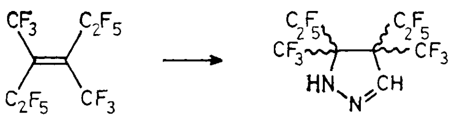
A Novel Rearrangement of a Strained Pyrazoline

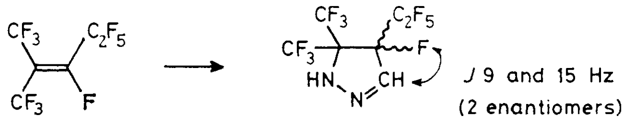
Martin R. Bryce, Richard D. Chambers,* and Graham Taylor

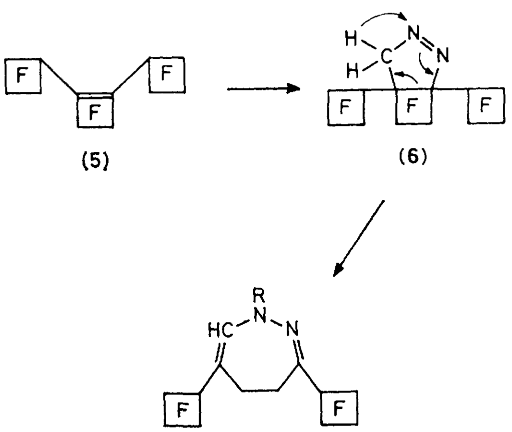
Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, U.K.

Perfluoroalkyl groups activate double-bonds towards cycloaddition reactions with diazomethane; a novel ring expansion is described, arising from a combination of eclipsing interactions and angle-strain.

We have an interest in developing the chemistry of systems having a number of perfluoroalkyl groups attached to a double bond[1] and we can now conclude from recent work that a perfluoroalkyl group is strongly activating, with respect to fluorine at the same position, for reactions with diazomethane. For example we now find that perfluoro-3,4-dimethylhex-3-


(1) (2) (93%)


(3) (4) (94%)


(5) (6)

(7) R = H (85%)
(8) R = Me

F in the centre of a ring signifies all bonds to fluorine.

ene (1) and perfluoro-2-methylpent-2-ene (3) react smoothly, in very high yield, with diazomethane giving the corresponding Δ^2-pyrazolines (2) and (4).† Only one regioisomer (4) was obtained and the structure follows simply from ^{1}H n.m.r. data which showed two doublets for the CH proton (J_{HF} 9 and 15 Hz); if the orientation of addition had been the reverse, then the CH proton would have appeared as a broadened singlet. In marked contrast, no reaction was observed between diazomethane and perfluoro-but-2-ene or -cyclohexene. These observations may be rationalised by the fact that π-LUMO energies are lowered by attachment to a perfluoroalkyl group more than by attachment to a fluorine atom.[2]

Strain, apparently, accounts for the reactivity of diazomethane with perfluoro(Dewar benzene), where a Δ^1-pyrazoline is obtained.[3] Compound (5) also reacts readily with diazomethane but, in this case, a pyrazoline is not isolated. Instead, the novel product (7) is obtained, arising from a remarkable rearrangement. In the presence of an excess of diazomethane, the corresponding *N*-methyl derivative (8) was obtained. The structure of (8) was indicated by spectroscopic data but has been unambiguously established by an *X*-ray crystallographic determination.[4]

It is clear that the first-formed pyrazoline (6) will suffer considerable eclipsing interactions involving the enforced cisoid arrangement of the perfluorocyclobutyl groups, attached to the fused ring system, as well as angle strain arising from the fused 4-membered ring itself. Therefore, the 1,5-H shift accompanied by the concomitant sigmatropic rearrangement (6) → (7) is driven by strain arising from a combination of these effects.

We are unaware of any analogous rearrangement.

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† Satisfactory elemental analyses were obtained for all compounds recorded here.