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SHORT COMMUNICATION

ACID – INDUCED DECOMPOSITION OF 5-PENTAFLUOROPHENYL-3,4,5-TRIAZATRICYCLO[5.2.1.$0^{2,6}$]DEC-3-ENE

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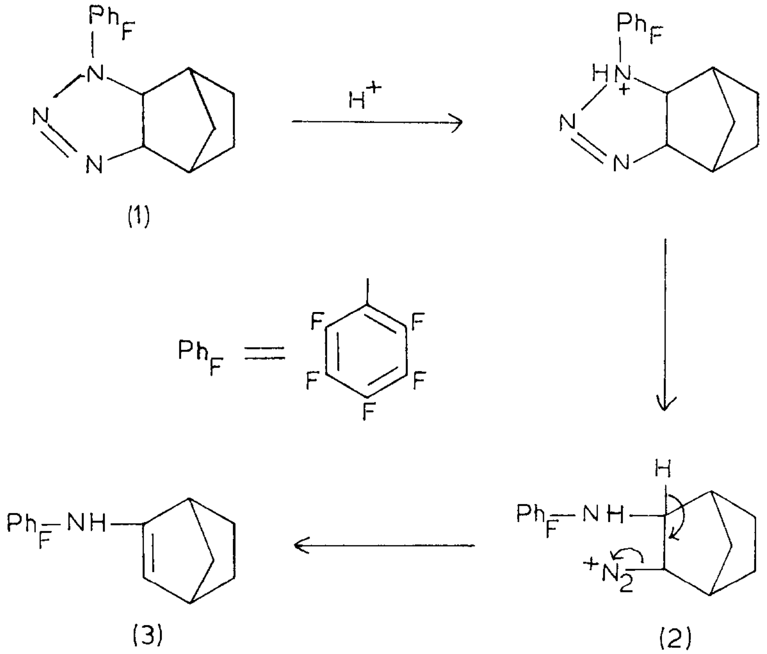
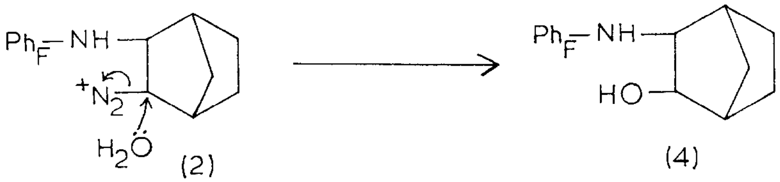
In a previous paper [1] it was reported that perfluoroazidobenzene undergoes 1,3-cycloaddition with norbornene in light petroleum at room temperature to give a triazoline, 5-pentafluorophenyl-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (1). Reported here is the acid-induced decomposition of the triazoline.

Triazolines are known to decompose rapidly and quantitatively, by acids, with a loss of nitrogen and nucleophilic substitution at the electron-deficient centre [2]. The acid-induced decomposition of the triazoline (1) with 2N HCl at room temperature provided the nucleophilic substituted product, 2-(pentafluorophenylamino)bicyclo(2,2,1)hepta-3-ol (4), in only 7% yield while the main product was identified as 2-(pentafluorophenylamino)bicyclo(2,2,1)hept-2-ene (3).

Isolation of the enamine (3) in upto 90% yield indicated that loss of proton from C_2 of the transition state (2), fascilitated by the -I nature of C_6F_5NH group, followed by intramolecular rearrangement and concerted loss of nitrogen (see Scheme 1) is preferred over the loss of nitrogen followed by the attack by an external nucleophile to give (4) (see Scheme 2).



SCHEME 1



SCHEME 2

EXPERIMENTAL

I.r. and n.m.r. (shifts to high field designated positive) spectra were obtained with a Perkin-Elmer spectrophotometer model 257 and a Perkin-Elmer R10 instrument (^{19}F at 56.46, ^{1}H at 60 MHz), respectively. Perfluoroazidobenzene was prepared by nitrosation of pentafluorophenylhydrazine [3] . The triazoline (1) was prepared by 1,3-cycloaddition of pentafluoroazidobenzene with norbornene [1] .

Decomposition of 5-pentafluorophenyl-3,4,5-triazatricyclo[5.2.1.0.^{2,6}]dec-3-ene. Dilute hydrochloric acid (2N; 5 ml) was added dropwise to a stirred solution of the above triazoline (1.2 g, 4.0 mmol) in acetone (25 ml) at room temperature. The reaction was spontaneous and a gas, presumably nitrogen, was evolved. The product was neutralised with a saturated aqueous solution of sodium carbonate. The contents were poured into water and extracted with ether (3 X 100 ml). The combined ether extract was dried ($MgSO_4$) and evaporated to give an oil. Examination of this oil by thin layer chromatography indicated it was a mixture of two components (TLC plate was developed in chloroform). The oil was subjected to column chromatography (silica gel) and elution with light petroleum (b.p. 60-80 °C) provided 2-(pentafluorophenylamino)bicyclo(2,2,1)hept-2-ene (1.0 g, 3.6 mmol; 90%) (Found: C,57.0; H, 3.9; F, 34.1; N, 5.0%. $C_{13}H_{10}F_5N$ requires C, 56.7; H, 3.6; F, 34.5; N, 5.1%), colourless oil, δ_H(neat liquid) +0.55 to +5.35 (br, complex),

δ_F(neat liquid) +83.0 (m, 2- and 6-F), +88.0 (m, 3- and 5-F) and +96.5 (m, 4-F) p.p.m. (rel. int. 2:2:1), λ_{max} (film) 2.92 (N-H str.) µm. Subsequent elution with chloroform provided white crystals of 2-(pentafluorophenylamino)bicyclo(2,2,1)hepta-3-ol (0.09 g, 0.31 mmol; 7.5%) (Found: C, 52.9; H, 4.0; F, 32.4; N, 4.5%. $C_{13}H_{12}F_5NO$ requires C, 53.2; H, 4.1; F, 32.4; N, 4.8%), m.p. 88-90 °C, δ_H(15% solution in benzene) -1.45 (br, singlet, OH) +1.4 to +6.3 (br, complex), δ_F(same soln.) +83.5 (m, 2- and 6-F), +88.0 (m, 3- and 5-F), and +96.5 (m, 4-F) p.p.m. (rel. int. 2:2:1), λ_{max}(mull) 3.0 (br, N-H and O-H str.) µm.

REFERENCES

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2) P. Scheiner, in B.S. Thyagarajan (Editor), Selective Organic Transformations, Vol. 1, Wiley-Interscience, New York, 1970, p. 349.
3) J.M. Birchall, R.N. Haszeldine and A.R. Parkinson, J.Chem.Soc., 1962, 4966.