An Unexpected Reaction of Diphenyldiazomethane with Perfluoro-2-nitrosopropane

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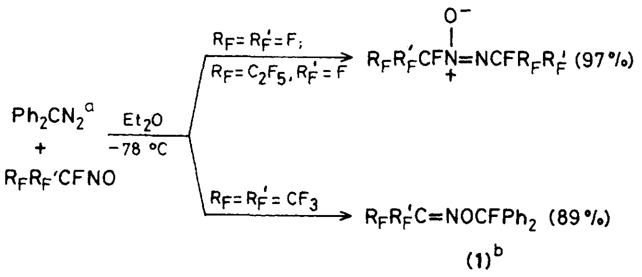
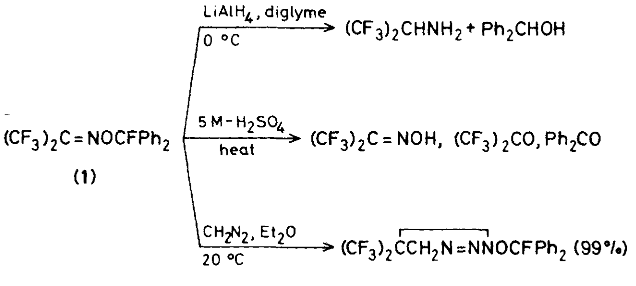
Diphenyldiazomethane reacts with perfluoro-2-nitrosopropane at low temperatures to yield the oxime ether $(CF_3)_2C{=}NOCFPh_2$, some chemistry of which has been explored.

Whilst attempting to synthesize the azoxy-compound $(CF_3)_2CF\overset{+}{N}(\overset{-}{O}){=}NCF(CF_3)_2$ for ^{15}N n.m.r. measurement, we have discovered that the pathway taken by the reaction between diphenyldiazomethane and perfluoro-2-nitrosopropane differs remarkably from that followed when primary nitrosoalkanes of the fluorocarbon class are employed (see Scheme 1).[1] The novel oxime ether formed, *O*-(fluorodiphenylmethyl)hexafluoroacetone oxime (**1**; b.p. 78—80 °C at *ca.* 0.3 mmHg), was identified by elemental analysis (C, H, F, and N) and spectroscopic methods [i.r., n.m.r. (^{13}C, ^{1}H, ^{19}F, and ^{15}N), and mass]. In addition to some standard conversions (see Scheme 2), the oxime ether suffers lethargic hydrolysis to



Scheme 1



Scheme 2

[a] In each case, the gaseous nitroso-compound was passed into the solution of the diazoalkane until the red colour characteristic of the latter disappeared. [b] The chloro-analogue $(CF_3)(CF_2Cl)C{=}NOCFPh_2$ (*E* and *Z* mixture) is obtained (84% yield) if one starts with $(CF_3)(CF_2Cl)CFNO$.[5]

the bis-oximino derivative $(CF_3)_2C{=}NOCPh_2ON{=}C(CF_3)_2$ when stored in glass at room temperature.

Apart from the work with trifluoronitrosomethane and its heptafluoro-n-propyl analogue (Scheme 1),[1] the sparse literature concerning reactions between perfluorinated nitroso-compounds and diazoalkanes[1—4] records the conversions $Ph_2CN_2 + (CF_3)_3CNO \longrightarrow Ph_2\overline{CON}C(CF_3)_3$[2] and $Ph_2CN_2 + C_6F_5NO \longrightarrow Ph_2C{=}\overset{+}{N}(\overset{-}{O})C_6F_5$.[3] The result of the diphenyldiazomethane–heptafluoro-2-nitrosopropane reaction, therefore, has not changed the intriguing situation that the nature of the product derived from this diazoalkane and a nitroso-compound of the fluorocarbon class depends dramatically on the structure of the latter. The pros and cons of adopting mechanisms with a common root will be presented in a full paper.

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