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POLYFLUOROCYCLOALKENES. PART XV [1]. REACTIONS OF DECAFLUOROCYCLOHEXENE WITH SECONDARY AMINES

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SUMMARY

Pyrrolidine, 3,3,4,4-tetrafluoropyrrolidine, and dimethylamine, react with decafluorocyclohexene to give the non-basic enamines, 1-pyrrolidino-, 1-(3',3',4',4'-tetrafluoropyrrolidino)- , and 1-dimethylamino-nonafluorocyclohex-1-ene, respectively.

DISCUSSION

A long-standing interest [2,3] in polyfluoroamines of various types continues in our group, and has been extended to compounds of biological significance [4]. Secondary amines have long been known to react with perfluoroalkenes to give tertiary amines, and in some cases enamines [5]. As a preliminary to future publications, this note reports some old (1962) work, on reactions of decafluorocyclohexene with pyrrolidine, a tetrafluoropyrrolidine, and dimethylamine.

Pyrrolidine and decafluorocyclohexene in diethyl ether gave a liquid product, 1-pyrrolidinononafluorocyclohex-1-ene (1) as evidenced by ir and nmr, and by oxidation to octafluoroadipic acid. The double bond of enamine (1) was much less susceptible to nucleophilic attack than that of decafluorocyclohexene; even under forcing conditions, it did not react further with pyrrolidine. Also, (1) was not basic. However, (1) was not very stable, it darkened on being kept at 15°. After being heated under reflux for 6 h in the presence of water there was obtained a crystalline solid (2). This had a strong selective UV absorption at

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3320 Å (cf. related -ene-ones [2]) and was oxidised to hexafluoroglutaric acid. The structure of (2) therefore was 1 pyrrolidino-3-oxo-heptafluorocyclohex-1-ene.

Decafluorocyclohexene was also reacted with 3,3,4,4-tetrafluoropyrrolidine [6]. Insufficiently basic to react alone, this amine gave a sodio-derivative with sodium hydride in dimethylformamide solution, and thence the expected product (3).

Dimethylamine reacted analogously to pyrrolidine, to give 1-dimethylaminononafluorocyclohexene (4), characterised as before. This enamine differed from earlier related products [7], made from dimethylamine and highly substituted perfluoroalkenes, in having a vinylic fluorine.

EXPERIMENTAL

Reaction of Decafluorocyclohexene and Pyrrolidine,

Pyrrolidine (10.8 g) in diethyl ether (20 cm^3) was added dropwise during 1.5 h to stirred decafluorocyclohexene (20.0 g) in ether (20 cm^3). After 4 h further, water (60 cm^3) was added cautiously, and the organic layer distilled (20 mm pressure) to give 1-pyrrolidinononafluorocyclohex-1-ene (1) nc (17.5 g), b.p. 99-101°/20 mm (Found: C, 38.5: H, 2.6. $C_{10}H_8F_9N$ requires C, 38.35; H, 2.6%); ν max 1670 cm^{-1} (vs; C=C): ^{19}F nmr (Mullard SL44 at 30 MHz) showed 4 peaks in ratios 2:2:4:1. Oxidation by potassium permanganate in acetone afforded octafluoroadipic acid, isolated as bis-anilinium and -S-benzylthiouronium salts [8].

Excess of pyrrolidine for longer times gave the same product (1), which was unchanged after further reaction with pyrrolidine.

Dry hydrogen chloride bubbled through (1) in ether gave no salt, and potentiometric titration of ethanolic hydrochloric acid against (1) in ethanol gave a curve superimposable on that from ethanol alone.

1-Pyrrolidino-3-oxoheptafluorocyclohex-1 (2)-ene (2).

Compound (1) (5.0 g) and water (0.4 cm^3) were refluxed together for 6 h. Extraction with light petroleum (b.p. 40-60°), and recrystallisation from the same solvent, gave compound (2) nc (1.2 g), m.p. 72° (Found: C, 41.3: H, 3.0 $C_{10}H_8F_7NO$ requires C, 41.2; H, 2.8%); λ max (EtOH) 3320 Å ($\varepsilon = 3.02 \times 10^4$); ν max 1675 cm^{-1} (s; C=C), 1595 cm^{-1} (vs; C=O): ^{19}F nmr showed 4 peaks in ratios 2:2:2:1.

Oxidation by potassium permanganate in acetone gave hexafluoroglutaric acid, isolated as its bis-anilinium and -S-benzylthiouronium salts [8].

Reaction of Decafluorocyclohexene and 3,3,4,4-Tetrafluoropyrrolidine. Sodium hydride (0.07 g) was added to a solution of 3,3,4,4-tetrafluoropyrrolidine (2.0 g) in dimethylformamide (25 g), and the mixture then added dropwise to refluxing decafluorocyclohexene (5.0 g) in dimethylformamide (75 cm^3) during 1.5 h. After being refluxed for a further 18 h, water (700 cm^3) was added, the organic layer evaporated, and the residue distilled in vacuo, to give 1-(3',3',4',4'-tetrafluoropyrrolidino)nonafluorocyclohex-1-ene (3) nc (1.8 g), b.p. 167-169°, (Found: C, 32.0; H, 1.3 $C_{10}H_4F_{13}N$ requires C, 31.2; H, 1.0%); ν max 1670 cm^{-1} (vs; C=C): ^{19}F nmr showed 5 peaks, relative areas 2:2:4:4:1.

Reaction of Dimethylamine and Decafluorocyclohexene. Decafluorocyclohexene (15.0 g) in diethyl ether (15 cm^3) was added dropwise to dimethylamine (6.0 g), cooled to -78° in a bath of solid CO_2/acetone. The solution was then warmed and refluxed for 2 h. The solid hydrofluoride formed was filtered off, and the filtrate distilled at 20 mm giving, as the least volatile component (b.r. 45-50°), 1-dimethylaminononafluorocyclohex-1-ene (4), nc (12.0 g) b.p. 149°, (Found: C, 33.3; H, 2.3. $C_8H_6F_9N$ requires C, 33.5; H, 2.1%); ν max 1660 cm^{-1} (s; C=C) : ^{19}F nmr showed 4 peaks ratios 2:2:4:1.

Oxidation went as for compound (1).

REFERENCES

1 Part XIV. M.J. Hamor, T.A. Hamor, C.M. Jenkins, R. Stephens, and J.C. Tatlow, J. Fluorine Chem., 10 (1977) 605.

2 P. Robson, J. Roylance, R. Stephens, J.C. Tatlow, and R.E. Worthington, J. Chem. Soc., (1964) 5748; A.M. Doyle and A.E. Pedler, J. Chem. Soc. (C), (1971) 282.

3 G.M. Brooke, J. Burdon, M. Stacey and J.C. Tatlow, J. Chem. Soc., (1960) 1768; J. Burdon, J. Castaner, and J.C. Tatlow, J. Chem. Soc., (1964) 5017.

4 P.L. Coe, J.H. Sleigh, and J.C. Tatlow, J. Fluorine Chem., 15 (1980) 339.

5 R.L. Pruett, J.T. Barr, K.E. Rapp, C.T. Bahner, J.D. Gibson and R.H. Lafferty, J. Amer. Chem. Soc., 72 (1950) 3646; D.C. England, L.R. Melby, M.A. Dietrich, and R.V. Lindsey, ibid., 82 (1960) 5116.

6 M.T. Chaudhry, G.A. Powers, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1964) 874.

7 H.H. Evans, R. Fields, R.N. Haszeldine, and M. Illingworth, J. Chem. Soc. Perkin I, (1973) 649; J.A. Oliver, R. Stephens, J.C. Tatlow, and J.R. Taylor, J. Fluorine Chem., 7 (1976) 555.

8 J. Burdon and J.C. Tatlow, J. Appl. Chem., 8 (1958) 293.