Preparation of a Polymer-supported Aryliodine(III) Difluoride and its Use to Fluorinate Olefins to Difluorides

By MARKO ZUPAN* and ALFRED POLLAK

(*J. Stefan Institute and Department of Chemistry, University of Ljubljana,* 61000 *Ljubljana, Yugoslavia*)

Summary A polymeric aryliodine(III) difluoride has been prepared and used to fluorinate several phenyl-substituted olefins to their difluorides in high yields under mild conditions.

THE advantage of polymer-supported organic reagents lies in the simplicity of preparative procedures, and there has been great interest in this field recently.[1] We report the preparation of the polymer-supported aryliodine(III) difluoride (**2**) and its reactions with phenyl-substituted olefins.

Aryliodine(III) difluorides have already been used for fluorination of 1,1-diphenylethene[2] and styrene,[3] but the resulting iodobenzene had to be separated from the geminal difluorides. With the polymer-supported aryliodine(III) difluoride (**2**) the separation procedure is reduced to filtration of the polymeric iodobenzene from the products of the reaction.

'Pop-corn' polystyrene (2·5 mmol g^{-1})[4] was iodinated[5], and reaction with XeF_2 in the presence of HF in CH_2Cl_2 at 25 °C gave (**2**) (Scheme). The quantity of active fluorine on the polymer resins was estimated by iodometry [75—90% of iodobenzene was converted into the difluoride (**2**)].

The products obtained by the treatment of (**2**) with various phenyl-substituted olefins are shown in the Table. The polymer is capable of fluorinating phenyl-substituted olefins under mild conditions resulting in rearranged products, *i.e.* geminal difluorides, in high yield. In a typical experiment, anhydrous HF (1 mmol) was introduced into a solution of the olefin (1 mmol) in CH_2Cl_2 (10 ml), and 0·5 g of the polymer (**2**) (containing 1·1 mmol fluorine) was added with stirring. After 2 h another 10 ml of CH_2Cl_2 were added and insoluble polymer resins were filtered off. As a routine work-up procedure, ^1H and ^{19}F n.m.r. and mass spectra were recorded on the crude reaction mixtures and the products were then purified by g.l.c. or t.l.c. Some of the difluorides were already known;[2,3] the structures of the unknown difluorides were assigned on the basis of their i.r., ^1H and ^{19}F n.m.r., and mass spectra.

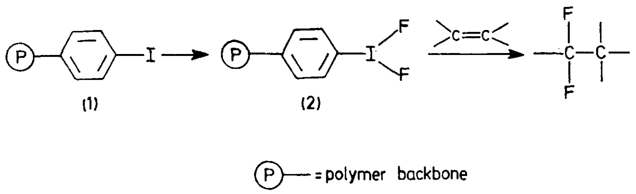

Table. Products from the reaction of (**2**) with olefins in CH_2Cl_2 at 25 °C.

Olefin	Product	Yield (%)
$Ph_2C{=}CH_2$	$PhCF_2CH_2Ph$	96
$Ph_2C{=}CHMe$	$PhCF_2CHMePh$	95
$PhCH{=}CH_2$	$PhCH_2CHF_2$	86
trans-$PhCH{=}CHMe$	$CHF_2CHMePh$	90
$PhC{=}CH[CH_2]_2CH_2$	$PhCHCF_2[CH_2]_2CH_2$	91
$PhC{=}CH[CH_2]_3CH_2$	$PhCHCF_2[CH_2]_3CH_2$	85

The conditions employed for the preparation of geminal-substituted difluorides were mild and the purity of the products was high as shown by g.l.c. or t.l.c. and n.m.r. spectra. After purification, the polymer iodobenzene could be reused several times for preparation of the polymer (**2**).

We thank Professors J. Slivnik for the XeF_2, and J. Marsel for facilities, Dr. V. Kramer for mass spectral data, and Dr. J. Kobe for n.m.r. spectra. The financial assistance of the Boris Kidrič Foundation and KRKA factory are acknowledged.

(*Received*, 23*rd June* 1975; *Com.* 715.)

---

[1] C. G. Overberger and K. N. Sannes, *Angew. Chem. Internat. Edn.*, 1974, **13**, 99; C. C. Leznoff, *Chem. Soc. Rev.*, 1974, **3**, 65.

[2] J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Amer. Chem. Soc.*, 1963, **85**, 1609.

[3] W. Carpenter, *J. Org. Chem.*, 1966, **31**, 2688.

[4] R. L. Letsinger, M. J. Kornet, V. Mahadevan, and M. J. Jeirna, *J. Amer. Chem. Soc.*, 1964, **86**, 5163.

[5] 'Methoden der Organischen Chemie (Houben-Weyl)', Makromolekulare Stoffe, Teil 2, Georg Thieme Verlag-Stuttgart, 1963, p. 682. Reaction time was 160 h at 110 °C.