Polyhalogenoheterocyclic Compounds. Part 36.[1] Additions of Diazomethane to Perfluoropolyalkylethenes. A Frontier Orbital Rationalisation of Reactions of Fluorinated Alkenes with 1,3-Dipoles and Nucleophiles

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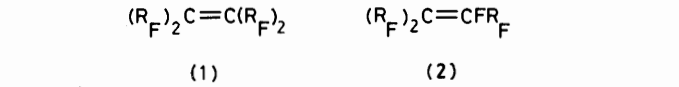
Additions of diazomethane to fluorinated alkenes have established the reactivity order $(R_F)_2C{=}C(R_F)_2 > (R_F)_2C{=}CFR_F \gg (R_F)_2C{=}CF_2$, $R_FCF{=}CFR_F$ (R_F = perfluoroalkyl). Highly regioselective addition occurs with the carbon of the dipole becoming attached preferentially to the site in the alkene most susceptible to nucleophilic attack. An approach based on considering frontier orbitals (F.O.) leads to a model for reactivity towards diazomethane in these systems. Also, consideration of F.O. is suggested as an alternative approach to accounting for reactions involving nucleophilic attack on fluorinated alkenes.

The literature on reactions that involve additions of diazomethane to alkene derivatives is concerned mainly with systems that have one or more electron-withdrawing groups attached to the double bond,[2,3] although additions to but-2-ene have been described.[4] Addition to cyclohexene does not occur but dihydropyrazoles are obtained, although only with difficulty, with cyclopentene and cyclobutene.[5] Surprisingly, however, there are comparatively few reports of reactions involving additions of diazomethane to fluorinated alkenes [6-9] and, except for the present study, we are unaware of any systematic investigation directed at establishing the effects of fluorine and perfluoroalkyl as substituent groups on the reactivity of alkenes towards diazomethane.

Fluoride-ion induced and related oligomerisation reactions of perfluorinated alkenes and cycloalkenes has led to a variety of novel compounds of general structures (1) and (2) [10,11] and we have a continued interest in developing the novel chemistry of these and related systems. This series of compounds has allowed us to investigate systematically the relationship of structure and reactivity of fluorinated alkenes towards diazomethane. In this paper we will attempt to provide a reasonable mechanistic model for diazomethane additions and link this with an alternative approach to explaining nucleophilic attack on fluorinated alkenes.

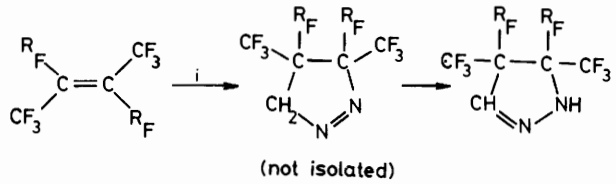
Systems of the type (1) are highly reactive towards diazomethane and addition to compound (3) gave an immediate reaction at 0 °C; presumably a Δ^1-dihydropyrazole (4) is the initial product but, so far, we have been unable to isolate this intermediate. Instead, we obtained the Δ^2-dihydropyrazole (5) (Scheme 1) whose structure is clear from the single vinylic proton, as well as from the broad N–H signal in the ^{1}H n.m.r. spectrum. Other workers [9c] have claimed the isolation of a Δ^1-dihydropyrazole from the closely related system (3a) but, in our hands, we have only been able to isolate a Δ^2-dihydropyrazole (5a) from this compound. The Δ^1-dihydropyrazole would be very susceptible to traces of acid [12] or base [12b] and it is possible that earlier workers were able to keep their system more free of acid or base than our own, although this was not discussed. A system with three perfluoroalkyl groups attached to the double bond, such as (6), was also surprisingly reactive giving, for the first time in our hands, an observable Δ^1-dihydropyrazole (7) (Scheme 2). This was the principal product and its structure follows from the n.m.r. data. The ^{13}C n.m.r. spectrum shows a CH_2 group and the ^{1}H n.m.r. spectrum contains these protons as part of an AB system, while no NH is present. A small amount (5—6%) of another regioisomer was observed but this was present as both the Δ^1-isomer (7a) and the Δ^2-isomer (7c). On standing, the Δ^2-isomer (7b) is formed from (7) and its structure follows from the n.m.r. data (see Experimental section). Coupling constant data for this isomer are not yet fully understood, but additional complexity may arise from slow inversion of the ring nitrogen in (7b) since it is established that the introduction of unsaturated sites as well as electron-withdrawing groups slows the inversion process.[13]

In an attempt to determine the relative reactivities of alkene



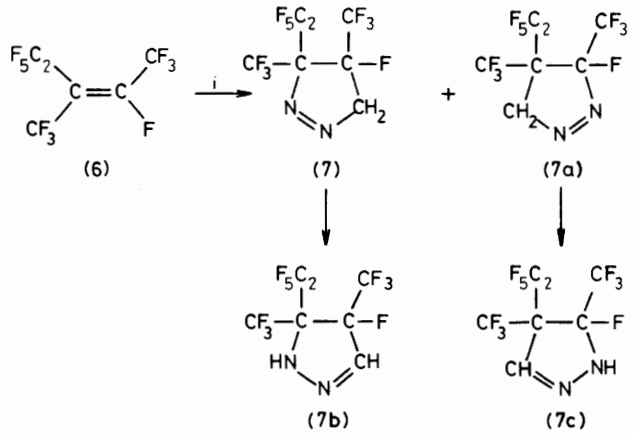
(1) (2)

R_F = perfluoroalkyl or part of a perfluorocycloalkyl group

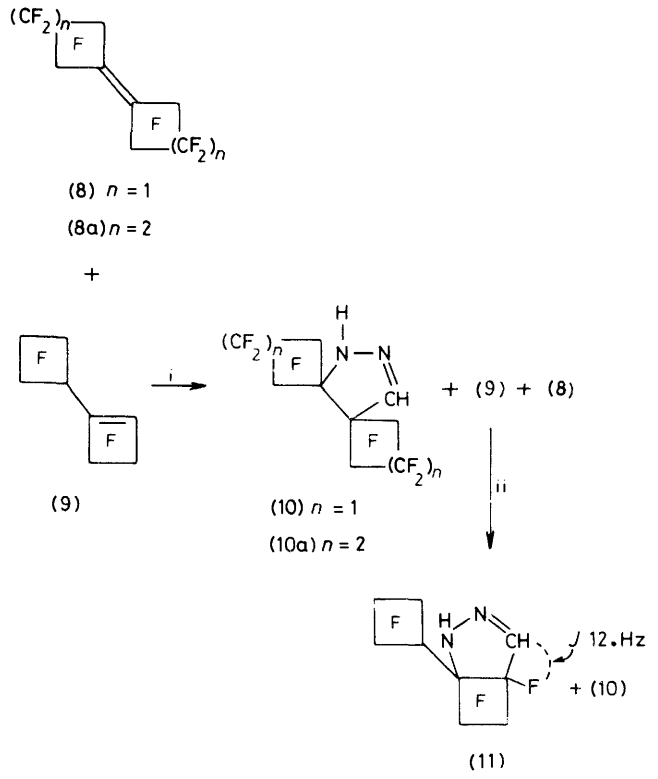


(3) $R_F = C_2F_5$ (*E* + *Z* isomers) (4) $R_F = C_2F_5$ (5) $R_F = C_2F_5$
(3a) $R_F = CF_3$ (4a) $R_F = CF_3$ (5a) $R_F = CF_3$

Scheme 1. *Reagents:* i, CH_2N_2, Et_2O, room temp.

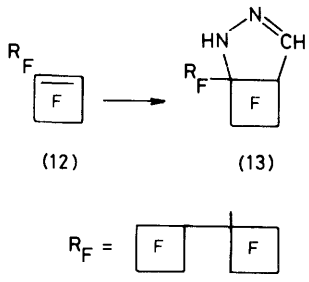


Scheme 2. *Reagents:* i, CH_2N_2, Et_2O, room temp.



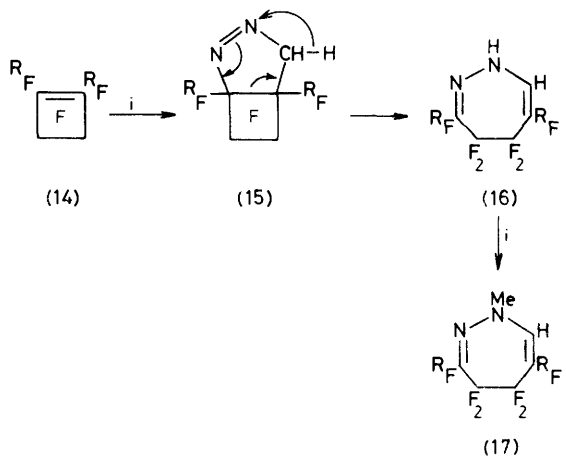
F in the centre of a ring denotes all unmarked bonds to F

Scheme 3. *Reagents:* i, Deficiency of CH_2N_2, room temp.; ii, excess of CH_2N_2, room temp.



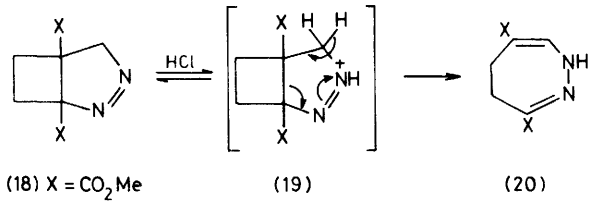
derivatives of the general types (1) and (2) we have carried out competition experiments between derivatives (3) and (6) for a deficiency of diazomethane; however, even at low temperatures only a slight preference for the system with four perfluoroalkyl groups, (3), was observed. A quite definite result was obtained, however, in competition reactions involving the mixture (8) and (9), where g.l.c. analysis of the reaction mixture showed that reaction occurred exclusively with the *exo*-isomer (8) giving the novel product (10) (Scheme 3) which has three rings joined through two spiro-centres. Further addition of diazomethane then led to reaction with the *endo*-isomer (9), again giving only one regioisomer (11). The structure of this isomer followed from the ^1H n.m.r. spectrum (see Experimental section) as both adducts (10) and (11) were characterised by separate experiments involving pure samples of the alkene derivatives (8) and (9) respectively. A further example of regiospecific addition occurred with the derivative (12), giving (13). In all of the cases of regiospecific addition, the carbon end of the dipole becomes attached to the site in the alkene which is also most susceptible to attack by nucleophiles (see later).

An isomer of (12), *i.e.* (14), reacted quite differently with

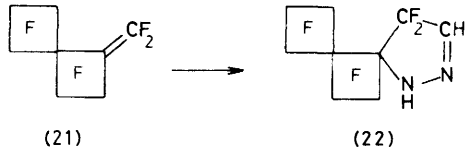


R_F = perfluorocyclobutyl

Scheme 4. *Reagents:* i, CH_2N_2, Et_2O, room temp.



Scheme 5.



diazomethane and led to an unusual rearrangement, indicated by the product (16) (Scheme 4); with excess of diazomethane, the *N*-methyl derivative (17) was also isolated. We were unable to determine the structures of (16) and (17) without some ambiguity by spectroscopic means, but this situation was resolved by an *X*-ray structure analysis of (17), determined by Professor King.[14]

Our attention has been drawn [12b] to reports of similar rearrangements (18; X = CO_2Me, X = CN), reported by Prinzbach and Martin,[15] *e.g.* the conversion (18) → (19) → (20) (Scheme 5) is promoted by acid. It is clear from a comparison of compounds (15) and (18) (X = CN, CO_2Me) that rearrangement is associated with strongly electron-withdrawing groups attached to the ring-junction sites. Also, rearrangement of (15) occurs more readily than in the systems (18); this we can attribute to the very unfavourable eclipsing interactions in (15) which are relieved by rearrangement.

Alkene derivatives of the type $(R_F)_2C{=}CF_2$ are frequently very hazardous, *e.g.* perfluoroisobutene has a toxicity level near that of nerve-gas [18] and limits the experiments that it is safe to conduct. We have, however, been able to add diazomethane to the novel spiro compound (21) to yield the dispiro product (22), albeit in only 40% yield, again demonstrating regiospecific addition. Nevertheless, this is a much more efficient reaction than with perfluorobut-2-ene, where no reaction was observed after prolonged contact with diazomethane. Therefore, it is reasonable to draw the overall conclusion that the order of reactivity towards diazomethane

$(R_F)_2C{=}CF_2$ (23) $R_FCF{=}CFR_F$ (24)

R_F = perfluoroalkyl

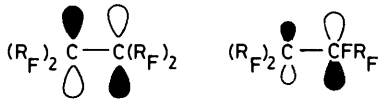
decreases in the series (1) ≥ (2) ≫ (23), (24) (R_F = perfluoroalkyl).

We have also sought to establish the effect on reactivity of fluorine as a substituent in comparison with hydrogen or chlorine atoms attached to the double bond. It has been reported [7] that $CF_3CH{=}CHCF_3$ gives a good yield of the corresponding Δ^2-dihydropyrazole with diazomethane, and we have now found that $CF_3CF{=}CHCF_3$ and diazomethane give a product that is probably a mixture of *both* regioisomers but only in very low yield and after prolonged contact. In contrast, $CF_3CCl{=}CClCF_3$ reacted very efficiently, again giving the corresponding Δ^2-dihydropyrazole. Therefore, we may reasonably conclude that the order of the activating influence of substituents at the double bond is perfluoroalkyl > chlorine > hydrogen > fluorine.

We have further posed the question of reactivity towards diazomethane, with decreasing perfluoro-alkyl or -cycloalkyl substitution at the double bond and find as, no doubt, others have found in the past, that alkene derivatives with two or more fluorine atoms directly attached to the double-bond are very unreactive. For example, we were unable to observe products from the reaction of diazomethane with perfluoro-cyclohexene, -but-2-ene, or -propene, even on prolonged contact. In contrast, perfluoro-cyclopentene and -cyclobutene each gave the corresponding Δ^2-dihydropyrazole, albeit very slowly indeed.

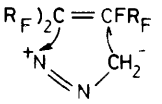
Mechanistic Considerations. A Frontier Orbital Approach.—It would be reasonable to anticipate that, if frontier orbitals govern the reactivity of fluorinated alkenes with diazomethane, then interaction of the LUMO of the fluorinated alkene with the HOMO of diazomethane would be the controlling process. Therefore, we need to consider the effect of fluorine and of perfluoroalkyl as substituents on the LUMO energy of an alkene. Electron-withdrawing substituents lower orbital energies and, consequently, perfluoroalkyl groups will have the effect of lowering the LUMO energy of the alkene. This is borne out by photoelectron spectroscopy [19,20] and the same technique points to the ambiguous nature of a fluorine atom directly attached to a double bond.[17,18] The ambiguity of a fluorine atom in a variety of locations is that, while it is inductively electron-withdrawing, interaction of the non-bonding electron pairs on fluorine with a double bond, or other centres, can lead to net electron-donation.[21] The effect of a fluorine atom on the LUMO energy appears, therefore, to be very little different from that of a hydrogen atom. Consequently, we can conclude that LUMO energies will be lowered for each perfluoroalkyl group introduced. Therefore, from the results described above, the reactivity towards diazomethane decreases in the series (1) > (2) ≫ (23), (24), *i.e.* with decreasing number of perfluoroalkyl groups and, hence, with increasing LUMO energy.

Regiospecific addition of diazomethane occurs with systems such as (6), (9), and (12), *i.e.* of the general form $(R_F)_2C{=}CFR_F$. To account for this we must further consider the effect of fluorine and perfluoroalkyl on coefficients. We have already deduced that the effect of fluorine attached to a double bond is not significantly different from that of hydrogen and so the *number* and *position* of perfluoroalkyl groups will be very important. The coefficients for the LUMO's in (1) and (2) may be represented by (1a) and (2a), *i.e.* in (1a) the effects of perfluoroalkyl are, obviously, symmetrical whereas in (2a) there is a clear polarisation of the system, with the carbon atom of the double bond, which is attached to fluorine, becoming the preferred site for attachment of a nucleophile.



(1a) (2a)

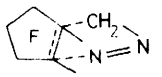
Therefore, it seems reasonable to argue that these concerted additions proceed with some character of a nucleophilic attack, *i.e.* as in structure (25).



(25)

Regiospecificity controlled by coefficients

The perfluorocycloalkenes are all, obviously, electronically equivalent to systems such as $R_FCF{=}CFR_F$ (24), but there is a clear variation in reactivity, in the order perfluoro-cyclohexene < -cyclopentene, -cyclobutene. A similar variation in reactivity has also been encountered in the corresponding hydrocarbon series [22a] and it seems reasonable to account for this on a stereochemical basis, *i.e.* that a planar transition state can be achieved with the four- and five-membered ring systems, *e.g.* (26).



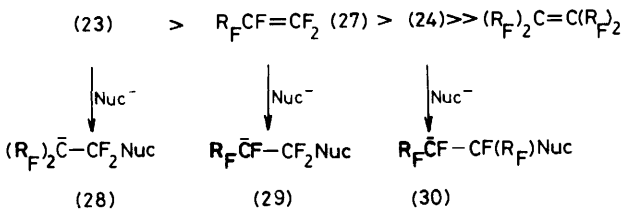
(26)

What is, perhaps, surprising on the model that we have now developed, to account for reactivity towards diazomethane, is that there is a qualitative similarity in reactivity between systems such as $R_FCF{=}CFR_F$ (R_F = perfluoroalkyl) and RCH=CHR (R = alkyl). We have already argued that perfluoroalkyl lowers the LUMO energy and activates and, therefore, we assume that this energy lowering effect of perfluoroalkyl is compensated for by fluorine atoms directly attached to the double bond. This is borne out by a qualitative order of reactivity that may be drawn from our results and those reported previously, *i.e.* $CF_3CH{=}CHCF_3$ [7] > $CF_3CF{=}CHCF_3$ > $CF_3CF{=}CFCF_3$. Since the corresponding dichloro derivative $CF_3CCl{=}CClCF_3$ is more reactive than any of the series, we can conclude that chlorine lowers the LUMO energy relative to hydrogen and fluorine.[22b]

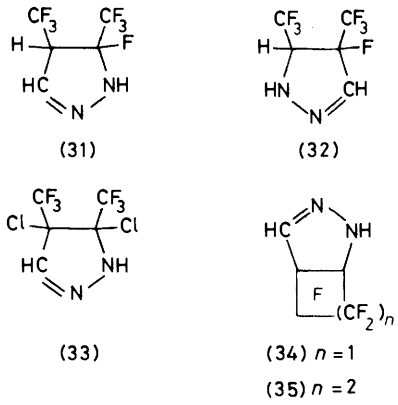
We feel, therefore, that the results described above and the frontier orbital rationale provide a reasonable basis for developing further the chemistry of highly halogenated alkenes in reactions with 1,3-dipoles. Furthermore, one of the features that emerges from the rationale, is a connection with reactions that involve nucleophilic attack and, below we show how the F.O. approach can be usefully applied to this series of reactions.

Nucleophilic Attack on Fluorinated Alkenes. A Frontier Orbital Approach.—Qualitatively, it is generally true [23,24] that

Reactivity order



Scheme 6.



the order of reactivity for polyfluorinated alkenes towards nucleophiles is that structures with a terminal difluoromethylene group (23) are more reactive than structures (27), which in turn are more reactive than (24). The order (27) > (24) > (1) has been established for at least one set of isomers (Scheme 6).[24]

It is common to account for reactivity and orientation of nucleophilic addition to fluorinated alkenes on the basis of relative stabilities of intermediate carbanions, and it is easy to rationalise the greater reactivity of systems such as (23) over (27) because the derived intermediate carbanion (28) will be much more stable than (29). This arises from the fact that fluorine directly attached to a carbanion centre, $\bar{C}-F$, may even be destabilising, whereas at the adjacent position, $\bar{C}-CF$, fluorine is strongly stabilising.[21] This approach becomes less convincing, however, in considering the reactivities of (27) and (24), where the only difference between the corresponding carbanions (29) and (30) lies in the relative stabilising influence of $\bar{C}-CF_2$ and $\bar{C}-CF(R_F)$. However, it is established [25] that both a fluorine atom and a perfluoroalkyl group in such a position, *i.e.* adjacent to a carbanion centre, have comparable effects. Consequently, there is insufficient justification for accounting for the greater reactivity of structures such as (27) over (24) on the basis of the difference in stability of carbanions (29) and (30).

An alternative approach to this problem lies in consideration of frontier orbitals and, in particular, the interaction between the HOMO of the nucleophile with the LUMO of the fluorinated alkene. We have outlined, earlier, the effects of a fluorine atom and of perfluoroalkyl on LUMO energies and concluded that the LUMO energy of a perfluoroalkene depends on the number of perfluoroalkyl groups present. Clearly, therefore, reactivity towards nucleophiles is not simply dependent on the total number of perfluoroalkyl groups present, as in diazomethane additions, because structures such as (1) are the *least* reactive of the possible isomers,[24] towards nucleophiles. Therefore, the coefficients must be important. As explained earlier, the effects of perfluoroalkyl groups on the same side of a double bond reinforce each other, as in the system (23), but *oppose* each other in the system (24), *i.e.* we have a situation similar to that in (1a) and (2a) for (23) and (24), respectively, and this accounts well for the otherwise puzzling low reactivity of systems such as (24). However, the greater reactivity towards nucleophiles of systems such as (2) than (1) may reasonably be attributed to the effect of the polar $\overset{\delta+}{C}-\overset{\delta-}{F}$ bond on the approach of a nucleophile.

The merit of the frontier orbital approach to the systems described in this paper is that we are able to rationalise reactions of systems not previously accounted for in a satisfactory manner and we are able to link both 1,3-dipolar additions and reactions of nucleophiles with fluorinated alkenes.

Experimental

Details of instrumentation have been described previously.[1] N.m.r. spectra for compounds (7), (7a), and (7c) were recorded on a Jeol FX 200 spectrometer. All n.m.r. spectra were recorded with $CFCl_3$ as solvent unless otherwise stated. Ether refers to diethyl ether.

Diazomethane Additions. General Procedure.—A solution of diazomethane in ether was added dropwise with stirring to the alkene at 0 °C until the yellow colour of CH_2N_2 persisted. The solution was allowed to warm to room temperature during 0.5 h, and the ether removed at room temperature. The crude product was purified by vacuum transfer or vacuum sublimation. Variations on this procedure are detailed where applicable.

Perfluoro-3,4-dimethylhex-3-ene (3).—Compound (3) (4.8 g, 12 mmol) and diazomethane yielded 4,5-*bis*(*pentafluoroethyl*)-4,5-*bis*(*trifluoromethyl*)-4,5-*dihydro*-1H-*pyrazole* (5), as an inseparable mixture of *E* and *Z* isomers (ratio 1 : 1) (4.8 g, 92%) (Found: C, 24.2; H, 0.2; F, 69.0; N, 6.7. $C_9H_2F_{16}N_2$ requires C, 24.4; H, 0.4; F, 68.8; N, 6.3%); *m/z* 442 (M^+); δ_F 62.7 (3 F, m, CF_3), 68.4 (3 F, m, CF_3), 81.0 (6 F, m, CF_3), and 106.6 (4 F, m, CF_2); δ_H 8.56 and 7.91 (each m, NH), and 4.60, 4.35 (each m, CH); $\nu_{max.}$ 3 400, 3 300 (br, NH), and 1 610 cm^{-1} (C=N).

Perfluoro-2,3-dimethylbut-2-ene (3a).—Compound (3a) (1.45 g, 4.8 mmol) and diazomethane yielded 4,4,5,5-*tetrakis*(*trifluoromethyl*)-4,5-*dihydro*-1H-*pyrazole* (5a) (0.92 g, 56%), as a white solid, m.p. 84—85 °C after sublimation and recrystallisation from CCl_4–CH_2Cl_2 (Found: C, 24.5; H, 0.5; F, 66.9; N, 7.3. $C_7H_2F_{12}N_2$ requires C, 24.6; H, 0.6; F, 66.6; N, 7.6%); δ_F 60.4 and 65.9 (each 6 F); δ_H ($CDCl_3$) 11.00 (br, NH) and 7.17 (q, *J* 5 Hz, CH); $\nu_{max.}$ 3 300 (NH), 1 610 cm^{-1} (C=N).

Perfluoro-2-methylpent-2-ene (6).—Compound (6) (3.0 g, 10 mmol) and diazomethane yielded, after removal of ether, an oil (3.25 g) shown by n.m.r. to consist of a mixture of (7) (*ca.* 95%), (7a) (*ca.* 3%), and (7c) (*ca.* 2%). Vacuum transfer separated 4-*fluoro*-5-*pentafluoroethyl*-4,5-*bis*(*trifluoromethyl*)-4,5-*dihydro*-3H-*pyrazole* (7) (2.80 g, 82%) as a colourless oil (Found: C, 24.4; H, 0.4; F, 67.0; N, 8.2. $C_7H_2F_{12}N_2$ requires C, 24.6; H, 0.6; F, 66.7; N, 8.2%); *m/z* 342 (M^+); δ_F ($CDCl_3$) 76.6, 83.4, 93.0 (each 3 F, m, CF_3), 122.7 (2 F, m, CF_2), and 176.0 (1 F, m, CF); δ_H ($CDCl_3$) 5.26 (1 H, dd, J_{HF} 72 and J_{HH} 19 Hz), 5.10 (1 H, dd, J_{HF} 90 and J_{HH} 19 Hz); δ_C ($CDCl_3$) 85.0 (dd, CH_2); $\nu_{max.}$ NH absent. The residual isomers (7a)

and (7c) could not be obtained free from each other (Found: C, 24.1; H, 0.6; F, 66.9; N, 8.8%); *5-fluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-4,5-dihydro-1H-pyrazole* (7a), δ_F ($CDCl_3$) 74.5, 80.0, 90.0 (each m, CF_3), 117.2 (m, CF_2), and 169.0 (m, CF); δ_H ($CDCl_3$) 5.69 (d, J_{HH} 19 Hz) and 5.05 (d, J_{HH} 19 Hz); δ_C ($CDCl_3$) 82.4 p.p.m. (s, CH_2). *5-Fluoro-4-pentafluoroethyl-4,5-bis(trifluoromethyl)-4,5-dihydro-1H-pyrazole* (7c), δ_F ($CDCl_3$) 78.2, 84.0, and 92.0 (each m, CF), 120.6 (CF_2), and 174.1 (m, CF); δ_H ($CDCl_3$) 7.28 (br, NH) and 6.95 (s, CH); δ_C ($CDCl_3$) 135.0 p.p.m. (d, CH=N); $\nu_{max.}$ 3 300 cm^{-1} (NH).

On standing at room temperature for 7 days, compound (7) isomerised quantitatively to *4-fluoro-5-pentafluoroethyl-4,5-bis(trifluoromethyl)-4,5-dihydro-1H-pyrazole* (7b) (Found: C, 24.9; H, 0.8; F, 66.3; N, 8.3%); δ_F 76.3, 83.0, and 89.0 (each 3 F, m, CF_3), 121.8 (2 F, m, CF_2), and 175.0 (1 F, m, CF); δ_H 9.25 (br, NH) and 7.60 (dd, J_{HF} 9 and 15 Hz); δ_C ($CDCl_3$) 136.7 p.p.m. (d, CH=N); $\nu_{max.}$ 3 300 (NH) and 1 607 cm^{-1} (C=N).

Perfluorobicyclobutylidene (8).—Compound (8) (1.7 g, 5.3 mmol) and diazomethane yielded *4,5-dihydro-1H-pyrazole-4,5-dispirobis(pefluorocyclobutane)* (10) (1.11 g, 57%), as a white solid, m.p. 37 °C (Found: C, 29.8; H, 0.8; F, 62.9; N, 8.0. $C_9H_2F_{12}N_2$ requires C, 29.5; H, 0.5; F, 62.3; N, 7.65%); *m/z* 366 (M^+); δ_F 119—135 (not assigned); δ_H ($CDCl_3$) 8.75 (br, NH) and 7.25 (d, *J* 34 Hz, CH); $\nu_{max.}$ 3 400, 3 310 (br, NH), and 1 600 cm^{-1} (C=N).

Perfluorobicyclopentylidene (8a).—Compound (8a) (2.3 g, 5.4 mmol) and diazomethane gave *4,5-dihydro-1H-pyrazole-4,5-dispirobis(perfluorocyclopentane)* (10a) (2.0 g, 79%), as a white solid, m.p. 81—82 °C (Found: C, 28.0; H, 0.3; F, 65.5; N, 6.1. $C_{11}H_2F_{16}N_2$ requires C, 28.3; H, 0.4; F, 65.2; N, 6.0%); *m/z* 466 (M^+); δ_F 108—135 (not assigned); δ_H [$(CD_3)_2CO$] 8.60 (br, NH) and 7.07 (s, CH); $\nu_{max.}$ 3 290 (br, NH) and 1 600 cm^{-1} (C=N).

Perfluoro-1-cyclobutylcyclobutene (9).—Compound (9) (0.170 g, 0.53 mmol) and diazomethane yielded *3a,4,4,5,5-pentafluoro-5a-heptafluorocyclobutyl-3a,4,5,5a-tetrahydro-1H-cyclobuta[d]pyrazole* (11) (0.154 g, 80%) as a viscous oil (Found: C, 29.6; H, 0.8; F, 62.8; N, 7.2%) *m/z* 366 (M^+); δ_F 112—133 (not assigned); δ_H 8.80 (br, NH) and 6.93 (q, J_{HF} 12.0 and 5.1 Hz, CH); $\nu_{max.}$ 3 320 (br, NH) and 1 595 cm^{-1} (C=N).

Perfluoro-1-(bicyclobutyl-1-yl)cyclobutene (12).—Compound (12) (2.6 g, 5.4 mmol) and diazomethane yielded the *3a,4,4,5,5-pentafluoro-5a-tridecafluorobicyclobutyl-1-yl-3a,4,5,5a-tetrahydro-1H-cyclobuta[d]pyrazole* (13) (2.4 g, 84%) as a viscous oil (Found: C, 30.0; H, 0.5; F, 64.6; N, 5.0. $C_{13}H_2F_{18}N_2$ requires C, 29.6; H, 0.4; F, 64.8; N, 5.3%); *m/z* 528 (M^+); δ_F 112—133 (not assigned); δ_H 8.68 (br, NH) and 6.86 (q, J_{HF} 12.2 and 5.3 Hz, CH); $\nu_{max.}$ 3 460, 3 280 (br, NH), and 1 600 cm^{-1} (C=N).

1,2-Bis(heptafluorocyclobutyl)cyclobutane (14).—Compound (14) (2.6 g, 5.4 mmol) and diazomethane afforded *4,4,5,5-tetrafluoro-3,6-bis(heptafluorocyclobutyl)-4,5-dihydro-1H-1,2-diazepine* (16) (2.4 g, 85%) as a white solid, m.p. 136—137 °C (Found: C, 29.8; H, 0.6; F, 64.5; N, 5.5%); *m/z* 528 (M^+); δ_F 120—140 (16 F not assigned), 154 and 164.0 (each 1 F, s); δ_H 7.90 (br, NH) and 6.60 (br, CH); $\nu_{max.}$ 3 290 (NH), 1 638, and 1 588 cm^{-1}.

Further reaction of (16) (1.05 g, 2.0 mmol) with diazomethane yielded *4,4,5,5-tetrafluoro-3,6-bis(heptafluorocyclobutyl)-1-methyl-4,5-dihydro-1H-1,2-diazepine* (17) (1.02 g, 95%), as white crystals, m.p. 85—86 °C (Found: C, 30.8; H, 1.2; F, 62.8; N, 4.8. $C_{14}H_2F_{18}N_4$ requires C, 31.0; H, 0.74; F, 63.1; N, 5.2%); *m/z* 542 (M^+); δ_F 120—138 (16 F unassigned), 154.0 and 164.1 (each 1 F, s); δ_H 6.97 (1 H, s, CH) and 3.83 (3 H, s, Me); $\nu_{max.}$ 1 642 and 1 592 cm^{-1}.

Perfluoro-1-methylenespiro[3.3]heptane (21).—Compound (21) [26] (0.85 g, 2.7 mmol) and diazomethane yielded *4,4-difluoro-4,5-dihydro-1H-pyrazole-5-spiroperfluorocyclobutane-2'-spiroperfluorocyclobutane* (22) (0.38 g, 40%) (Found: C, 29.1; H, 0.4; F, 62.8; N, 8.2%); *m/z* 366 (M^+); δ_F 108—133 (not assigned); δ_H 8.62 (br, NH) and 6.71 (br, d, *J ca.* 74 Hz, CH); $\nu_{max.}$ 3 310 (NH) and 1 605 cm^{-1} (C=N).

2H-Heptafluorobut-2-ene.—*2H*-Heptafluorobut-2-ene (3.6 g, 20 mmol) and diazomethane (excess) were sealed in a tube and stirred at room temperature for 15 days. Removal of ether left an oil (32 mg, 1%), tentatively identified as an impure mixture of the Δ^2-dihydropyrazoles (31) and (32); δ_F 57.3, 58.2, 59.2, and 62.0 (s, CF_3), and 152.8, 166.8 (both s, CF); δ_H 8.51 and 7.99 (both br, NH), 7.80 (m, br, N=CH of both isomers), and 5.4—5.0 (m, br, tertiary CH of both isomers); $\nu_{max.}$ 3 200 (NH) and 1 610 cm^{-1} (NH).

2,3-Dichlorohexafluorobut-2-ene.—The title compound (4.6 g, 20 mmol) and diazomethane yielded *4,5-dichloro-4,5-bis(trifluoromethyl)-4,5-dihydro-1H-pyrazole* (33) (3.6 g, 66%) (Found: C, 21.5; H, 0.5; F, 41.9; N, 10.2. $C_5H_2Cl_2F_6N_2$ requires C, 21.9; H, 0.7; F, 41.6; N, 10.2%); δ_F 57.3 and 62.0 (both s, CF_3); δ_H 10.43 (br, NH) and 7.98 (s, CH); $\nu_{max.}$ 3 250 (NH) and 1 575 cm^{-1} (C=N).

Hexafluorocyclobutene.—A mixture of hexafluorocyclobutene (3.2 g, 20 mmol) and excess of diazomethane, contained in a tube sealed under vacuum, was stirred at room temperature for 14 days, to yield *3a,4,4,5,5,5a-hexafluoro-3a,4,5,5a-tetrahydro-1H-cyclobuta[d]pyrazole* (34) (2.2 g, 55%) (Found: C, 28.8; H, 1.1; F, 56.5; N, 13.3. $C_5H_2F_6N_2$ requires C, 29.4; H, 1.0; F, 55.9; N, 13.7%); δ_F 124—143 (not assigned); δ_H 8.18 (br, NH) and 6.90 (q, J_{HF} 13.8 and 5.0 Hz); $\nu_{max.}$ 3 280 (NH) and 1 610 cm^{-1} (C=N).

Octafluorocyclopentene.—A mixture of octafluorocyclopentene (4.2 g, 20 mmol) and excess of diazomethane contained in a tube sealed under vacuum was stirred at room temperature for 14 days, to yield *3a,4,4,5,5,6,6,6a-octafluoro-1,3a,4,5,6,6a-hexahydrocyclopenta[d]pyrazole* (35) (1.25 g, 25%) (Found: C, 28.9; H, 0.7; F, 59.2; N, 12.0. $C_6H_2F_8N_2$ requires C, 28.4; H, 0.8; F, 59.8; N, 11.0%); δ_F 122—142 (not assigned); δ_H 7.26 (br, NH) and 6.95 (br, s, CH); $\nu_{max.}$ 3 470, 3 310 (NH), and 1 595 cm^{-1} (C=N).

Perfluoro-cyclohexene, -but-2-ene, and -propene did not yield any product on stirring with excess of diazomethane in sealed tubes at room temperature for 14 days.

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