal mol^{-1} (error)	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} (error)	Ref.
 (40)			Vapour phase	1	42.4	—	+11.2	13
 (36)			Vapour phase	68	32.6	—	−1.1	10
 (41)			Vapour phase	23	37.3	—	+8.7	13
 (42)			Benzene	360 000	27.6 (0.5)	—	+6.5	14
			CH_3CN	200 000	28.8 (0.5)		+8.3	14
 (43)			CH_3CN	450 000	28.0 (0.5)		+8.1	14
 (44)			Vapour phase	5.4	37.7	—	+4.6	13
	X	Y						
 (33)	Me	Me	Hexadecane	0.041	—	44.9 (1.0)	+12.6 (0.5)	This work
	Cl	Cl	Hexadecane	0.078	—	45.1 (1.1)	+14.3 (0.5)	This work
	CO_2Et	CO_2Et	Hexadecane	0.26	—	38 (3)	+2.0 (0.7)	This work
	H	CO_2Et	Hexadecane	0.28	—	41.4 (1.4)	+9.0 (0.3)	This work
	Ph	Ph	Hexadecane	0.43	—	39.5 (0.8)	+5.9 (0.2)	This work
	H	Bu^t	Hexadecane	0.61	—	41.0 (1.2)	+9.7 (0.3)	This work
	H	Me	Hexadecane	0.65	—	40.3 (1.5)	+8.5 (0.3)	This work
	CN	CN	Hexadecane	1.1	—	39.0 (0.2)	+6.7 (0.2)	This work
	H	Cl	Vapour phase	1.6	—	—	—	3
	H	H	Hexadecane	2.5	—	36.9 (1.0)	+4.1 (0.2)	This work
	H	Ph	Hexadecane	3.8	—	38.3 (1.0)	+7.6 (0.2)	This work

true for all of the α-methylated systems studied. One trend which is apparent from the data in Table 1 is that doubling up of a substituent [X, Y = Ph_2 rather than Ph, H or Me_2, rather than Me, H or $(CO_2Et)_2$ rather than CO_2Et, H or Cl_2 rather than Cl, H] always slows down



(47)



(48)

the reaction. This suggests that complete orthogonality is perhaps confined to the most sterically congested systems and that in the mono-substituted compounds and the ' parent ' system (X=Y=H) a little conjugation does develop in the transition state. The effect is, however, small and it is difficult to know whether it should be related to the effect of the substituents on the conformation of the pyrazoline, or the reaction intermediate, or on both of these. It must also be remembered that there is no compelling evidence as to whether the first formed intermediate is a TMM or a diazenyl biradical. If it is a TMM then these kinetic results are at least consistent with the idea, developed in the previous paper,[19] that the singlet TMM *in this tetramethylated series* is generated in a bis-orthogonal rather than a planar or a mono-orthogonal geometry.

EXPERIMENTAL

Flash vacuum pyrolyses were performed using the apparatus previously described [21] and at a pressure of 10^{-3}—10^{-4} mmHg.

Pyrolysis of 3,3,5,5-*Tetramethyl*-4-(2,2,4,4-*tetramethylthietan*-3-*ylidene*)-1-*pyrazoline* S,S-*Dioxide* (13).—A solution of the pyrazoline in benzene heated at 200 °C in a sealed tube for 24 h gave a quantitative yield of 2,2,4,4-*tetramethyl*-3-(2,2,3,3-*tetramethylcyclopropylidene*)*thietan* S,S-*dioxide* (14) identical in all respects with that prepared photochemically.[20]

A solution of the pyrazoline (40 mg) in diphenyl ether (1 cm^3) was sealed in an n.m.r. tube and heated at 200 °C. The reaction was monitored by n.m.r. spectroscopy and showed first a quantitative formation of the cyclopropane (14) and then of 2,2,4,4-*tetramethyl*-3-(2,4-*dimethylpent*-1-*en*-3-*ylidene*)*thietan* S,S-*dioxide* (15) which was purified by chromatography on Kieselgel (eluant chloroform), m.p. 117—120 °C [after recrystallisation from chloroform–light petroleum (b.p. 40—60 °C)] (Found: C, 65.4; H, 9.2; S, 12.6%; M^+, 256.149 0. $C_{14}H_{24}SO_2$ 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 1.04 (6 H, d, *J* 7 Hz, Me_2CH), 1.61, 1.70 (each 6 H, s, thietan CMe_2), 1.90 (3 H, broad s, vinyl Me), 2.69 (1 H,

septet, J 7 Hz, Me_2CH), and 4.63, and 5.12 (each 1 H, broad s, CH_2=C); *m/e* 256 (M^+, <0.1%), 192 ($C_{14}H_{24}^+$, 11), 177 ($C_{13}H_{21}^+$, 39), 149 ($C_{11}H_{14}^+$, 80), and 135 ($C_{10}H_{15}^+$, 100).

Pyrolysis of 4-(2,2-*Dimethylpropylidene*)-3,3,5,5-*tetramethyl*-1-*pyrazoline* (16).—A solution of the pyrazoline (16) (45 mg) in benzene (1 cm^3) in a sealed n.m.r. tube was heated at 196 °C and the reaction monitored by n.m.r. spectroscopy. After 2 days no starting material and very little (2,2-dimethylpropylidene)-2,2,3,3-tetramethylcyclopropane (17) remained. Chromatography on Kieselgel [eluant light petroleum (b.p. 40—60 °C)] gave a colourless oil which was bulb distilled. G.l.c.–mass spectroscopy showed this to be a 68 : 18 : 12 mixture of three isomeric hydrocarbons each M^+, *m/e* 166 (main component M^+, 166.172 3. $C_{12}H_{22}$ requires M^+, 166.172 1). These were most probably the dienes *E*- and *Z*-3-isopropyl-2,5,5-trimethylpenta-1,3-diene (18) and (19) and 3-isopropylidene-2,5,5-trimethylpent-1-ene (20), δ_H 0.8 (s, Bu^t), 0.85—1.2 (m, Pr^i), 1.48, 1.62 (broad singlets, vinyl Me), 2.6, 2.7 (singlets), and 4.62, 4.68, 5.22, and 5.35 (broad singlets, vinyl H). The product from this reaction in chloroform was mixed with liquid sulphur dioxide, sealed in a tube, and heated on a steam-bath for 18 h. The tube was opened, the solvent and excess of sulphur dioxide removed under reduced pressure, and the residue chromatographed on Kieselgel (eluant chloroform) to give 3-*isopropyl*-4-*methyl*-2-t-*butyl*-3-*thiolen* S,S-*dioxide* (21), as a white solid, m.p. (after recrystallisation from chloroform–ether) 117—119 °C (Found: C, 62.9; H, 9.7%; M^+, 230.134 7. $C_{12}H_{22}SO_2$ requires C, 62.6; H, 9.6%; M^+, 230.134 0), $\nu_{max.}$ ($CHCl_3$) 1 120 and 1 305 cm^{-1} (SO_2); δ_H 1.12 (9 H, s, Bu^t), 1.20 (6 H, d, Me_2CH), 1.94 (3 H, broad s, vinyl Me), 2.5 (1 H, septet, Me_2CH), and 3.2—3.8 (3 H, m, CH_2SO_2CH); *m/e* 230 (M^+, 3%) and 174 ($M^+ - C_4H_8$, 100).

Pyrolysis of 3,3,5,5-*Tetramethyl*-1-*pyrazolin*-4-*ylidenemalonitrile* (22).—The pyrazoline (22) (30 mg) in benzene (0.5 cm^3) was sealed in an n.m.r. tube, heated at 195 °C, and the reaction monitored by n.m.r. spectroscopy. The initial product appeared to be 2,2-dicyano-1-isopropylidene-3,3-dimethylcyclopropane (23) but almost as quickly as it was formed it was converted into 2,4-*dimethylpent*-1-*en*-3-*ylidenemalonitrile* (24). After 6 h this was the only product (n.m.r.). The solvent was removed under reduced pressure and the residue chromatographed on Kieselgel [elution with light petroleum (b.p. 30—40 °C)–ether (6 : 1)]. Bulb distillation gave the *diene* as a pale yellow oil (Found: C, 74.6; H, 7.7; N, 17.4%; M^+, 160.099 7. $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.5; N, 17.6%; M^+, 160.100 4), $\nu_{max.}$ ($CHCl_3$) 2 238 (CN) and 1 573 (C=C) cm^{-1}; δ_H 1.22 (6 H, d, J 7 Hz, Me_2CH), 2.00 (3 H, m, vinyl Me), 3.24 (1 H, septet, J 7 Hz, Me_2CH), and 4.97 and 5.34 (each 1 H, broad s, CH_2=C); *m/e* 160 (M^+, 25%), 145 (M^+ — Me, 100), 132 (19), and 118 (70).

Flash vacuum pyrolysis at 432 °C gave a mixture of the cyclopropane (23) and the diene (24).

Flash vacuum pyrolysis of the pyrazoline (120 mg) at 580 °C gave a white solid (presumably a dihydropyridine) which on exposure to the air reverted to a yellow oil which was purified by chromatography on Kieselgel (elution with chloroform) and low-temperature recrystallisation from ether–light petroleum (b.p. 30—40 °C) to give 3-*cyano*-4-*isopropenyl*-5-*methylpyridine* (27) (35 mg, 35%) as a low-melting solid, m.p. *ca.* 25 °C (Found: M^+, 158.084 0. $C_{10}H_{10}N_2$ requires M^+, 158.084 4), $\nu_{max.}$ ($CHCl_3$) 2 238 (CN) and 1 580 cm^{-1}; δ_H 2.08 (3 H, broad s, vinyl Me), 2.32 (3 H, s, ring Me), 5.01 and 5.48 (each 1 H, m, C=CH_2), and 8.56 and 8.67 (each 1 H, s, ring H); *m/e* 158 (M^+, 100%), 157 (70), and 143 (M^+ — Me, 40). The pyridine was converted into its *picrate*, m.p. 124—128 °C, after recrystallisation from methanol (Found: C, 49.4; H, 3.8; N, 17.8. $C_{16}H_{13}N_5O_7$ requires C, 49.6; H, 3.4; N, 18.1%), δ_H 2.10 (3 H, broad s, vinyl Me), 2.33 (3 H, s, ring Me), 3.69 (1 H, broad s, NH), 5.50 and 5.82 (each 1 H, broad s, CH_2=C), 7.26 (2 H, s, ArH), and 9.19 (2 H, broad s, pyridine ring H).

Pyrolysis of 4-*Dichloromethylene*-3,3,5,5-*tetramethyl*-1-*pyrazoline* (28).—Flash vacuum pyrolysis of the pyrazoline (28) at 440 °C gave recovered starting material, 1-dichloromethylene-2,2,3,3-tetramethylcyclopropane (29),[20] and (mainly) 2,2-dichloro-1-isopropylidene-3,3-dimethylcyclopropane (30). This last compound could be obtained pure by photolysing the pyrazoline in benzene and heating the resultant solution of 1-dichloromethylene-2,2,3,3-tetramethylcyclopropane [20] in a sealed tube for 2 h at 196 °C. Removal of the solvent and bulb distillation gave 2,2-*dichloro*-1-*isopropylidene*-3,3-*dimethylcyclopropane* (30) as a clear liquid (Found: C, 53.7; H, 6.8%; M^+, 178.031 4, 180.028 4, 182.026 6. $C_8H_{12}Cl_2$ requires C, 53.5; H, 6.8%; M^+, 178.031 6, 180.028 2, 182.025 7), δ_H 1.40 (6 H, s, cyclopropyl CMe_2), 1.83, and 1.97 (each 3 H, s, vinyl CMe_2); δ_C (C_6D_6) 21.06, 21.94 (methyls), 32.33 (CMe_2), 63.8 (? very weak, CCl_2), 128.45 (C=CMe_2), and 131.69 (C=CMe_2); *m/e* 182, 180,

TABLE 2

Rate data for the deazetisation of 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines (33)

Substituents X	Substituents Y	T/°C	10^4k/s^{-1}	T/°C	10^4k/s^{-1}	T/°C	10^4k/s^{-1}	T/°C	10^4k/s^{-1}
Me	Me	169.4	0.003 72	187.0	0.0264	192.0	0.0372	201.2	0.117
		216.4	0.662	223.0	0.993	230.4	1.78		
Cl	Cl	170.2	0.006 51	195.0	0.0112	199.8	0.223	223.0	1.77
		230.4	3.44						
CO_2Et	CO_2Et	169.4	0.0405	180.0	0.0950	187.0	0.163	201.2	0.802
H	CO_2Et	169.4	0.0310	173.0	0.0515	180.0	0.0911	187.0	0.178
		192.0	0.308	201.2	0.865				
Ph	Ph	169.4	0.0561	187.0	0.306	192.0	0.497	201.2	1.24
H	Bu^t	169.4	0.0703	191.6	0.641	201.2	1.75		
H	Me	169.4	0.0823	191.6	0.709	201.2	1.97		
CN	CN	169.4	0.154	173.0	0.193	180.0	0.408	187.0	0.794
		192.0	1.34	201.2	3.03				
H	H	169.4	0.391	187.0	1.86	191.6	3.03	201.2	7.06
H	Ph	169.4	0.536	173.0	0.736	180.0	1.38	187.0	3.16
		192.0	4.59	201.2	10.1				

178 (M^+, 0.4, 3.9, 6.5%), 145, 143 (M^+ − Cl, 19, 58), 107 (100), and 91 (93).

Flash vacuum pyrolysis of the pyrazoline (28) at 540 °C gave some 2,2-dichloro-1-isopropylidene-3,3-dimethylcyclopropane (30) and some of the acetylene (32) (total *ca.* 15%) but mainly (*ca.* 85%) 3,4-dichloro-2,5-dimethylhexa-2,4-diene (31) (M^+ 178.031 3. $C_8H_{12}Cl_2$ requires 178.031 6), δ_H 1.77 and 1.95 (each 6 H, s); δ_C (C_6D_6) 20.7, 20.8 (CMe_2), and 123.6 and 134.1 (C=C); *m/e* 178, 180, 182 (M^+, 19, 12, 1%), 143, 145 (56, 17), 107 (78), and 91 (100). This product showed identical spectroscopic properties and g.l.c. behaviour with authentic material prepared by the method of Loewenthal.[22]

Flash vacuum pyrolysis of the pyrazoline (28) or of the diene (31) at 840 °C gave 2,5-dimethylhexa-1,5-diene-3-yne (32), $\nu_{max.}$ (film) 895 (CH_2=C), 1 605 (C=C), and 3 095 cm^{-1} (CH_2=C); δ_H 1.89 (6 H, m, collapsed to a singlet by irradiation of the signal at δ 5.23, CH_3) and δ 5.23 (4 H, m, collapsed to an AB quartet, *J* 2 Hz, on irradiation of the signal at δ 1.89, CH_2); δ_C (C_6D_6) 23.5 (Me), 90.3 (C≡C), 121.6 (CH_2), and 127.4 (CH_2=*C*); *m/e* 106 (M^+, 100%), 91 (M^+ − CH_3, 75), and 65 (M^+ − C_3H_5, 38). This product showed identical spectroscopic properties and g.l.c. behaviour to authentic material prepared by phosphoric acid dehydration of 3,5-dimethylhex-4-yne-3,5-diol.[22]

When a sample of the pyrazoline (28) was heated at *ca.* 200 °C in benzene solution and the reaction monitored by n.m.r. spectroscopy the first three stages of this sequence pyrazoline (28)→cyclopropane (29)→cyclopropane (30)→diene (31) were also observed but the solution became very dark and evidently by-products were also formed.

Kinetic Studies.—The pyrazoline (*ca.* 6 mg) was dissolved in hexadecane (*ca.* 2.5 ml) in a Pyrex cell made from 5 mm i.d., 12 mm i.w. rectangular tubing (Jencons) which was then attached to the vacuum line. After degassing the solution the cell was sealed off and the u.v. spectrum recorded on a Unicam SP 800 instrument using a similar cell containing hexadecane as the reference. The cell was completely immersed in a thermostatted bath and after a period of time removed and rapidly cooled to room temperature. The spectrum was recorded once again and the process repeated many times. The kinetics were monitored from the disappearance of the N=N n→π* band at *ca.* 325 nm. With the exception of two systems (X=Y=Ph and X=Y=CO_2Et, see main text) there were no difficulties in obtaining good 'infinity' reading and good first-order behaviour was observed over at least four half-lives. Rate constants were obtained by a simple 'least squares' procedure and are collected together in Table 2. Temperatures were determined using standard, calibrated thermometers. Activation parameters were also obtained using a simple 'least squares' program and values are given in Table 1. As a check on our general procedures we first measured the kinetics of deazetation of the pyrazoline (40) in acetonitrile and obtained activation prameters essentially the same as those reported in the literature.[14] Unfortunately, however, there is a large discrepancy between the values which we obtained for pyrazoline (1) ($\Delta H^{\ddagger}$, 44.9 ± 1; $\Delta S^{\ddagger}$, + 12.6 ± 0.5) and those recorded by Engel and Shen [23] for the same compound ($\Delta H^{\ddagger}$, 38.8; $\Delta S^{\ddagger}$, 0.5). The reasons for this discrepancy can be appreciated by reference to Figure 2. The actual rates obtained by Engel and Shen are close to those which we obtained at the upper end of the temperature range. The erroneous slope of the line based on their data arises mainly from the small temperature range which they investigated. It may also be significant that the method of repeatedly heating and cooling a cell is subject to a cumulative error arising from the time taken for the cell to reach 'bath' and 'room temperatures' respectively and this cumulative error is most significant at high reaction rates, *i.e.* the upper end of the temperature scale.

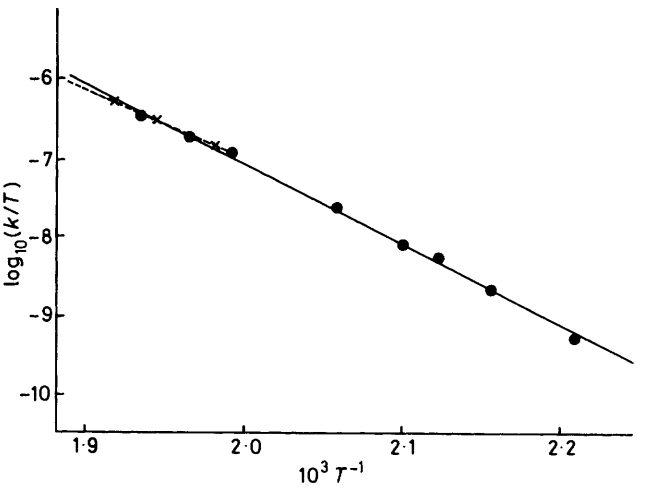


FIGURE 2 Kinetic data for the elimination of nitrogen from 3,3,5,5-tetramethyl-4-isopropylidene-1-pyrazoline obtained by Engel and Shen [23] (– – × –) and as part of the present work (——●——)

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