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PRELIMINARY NOTE

[2+3]Cycloadditions of fluoroolefins : Synthesis of 3,4-Difluoro-1-*t* butyl-pyrrole

J. LEROY, M. RUBINSTEIN and C. WAKSELMAN

C.N.R.S.-C.E.R.C.O.A., 2 rue Henri Dunant, 94320 Thiais (France)

SUMMARY

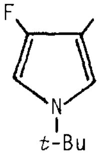
3,4-Difluoro-1-*t*-butyl-pyrrole was synthesized by the thermal [2+3] cycloaddition of 2-carbomethoxy-1-*t*-butyl-aziridine with chlorotrifluoroethylene, followed by treatment with sodium methoxide then with alcoholic potassium hydroxide. Thermal decarboxylation afforded the title compound.

INTRODUCTION

Although (poly)-halopyrroles (chloro, bromo, iodo) are well known [1,2], (poly)-fluoropyrroles have been less studied. We showed that 2-perfluoroalkylpyrroles could be obtained by condensation of R_FI with N-alkylpyrroles [3]. Recently, 3,4-bis[trifluoromethyl]-1-*H*-pyrroles have been synthesized by a Diels-Alder reaction between N-protected pyrroles and perfluoro-2-butyne [4,5]. Furthermore, we showed that [2+3] thermal cycloadditions of aziridines with perfluoroolefins could also lead to 3,4-perfluoroalkylpyrroles [4,6].

Pyrroles bearing electron-withdrawing substituents at the C3 and (or) C4-position are of interest ; synthesis of phorphyrins bearing either polyfluoroalkyl groups [7] or a trifluoromethyl group [8] have been reported recently.

With the aim of preparing several 3,4-difluoropyrroles, we first explored a route to the attractive compound (1).



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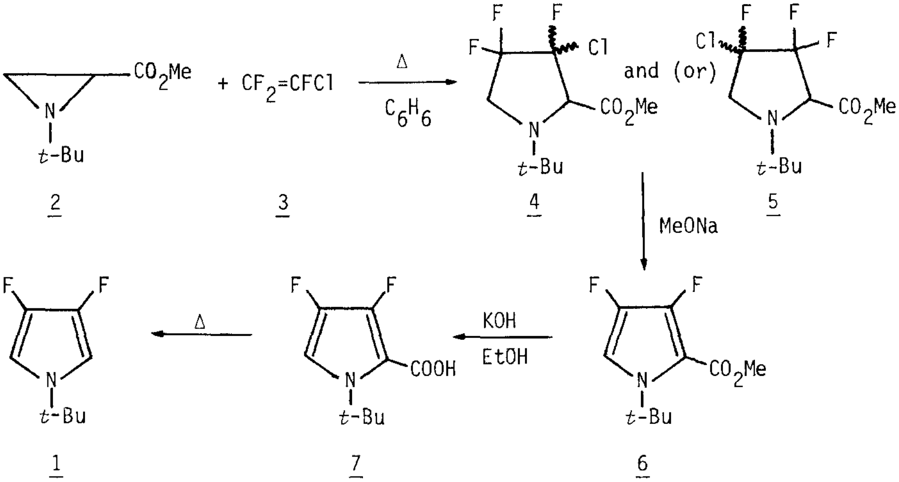
RESULTS

2-Carbomethoxy-1-*t*-butyl-aziridine was condensed with chlorotrifluoroethylene in an autoclave as described earlier for perfluoropropene [6]. However, the temperature range for the condensation with the reactive chlorotrifluoroethylene was very narrow. A complex mixture of chlorofluoropyrrolidines (4) and (or) (5) was obtained. Aromatization of this mixture was performed with sodium methoxide, giving 3,4-difluoro-2-carbomethoxy-1-*t*-butyl-pyrrole (6). Saponification of (6) with alcoholic potassium hydroxide afforded the acid (7). The last step involved thermal decarboxylation of this acid. This decarboxylation was much easier than in the case of some trifluoromethylpyrroles [4,6].



The ^{1}H and ^{19}F NMR spectra of pyrrole 1 are noteworthy in that they are deceptively simple. Instead of the expected AA'XX' patterns for the two equivalent fluorine atoms and the two protons, as observed for the 3,4-difluoro-thiophene [9], only a doublet is observed for each nucleus, with J=1.5 Hz.

EXPERIMENTAL

All compounds (except chlorofluoropyrrolidines) exhibited correct elemental analysis.

Chlorofluoropyrrolidines (4) and (or) (5). A 50 ml stainless steel autoclave was charged with the freshly distilled aziridine (2) (4 g ; 25.4 mmol) in benzene (8 ml). The autoclave was closed, cooled to about -70°C, then evacuated. Chlorotrifluoroethylene was introduced (≃ 19 g, 0.16 mol). After warming-up, the autoclave was placed in a rocking-oven and heated to 200°C for 2 h 1/4 (this temperature was reached within 3/4 h). The hot bomb was removed from the oven and allowed to cool. After cautious degassing and opening, the solvent was removed *in vacuo* then the brown oily residue (5.8 g) roughly purified by a bulb-to-bulb distillation at 120°C (0.05 torr) giving 2.9 g of a colorless oil consisting essentially of a mixture of isomers of (4) and (or) (5).
^{1}H NMR ($CDCl_3$) $\delta \simeq 2.8$ to 4.5 (m, H cycle), 3.8 and 3.82 ppm (s, CH_3).
^{19}F NMR ($CDCl_3$) $\delta \simeq 96$ to $\simeq 130$ ppm, ten massifs of multiplets of various intensity (pattern and distribution reproducible).$\{^{1}H\}$ did not allow easy analysis.

3,4-Difluoro-2-methoxycarbonyl-1-*t*-butyl-pyrrole (6) was obtained from the pyrrolidines (4) and (or) (5) as described earlier [6] (25 % yield from aziridine (2)), after silica gel chromatography (Merck 60, methylene dichloride as eluent, $R_f \simeq 0.9$). Mp 46°C.
^{1}H NMR ($CDCl_3$) δ 6.82 (dd, 1H, $^{3}J_{HF}=1.9$ Hz, $^{4}J_{HF}=5.1$ Hz, H_5), 3.83 (s, 3H, CH_3), 1.65 ppm (s, 9H, CH_3).
^{19}F NMR ($CDCl_3$) δ 157.8 (dd, 1F, $^{3}J_{FF}=13.4$ Hz, $^{4}J_{FH}=5.1$ Hz, F_3), 182 ppm (dd, 1F, $^{3}J_{FF}=13.4$ Hz, $^{3}J_{FH}=1.9$ Hz, F_4).

3,4-Difluoro-2-carboxy-1-*t*-butyl-pyrrole (7) was obtained by saponification pyrrole (6) as described earlier [6], in 88 % yield. Mp 112°C.

3,4-Difluoro-1-*t*-butyl-pyrrole (1). Refluxing pyrrolecarboxylic acid (7) at 160°C for 1 h afforded, after a bulb-to-bulb distillation (≈90°C/0.05 torr), pyrrole (1) as a sweet-smelling colorless liquid in 85-90 % yield. Bp 192° (Siwoloboff's method). Mp 19-20°C.
^{1}H NMR ($CDCl_3$) δ 1.43 (s, 9H, CH_3), 6.42 ppm (d, 2H, J=1.5 Hz, H_2, H_4).
^{19}F NMR ($CDCl_3$) δ 181.5 ppm (d, J=1.5 Hz, F_3, F_4).

REFERENCES

1 R.A. Jones, G.P. Bean, The Chemistry of Pyrroles, Academic Press, London, 1977, p. 129.
2 R.J. Motekaitis, D.H. Heinert and A.E. Martell, J. Org. Chem., 35 (1970) 2504.
3 D. Cantacuzene, C. Wakselman and R. Dorme, J. Chem. Soc. Perkin Trans.I (1977) 1365. See also : Y. Kobayashi, I. Kumadaki, A. Ohsawa, S. Murakami, T. Nakano, Chem. Pharm. Bull., 26 (1978) 1247. Y. Girard, J.G. Atkinson, P.C. Belanger, J.J. Fuentes, J. Rokach, C.S. Rooney, D.C. Remy and C.H. Hunt, J. Org. Chem., 48 (1983) 3220.
4 J. Leroy, D. Cantacuzene, C. Wakselman, Synthesis (1982) 313.
5 R.W. Kaesler and E. Le Goff, J. Org. Chem., 47 (1982) 4779.
6 J. Leroy and C. Wakselman, Can. J. Chem., 54 (1976) 218.
7 R.W. Kaesler and E. Le Goff, J. Org. Chem., 47 (1982) 5243.
8 M. Homma, K. Aoyagi, Y. Aoyama and H. Ogoshi, Tetrahedron Lett., 24 (1983) 4343.
9 H. Christiansen, S. Gronowitz, B. Rodmar, S. Rodmar, U. Rosen and M.K. Sharma, Arkiv Kemi, 30 (1969) 561.