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REACTIONS OF HEXAFLUOROPROPENE WITH C,N-DIPHENYLNITRONE; A NOVEL SYNTHESIS OF 2-AZETIDINONE

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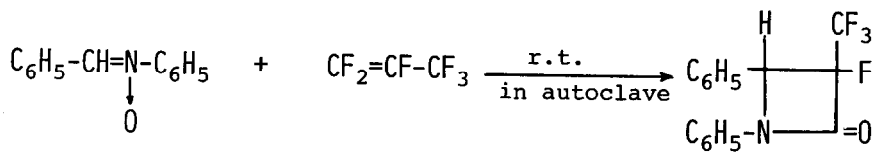
Little has been reported about the reaction of 1,3-dipoles with hexafluoropropene(HFP)[1,2]. In general, five-membered ring compounds are obtained in the reactions of 1,3-dipoles with alkenes[3]. In the course of the study of cycloaddition of 1,3-dipoles with alkenes, we found, however that the reaction of C,N-diphenylnitrone with HFP gave 2-azetidinone instead of a five-membered ring compound. This is a novel example that a four-membered ring compound was obtained from the reaction of a 1,3-dipole and an alkene so far as the authors know[4]. This paper describes the elucidation of the structure of resulting product and a possible mechanism to give it.

The reaction of C,N-diphenylnitrone with HFP was carried out in an autoclave at room temperature. From the dark-brown reaction mixture colorless crystals were obtained[5], mp.;110.0-110.5, which were identified as 1,4-diphenyl-3-fluoro-3-trifluoromethyl-2-azetidinone(1).



(1)

The structure of (1) was determined by the spectroscopic methods. ir(KBr): 1762cm^{-1} (C=O), 1192cm^{-1} (C-F). The amide carbonyl band at 1762cm^{-1} strongly suggests a strained ring structure. ^{1}H-nmr($CDCl_3$,ppm(TMS)): 5.36(1H, doublet, C_4-H, J_{H-F}=3.4Hz), 7.1-7.4(10H, multiplet, phenyl); ^{19}F-nmr($CDCl_3$, ppm(CF_3COOH)): 0.0(3F, doublet, CF_3, J_{F-F}=11.2Hz),+103.5(1F, doublet of quartet, CF, J_{H-F}=3.4Hz, J_{F-F}=11.2Hz); mass(m/e, (rel.int.)(fragmentation)(calcd.)): 309.0763(134)(M)(309.0777), 190.0403(255)(M-C_6H_5NCO)(190.0406), 119.0379(255)(C_6H_5NCO)(119.0371), 91.0405(162)(C_6H_5N)(91.0422), 77.0384(145)(C_6H_5)(77.0391); elemental analysis(obs.(calcd.)): C;61.93(62.14), N;4.48(4.53), H;3.55(3.58), F;24.72(24.57); UV.: λmax=257nm.

Two fluorine atoms were eliminated in the reaction product. The fact that

Table 1 Yields of (1) under Several Reaction Conditions

Solvent	Reaction Time(hour)	Compound added	Yield(%)
Acetone	40	none	14
"	117	H_2O (2ml)	16
"	26	Pyridine (2.5 mol.eq.)	22
"	24	Et_3N (2.7 mol. eq.)	trace[a]
CH_2Cl_2	47	none	2.5
Toluene	46	none	15

a) from thin layer chromatography (Rf=0.56, benzene, silica-gel)

the reaction mixture was strongly acidic indicated the generation of hydrofluoride Table 1 shows the yield of (1) under several conditions. On addition of pyridine to the reaction system, pyridine hydrofluoride was obtained and a higher yield of (1) resulted in a shorter reaction time. Triethylamine did not give a good result presumably because it induced the oligomerization of HFP[6]. It was reported that acetone reacted with hexafluoropropene dimer[7]. Therefore it is quite possible that acetone has reacted as a proton donner in the generation of hydrofluoride since dichloromethane gave a much lower yield of (1) when used as the solvent.

In the reaction of 1,3-dipoles with HFP, five-membered ring compounds formed first[2], and such cycloadducts are relatively difficult to be isolated[8]. Therefore it is quite possible that an isoxazolidine forms first and then it chages to (1) giving off two fluorine atoms, though our attempts to isolate such an intermediate were unsuccessful. Details of the reaction mechanism are under investigation, but it seems quite certain that 2-azetidinone is formed by this ring contraction reaction.

References and footnotes

1) E.A.Mailey and L.R.Ocone; *J.Org.Chem.* 33 3343 (1968)

2) R.E.Banks, R.N.Haszeldine and J.M.Robinson; *J.C.S.Perkin I* 1226 (1976)

3) See for examples; R.Huisgen; *Angew.Chem.Int.Ed.Engl.* 2 565 (1963), R.Huisgen *ibid* 2 633 (1963), D.St.C.Black, R.F.Crozier and V.C.Davis; *Synthesis* 205 (1975)

4) There has been a paper that 2-azetidinones were obtained by the reactions of C,N-diphenylnitrones with copper acetylides. L.K.Ding and W.J.Irwin; *J.C.S.Perkin I* 2382 (1976)

5) Column chromatography was used (200 mesh silica-gel).

6) See for examples; Martini and Thomas; *Ger.Offen.* 2306439 (1974) R.D.Dresdner, F.N.Tlumac and J.A.Young; *J.Org.Chem.* 30 3524 (1965)

7) S.Yanagida, Y.Noji and M.Okahara; *Tetrahedron Lett.* 2337 (1977)

8) There was only one paper that isoxazolidines were isolated in the reactions of HFP with acyclic nitrones; I.L.Knunyants, E.G.Bykhovskaya, V.N.Frosin, I.V. Galakhov and L.I.Regulin; *Zhur.Vsesoyuz.Khim.obshch.im.D.T.Mendeleeva* 17 356 (1972)