Journal of Fluorine Chemistry, 34 (1986) 281–285

Received: July 28, 1986; accepted August 22, 1986

PRELIMINARY NOTE

Polymeric Analogues of Electrophilic Fluorinating Agents of the N-F Class

RONALD ERIC BANKS* and EFTHIMIOS TSILIOPOULOS

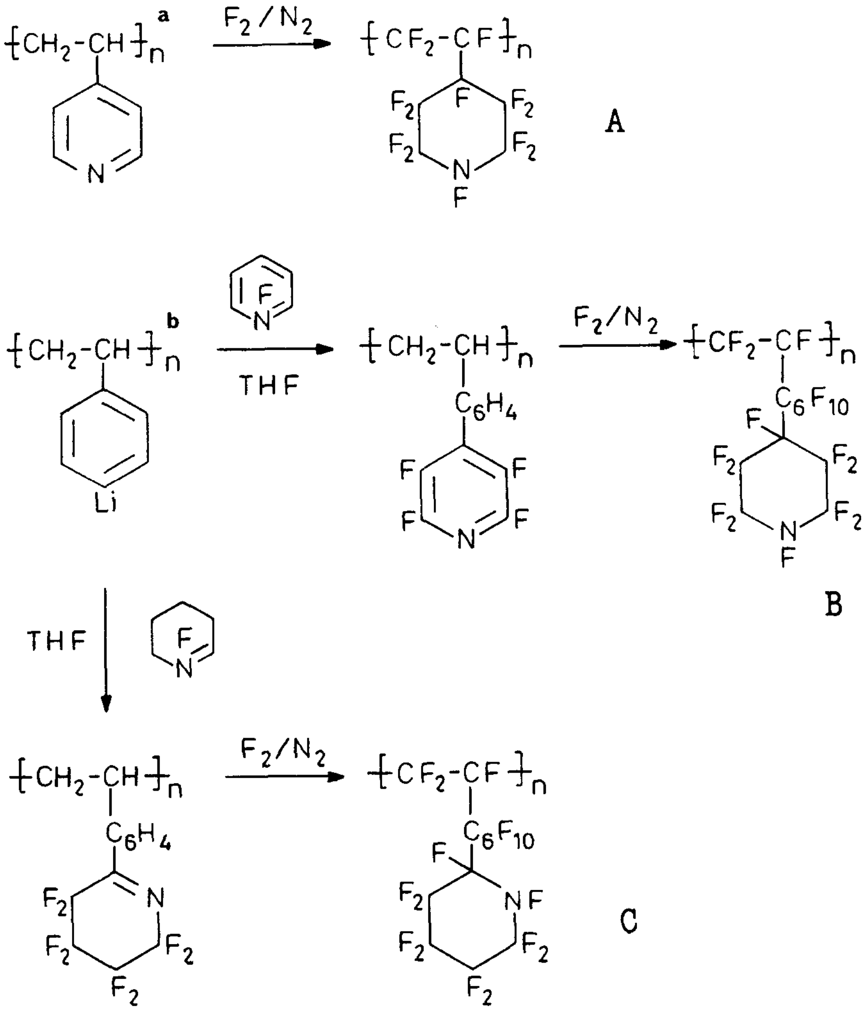
Chemistry Department, The University of Manchester
Institute of Science and Technology, Manchester M60 1QD
(U.K.)

SUMMARY

Polymeric reagents capable of effecting the conversions $Ph\bar{C}(CO_2Et)_2\ Na^+ \longrightarrow PhCF(CO_2Et)_2$ and $\overline{CH_2(CH_2)_3CH=C}H-\overline{N(CH_2)_2OCH_2CH_2} \longrightarrow$ (after hydrolytic work-up) $\overline{CH_2(CH_2)_3CHFC}=O$ have been prepared via direct fluorination of polymers derived from 4-vinylpyridine and from treatment of lithiated poly(styrene) with perfluoropyridine or perfluoro-1-azacyclohexene.

The current high level of interest in low-molecular-weight electrophilic fluorinating agents of the O-F [1] and N-F [2] classes [3] prompts us to disclose our involvement with the development of polymeric analogues . Specifically here we wish to report that direct fluorination by a LaMar procedure [4] of crosslinked poly(4-vinylpyridine) yields a fluoropolymer that mimics perfluoro-N-fluoropiperidine[5-7] with respect to its ability to deliver "positive fluorine" to carbanionic sites. Similar macromolecular fluorinating agents, i.e. possessing the activity expected of polymer-anchored perfluoro-N-fluoropiperidine, can be obtained by direct fluorination of macromolecules carrying tetrafluoro-4-pyridyl or perfluoro-1-azacyclohexen-2-yl pendant groups.

0022-1139/86/$3.50



Scheme

[a] Reillex^{TM} (Reilly Tar & Chemical Corp.,Indianapolis) 402 (2% crosslinked) and 425 (25% crosslinked) polymers based on 4-vinylpyridine and divinylbenzene were used.

[b] Prepared by standard procedures (bromination then lithiation) [8] from linear poly(styrene).

The synthetic strategies involved are shown in the Scheme, where idealized formulae [cf.4] are written for the novel polymeric fluorinating agents obtained.

Like perfluoro-N-fluoropiperidine[9], each of the final nitrogeneous polymers shown in the Scheme readily liberated iodine from potassium iodide dissolved in aqueous acetone - a diagnostic test for the NF group [10] which also enabled the apparent NF-loadings (mmol g^{-1}) to be determined [1 NF $\equiv$ 1 I_2 (titrated against $Na_2S_2O_3$)] [11].

Flow fluorination for 94 hours (1 F_2 : 10 N_2 v/v for 48 h, 1 F_2 : 7 N_2 v/v for 46 h) at ambient temperature of poly(4-vinylpyridine) (Reillex^{TM} 402, 1.5 g; Found: C, 77.9; H. 6.9; N, 12.2%) gave a white fluoropolymer [A, 2.2 g; Found: C, 26.9; H, 0.6; F, 63.9; N, 3.5%; NF content 0.7 mmol g^{-1}]. When a slurry of this polymer in tetrahydrofuran was treated with an excess of sodio diethyl phenylmalonate in the same solvent, diethyl 2-fluoro-2-phenylmalonate was formed in 17% yield (determined by n.m.r. analysis); similarly, treatment of 1-(N-morpholinyl)cyclohexene in methylene chloride with the polymer, followed by the addition of 1M-hydrochloric acid, gave 2-fluorocyclohexanone in 15% yield based on the oxidising power of the polymer towards potassium iodide. The best yield (23%) of the fluoromalonate $PhCF(CO_2Et)_2$ was achieved with a presumptive NF-polymer of type C; polymer of type B provided the product in 19% yield.

Although a much higher yield (68%) of $PhCF(CO_2Et)_2$ can be achieved using perfluoro-N-fluoropiperidine(I) as the fluorinating agent, this compound (not available commercially) would prove more troublesome to prepare in laboratories not equipped with Simons electrochemical fluorination apparatus {pyridine or 2-fluoropyridine $\longrightarrow$ (ECF in AHF) (I; 8 and 13% yield, respectively) [9]} than the polymeric analogues of type A. The lithiation route to type B and C polymers is tedious, and in any case the perfluoro-1-azacyclohexene required in the synthesis of the latter is best prepared by defluorination of perfluoro-N-fluoropiperidine[6,12]. Note that when using polymers of type A-C to fluorinate carbanions, it is impossible to escape the possibility of losing perhaps valuable starting material via reaction with imidic entities generated during the halogenation reaction, as with perfluoro-N-fluoropiperidine itself [7] : $Nu^- + (I) \longrightarrow NuF + F^- + \overline{CF_2(CF_2)_3N{=}C}F \longrightarrow$ (with Nu^-) $\overline{CF_2(CF_2)_3N{=}C}Nu + F^-$.

We are indebted to Dr Eric F.V. Scriven of the Reilly Tar & Chemical Corporation for providing samples of poly(4-vinylpyridine) and Koch-Light/Genzyme (UK) for financial assistance.

1 See, for example, M.J. Fifolt, R.T. Olczak and R.F. Mundhenke, J.Org.Chem., 50 (1985) 4576; J.B. Levy and D.M. Sterling, ibid., p.5615; G.K. Mulholland and R.E. Ehrenkaufer, ibid., 51 (1986) 1482; G.W.M. Visser et al., ibid., pp.1466, 1886.

2 W.E. Barnette, J.Am.Chem.Soc., 106, (1984) 452; idem , US Pat. 4 479 901 (1984) (to Du Pont); S.T. Purrington and W.A. Jones, J.Org.Chem., 48 (1983) 761; idem, J.Fluorine Chem., 26 (1984) 43; D.D. DesMarteau, C.W. Bauknight, B.A. O'Brien and S.Singh, paper read (by D.D. DM.) in the Fluorine Division of the 191st ACS National Meeting, April 15, 1986 (New York City) {see also Chem. and Eng. News, 64 [(4), January 27] (1986) 20}; R.E. Banks, R.A. Du Boisson, and E. Tsiliopoulos, J.Fluorine Chem., 32 (1986) 461.

3 For a recent review, see A. Haas and M. Lieb, Chimia , 39 (1985) 134.

4 R.J. Lagow and J.L. Margrave, Progr.Inorg.Chem., 26 (1979) 162.

5 R.E. Banks and G.E. Williamson, Chem. and Ind., (1964) 1864.

6 R.E. Banks, K. Mullen, W.J. Nicholson, C. Oppenheim, and A. Prakash, J.Chem.Soc., Perkin Trans.I, (1972) 1098.

7(a) R.E. Banks and R. Hatton, unpublished work (see R.Hatton, PhD Thesis, University of Manchester, 1967);

(b) R.E. Banks and E. Tsiliopoulos, work in progress.

8 M.J. Farrall and J.M.J. Fréchet, J.Org.Chem., 41 (1976) 3877; M. Bernard and W.T. Ford, ibid., 48 (1983) 326.

9 R.E. Banks, W.M. Cheng, and R.N. Haszeldine, J.Chem.Soc., (1962) 3407.

10 R.E. Banks and E.D. Burling, J.Chem.Soc., (1965) 6077.

11 R.E. Banks, 'Fluorocarbons and their Derivatives', MacDonald, London (1970) (2nd edn.), p. 133.

12 R.E. Banks and G.E. Williamson, J.Chem.Soc., (1965) 815.