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PERMETHYL-44'-BIS-$\Delta^{1,2}$-PYRAZOLINYLIDENE (4)

THE SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STRUCTURE OF A HIGHLY CROWDED OLEFIN

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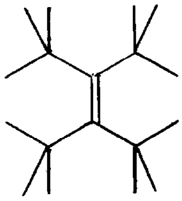
In recent years there has been considerable interest in the synthesis and properties of highly crowded olefins.[1] Much of this effort has been concentrated on obtaining tetra*tert*butyl ethylene (1). Whilst this has remained an elusive goal some olefins which approach its high degree of steric crowding (for example 2 and 3) have been obtained. One of the most effective methods for synthesising such systems has been developed by the groups of Barton[2] and Kellog[3] and involves a double elimination from a Δ^3-1,3,4-thiadiazoline or Δ^3-1,3,4-selenodiazoline intermediate. We have employed this route in the formation of the highly hindered olefin 4. Like tetra*tert*butyl ethylene 1 and fenchylidenefenchane 3 this has four quaternary carbons attached to the double bond but, as in 3, the steric crowding is somewhat reduced by "tying" the substituents back in a ring.



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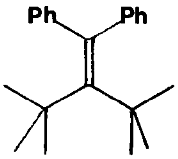

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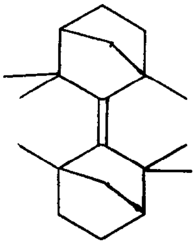

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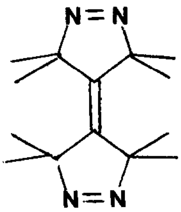

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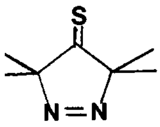
When the thioketone 5[4] and the diazo compound[5] 6 are allowed to react in ether at 0 °C and the mixture cooled to -70 °C the thiadiazoline 7 precipitates out as a white powdery solid (70%, m.p. 210-12° dec., δ ($CDCl_3$) 1.38, broad). If this is heated in solution 5 and decomposition products of 6 are obtained. If it is heated as the solid, however, (120 °C, 30 min) it gives the episulphide 8 (m.p. 210° dec., δ 1.57 and 1.66) which on heating with trimethyl phosphite gives the olefin 4 (m.p. 214.5° dec., δ 1.65). These last two stages proceed in almost quantitative yield. The difference between the solution and solid phase thermolysis of 7 is interesting. Presumably, if it reverts to 5 and 6 in the solid phase, these are held sufficiently close for them to recombine before 6 has a chance to decompose.



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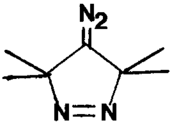

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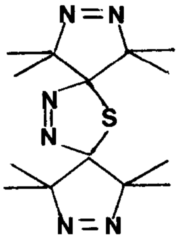

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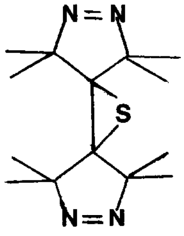

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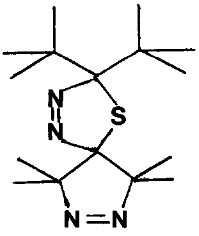

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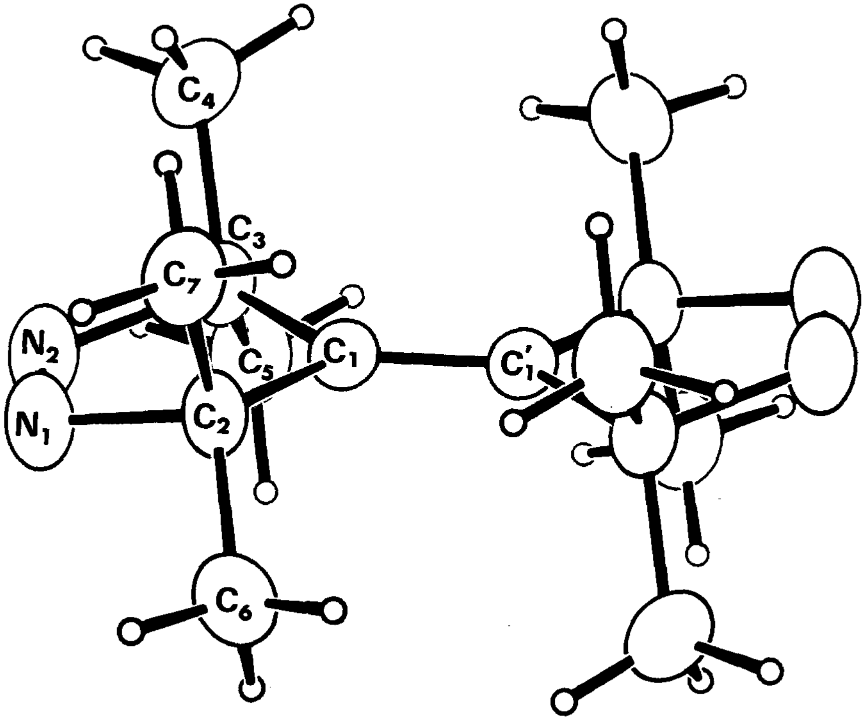
In an attempt to extend these syntheses to even more crowded systems it was shown that the thioketone 5 with di*tert*butyl diazomethane gave the thiadiazoline 9. When 9 is heated in solution it reverts to starting materials and the thioketone 5 is recovered. When it is heated in the solid phase both 5 and the episulphide 8 are produced. This latter compound presumably arises from a combination of 5 and 6 produced by a retro 2π + 4π reaction of 9 in both possible senses.

The structure of compound 4 was determined by X-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, with a = 9.061 (1), b = 12.909 (2), c = 5.984 (1) Å and β = 95.53 (2)°. With two molecules per cell the molecule has crystallographic symmetry C_i. The structure analysis used the 837 independent F_o having $I > 3\sigma(I)$ and least-squares refinement with anisotropic vibration parameters for C and N and isotropic parameters for H gave a final R of 3.70%. The structure is shown in the Figure.



ORTEP drawing of the molecular structure of **4**

Principal dimensions are:- C(1) - C(1') 1.356(2)Å, C(1) - C(2) 1.536(2)Å, C(1) - C(3) 1.544(2)Å, C(2) - N(1) 1.505(2)Å, C(3) - N(2) 1.502(2)Å, N(1) - N(2) 1.235(2)Å.

Principal bond angles are:- C(1') - C(1) - C(2) 128.4(1)°, C(1') - C(1) - C(3) 127.8(1)°, C(2) - C(1) - C(3) 103.8(1)°, C(1) - C(2) - C(6) 118.4(1)°, C(1) - C(2) - C(7) 114.6(1)°, C(1) - C(3) - C(4) 114.8(1), C(1) - C(3) - C(5) 117.6(1), C(2) - N(1) - N(2) 112.9(1)°, C(3) - N(2) - N(1) 113.6(1)°.

Force field calculations on hindered olefins[6] suggest that steric crowding is often relieved by twisting about the double bond and for tetra*tert*butyl ethylene this twist is calculated as ca. 75°. X-Ray crystallographic studies have revealed a twist of 24° in the case of the diphenyldi*tert*butyl olefin **2**[7] and 11.8° in the case of fenchylidenefenchane **3**.[8] In the present compound the crystallographically imposed centre of symmetry precludes any such twist, and the central olefinic unit is essentially planar. Steric hindrance is relieved by the "tying back" to give a C(2) - C(1) - C(3) angle of 104° with a consequent increase of the other angles at C(1) to 128°. There is also a "bending back" of the methyl substituents as shown by the C-C-Me angles of 115° and 118° in contrast to the N-C-Me angles which are in the range 103.2 - 103.9(1)°. In spite of the presence of the sp^2 hybridised carbon atom the dimensions of the pyrazoline ring are similar to those in other $\Delta^{1,2}$-pyrazolines[9] except that the ring is somewhat flattened with C(1) displaced 0.26 Å from the plane of the other four ring atoms (c.f. typical[9] values of 0.49, 0.49, 0.58, 0.24 and 0.45 Å). This is, presumably, the result of the clash of the methyl groups across the top of the ring and is consistent with the predictions (on kinetic grounds) of Crawford and Tokunaga.[10]

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