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A Convenient New Synthesis of 4-Alkylidene-3,3,5,5-Tetramethyl-$\Delta^{1,2}$-Pyrazolines.

Potential Precursors of T.M.M.

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Probably the best precursors for T.M.M. biradicals (1 and derivatives thereof) are the 4-alkylidene-$\Delta^{1,2}$-pyrazolines first studied by Dowd[1]. Unfortunately the parent system 2 tends to undergo isomerisation[1,2] to give conjugated dienes, such as 3, and this may compete with the desired elimination of nitrogen. Day[3] has overcome this problem by working with the α-methylated systems 4 and Berson[4] by using the bicyclic systems 5.

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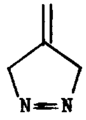

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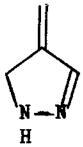

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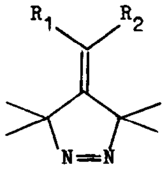

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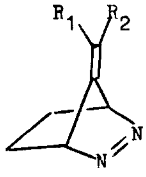

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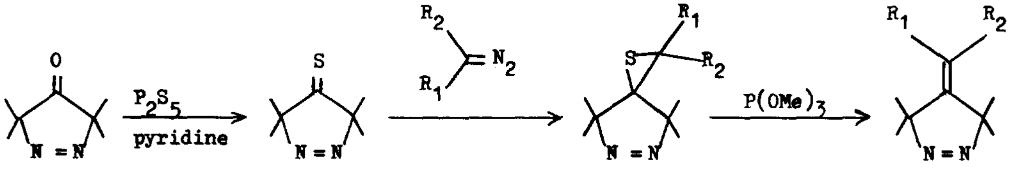
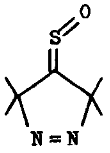
In order to unravel the complex relationship between structure and the balance between the singlet and triplet states of T.M.M. it is desirable to develop syntheses of compounds related to 4 and 5 in which the nature of the substituents R_1, R_2, the ring size (as in 5), and other structural features can be varied as widely as possible[5]. We have found that for the α-methylated systems the synthetic scheme outlined on the next page (which is based on our earlier syntheses of 3-alkylidenethietane dioxides[6]) is the most satisfactory and allows a wider variation in substituents than other routes which are currently available[7]. The intermediate thioketone 6 is a surprisingly stable, red, crystalline compound which is very readily sublimed. With permaleic acid it can be oxidised to a moderately stable sulphine 8. Both 6 and 8 form adducts with diazoalkanes (7 and 9[8]) which can be converted to the desired pyrazolines 4 but the best yields were obtained via. the episulphide 7 as shown.



6 7 4

R_1 = H	R_2 = H	99%	66%
Me	Me	86%	89%
Ph	Ph	75%	94%
H	Bu^t	74%	78%
H	Ph	82%	98%
H	CO_2Et	82%	90%

Flash vacuum pyrolysis of the isopropylidene pyrazoline (4, $R_1 = R_2$ = Me) under the same conditions[6] as were employed for the thietane 10 produced the same diene 11 (94% yield). This is consistent with a common intermediate for both reactions which may well be the hexamethyl-T.M.M. 12.



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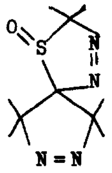

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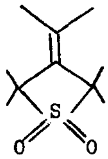

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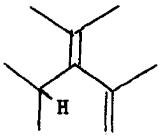

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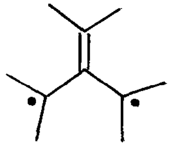

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