

NITRENE ADDITION TO ALLENES 1,4-DIAZASPIRO[2.2]PENTANES

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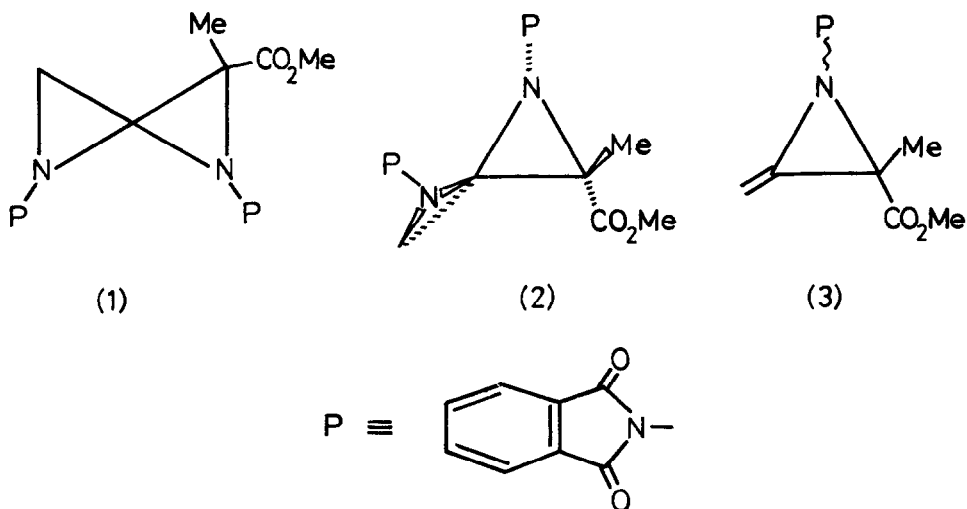
Summary A crystalline product isolated from addition of phthalimidonitrene to methyl 2-methylbuta-2,3-dienoate is formulated on spectroscopic grounds as 2-methoxycarbonyl-2-methyl-1,4-diphthalimido-1,4-diazaspiro[2.2]pentane

Ethoxycarbonylnitrene has recently been shown to add to allenes to yield methylene-aziridines¹ We have added phthalimidonitrene² to methyl 2-methylbuta-2,3-dienoate and obtained a crystalline product, m p 172-173.5°C in 14% yield On the basis of the following spectroscopic evidence, this product is formulated as the diazaspiro[2.2]pentane (1), a previously unknown strained ring system³ m/e 432 (8%, M⁺), 373 (24%), 286 (9%), 258 (12%), 147 (100%) and 104 (79%), $\nu_{\max}^{\text{nujol}}$ 1782 (w), 1766 (sh), 1755 (sh), 1744, 1736 and 1718 cm⁻¹ In the n.m.r. spectrum (CDCl₃), 2 invertomers at the aziridine ring nitrogens are clearly visible with δ 7.76 (8H, m), 4.20 (1H, d, J = 1.3 Hz), 3.66 (1H, d, J = 1.3 Hz), 3.46 (3H, s), 1.79 (3H, s) and 7.76 (8H, m), 4.71 (1H, d, J = 3.4 Hz), 3.88 (3H, s), 3.33 (1H, d, J = 3.4 Hz), 1.72 (3H, s) in a ratio of 70:30 respectively

Compound (1) may exist as two diastereoisomers and the capability for slow inversion at two nitrogen centres in each leads to a total of eight possible stereoisomeric forms In fact, examination of the crude reaction product by n.m.r. spectroscopy suggests that only one of the diastereoisomers is formed in significant yield. That (1) contains a mixture of invertomers and not diastereoisomers was shown by crystallisation from CHCl₃/EtOAc, dissolution of the crystals in CDCl₃ at -30°C and measurement of the n.m.r. spectrum at that temperature⁴ The spectrum corresponded with that of the major invertomer (better than 90% pure) Equilibration occurred at ca -5°C as shown by the appearance of signals due to the minor invertomer, leaving a spectrum identical to that described above for the mixture

Estimation of probable relative thermodynamic stabilities in this series and analysis of the n.m.r. spectrum leads to the tentative suggestion that the major invertomer is (2) The higher field chemical shift of the ester methyl group in the major invertomer, for 4305

example, points to a cis-relationship with the N-phthalimido group whose pronounced shielding effect in such a situation is well established⁵ This is the diastereoisomer which would be expected if addition of the second phthalimidonitrene were to take place from the less hindered side of an intermediate methyleneaziridine (3) in which the major invertomer is assumed to have the ester and phthalimido groups cis.⁴ It is also the diastereoisomer anticipated should addition of the second phthalimidonitrene occur before thermodynamic equilibration at this methyleneaziridine ring nitrogen since the kinetically formed invertomer of (3) is also expected to have phthalimido and ester groups cis.⁶



References

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