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# Tetraphenylphosphonium Salts-Grafted Copolymers as Catalysts for Halogen-Exchange Fluorinations

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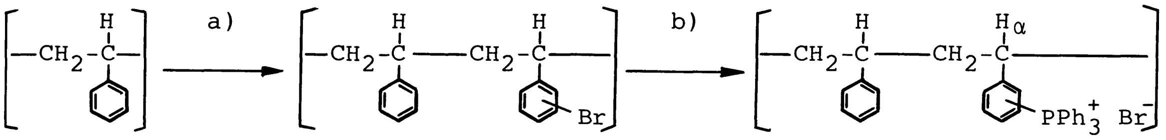
Cross-linked styrene/2-(4-chlorophenyl)propene copolymer-grafted tetraphenylphosphonium salt was an effective and reusable catalyst for the reaction of aromatic chlorides with anhydrous potassium fluoride to afford the corresponding aromatic fluorides in good yields.

Tetraphenylphosphonium bromide ($Ph_4PBr$) has recently much attention as a thermally stable catalyst for the halogen-exchange fluorination reactions of aromatic chlorides.$^{1)}$ Though the use of $Ph_4PBr$ has made possible syntheses of wide variety of aryl fluorides which had been difficult to obtain by simple halogen-exchange fluorination reactions, the salt seems to be somewhat expensive for the industrial use.

Previously, the authors explored a polystyrene-supported aminopyridinium salt as a versatile catalyst for halogen-exchange fluorinations.$^{2)}$ The catalyst was reusable more than 8 times without significant loss in activity on the reaction of 4-chloronitrobenzene (PCNB) with potassium fluoride (KF) in tetrahydrothiophene 1,1-dioxide (sulfolane, $TMSO_2$). Although we succeeded in preparing various aryl fluorides by using of the catalyst, the development of much more efficient and practical catalysts has been desired.



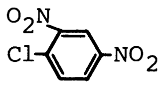
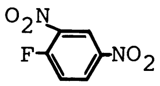
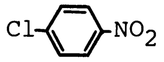
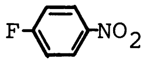
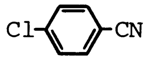
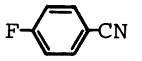
2% DVB cross-linked polystyrene gel

**1** (1.12 mmol/g)

a) Ref. 3 b) $Ph_3P$-$NiBr_2$ in $C_6H_5CN$, reflux, 5.5 h

Scheme 1.

Table 1. Halogen-Exchange Fluorination Reactions in the Presence of **1**

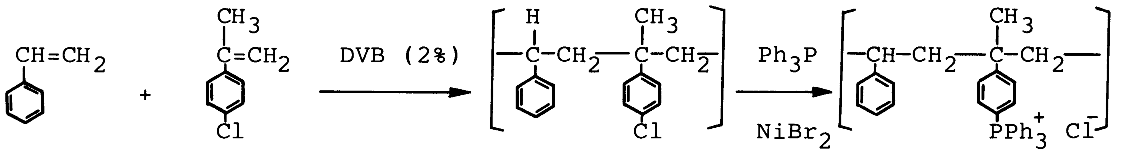
| Run | Reactant | Product | Catalyst | Solv. | Temp °C | Time h | Yield[a)] % | Recovered catalyst/% |
|---|---|---|---|---|---|---|---|---|
| 1 |  |  | **1** | $CH_3CN$ | 80 | 12 | 98 | 90 |
| 2 | " | " | **1**[b)] | " | " | " | 91 | 90 |
| 3 | " | " | **1**[c)] | " | " | " | 100 | 90 |
| 4 | " | " | none | " | " | 9 | 11 | — |
| 5 |  |  | **1** | $TMSO_2$ | 180 | 4 | 72[d)] | 0 |
| 6 | " | " | none | " | " | " | 10 | — |
| 7 |  |  | **1** | $TMSO_2$ | 215 | 5 | 62 | 0 |

a) GLC yields. b) Reused catalyst. c) Second reuse of catalyst.
d) Isolated yield.

This paper reports novel polymer supported tetraphenylphosphonium salts as other candidates which are repeatable catalysts for the halogen-exchange fluorination. First of all, we prepared the polymer analogue of $Ph_4PBr$. Thus, commercial 2% divinylbenzene (DVB) cross-linked polystyrene was brominated and then quaternized to give polymer supported tetraphenylphosphonium bromide (**1**). (Scheme 1)

The reaction of 2,4-dinitrochlorobenzene (1 equiv.) with spray dried KF (1.5 equiv.) in the presence of catalyst **1** (0.1 equiv.) in acetonitrile at 80 °C for 12 h gave 2,4-dinitrofluorobenzene in 98% yield. Resin **1** recovered from the reaction mixture by simple filtration could be effectively used in the repeated experiment. (Table 1) The reaction of PCNB with KF in $TMSO_2$ at elevated temperature (180 °C) gave 4-fluoronitrobenzene (PFNB) in 72% yield, but the catalyst beads have dissolved in the reaction mixture and could not be recovered by filtration, i.e., after distillation of volatile components only an oily residue was obtained. Dissociation of the α-proton of polymer **1**, induced by strong base KF, seems to initiate degradation of the polymer backbone.

We have next designed phosphonium chloride such as polymer **2**, supported on a copolymer having α-methyl group, in order to obtain the more



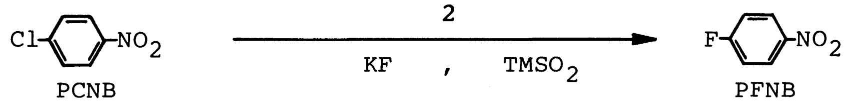
( 78 : 20 )

**2**

(1.19 mmol/g)

Scheme 2.

Table 2. Repeated Experiment of **2** for the Reaction of PCNB with KF



| Reuse number | Time<br>h | Product compositions/%<br>PCNB | <br>PFNB | Isolated yield<br>of PFNB/% |
|---|---|---|---|---|
| 1 | 5 | 2 | 98 | 83 |
| 2 | 5 | 0.4 | 97 | |
| 3 | 5 | 8 | 92 | 84 |
| 4 | 7 | 4 | 91 | |
| 5 | 7 | 13 | 84 | 77 |

All experiments were carried out with PCNB (50 mmol), spray dried KF (75 mmol), **2** (5 mmol), and $TMSO_2$ (30 g) at 180 °C. Virgin **2** of an amount of lossed polymer in the reaction (5-7%) was added each time.

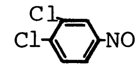
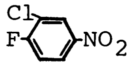
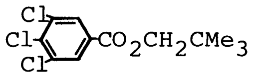
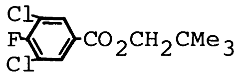
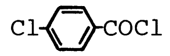
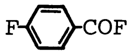
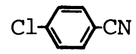
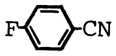
stable catalyst. Polymer **2** could be readily prepared by the reaction shown in Scheme 2.$^{4)}$

As expected, polymer **2** without α-proton adjacent to the active site exhibited high catalytic activity for the reaction of PCNB with KF in $TMSO_2$ at 180 °C and could be recovered by simple filtration from the reaction mixture. Thus, a mixture of PCNB (7.88 g, 50 mmol), spray dried KF (4.36 g, 75 mmol), and $\mathbf{2}^{4)}$ (4.20 g, 5 mmol) in $TMSO_2$ (30 g) was stirred for 5 h at 180 °C after treatment of dehydration with toluene (40 ml). The mixture was then cooled to room temperature and filtered, and the resin was washed with dichloromethane. The combined filtrate was concentrated and distilled to give 5.84 g (83%) of PFNB, bp 77-83 °C/6 mmHg (lit.,$^{2)}$ bp 77-82 °C/6 mmHg). (1 mmHg=133.32 Pa) Recovered resin catalyst **2** (3.92 g, 93%), which was washed with water and dried in vacuo, was submitted to the repeated run. The result was shown in Table 2. After reuse of 5 times, polymer **2** seems to be somewhat decomposed. The higher stability of polymer **2** compared with that of polymer **1** seems to support the degradation mechanism of **1** involving α-proton.

The synthetic utility of **2** is further demonstrated in Table 3 by the successful fluorination of aryl chlorides. In general, the yields obtained with polymer catalyst **2** are comparable to those of the current best methods catalyzed by $Ph_4PBr$, though catalyst **2** decomposed at 210 °C.

In conclusion, polymer supported catalyst **2** has high activity for fluorinations and high chemical stability, and is promising as a new practical catalyst.

Table 3. Preparation of Aryl Fluorides Catalyzed **2** in $TMSO_2$

| Run | Substrate | Catalyst | KF (equiv.) | Temp °C | Time h | Product | Yield/%[a)] |
|---|---|---|---|---|---|---|---|
| 1 |  | **2** | 1.5 | 160 | 3 |  | 97 (85) |
| 2 | " | Recovered **2** | " | " | " | " | 94 (86) |
| 3 | " | **2** | 2.5 | 210 | 7 | " | 64[b)] |
| 4 |  | **2** | 1.5 | 200 | 5 |  | 83 (76) |
| 5 |  | **2** | 2.5 | 210 | 3 |  | 57[c)] |
| 6 |  | **2** | 1.5 | 210 | 4 |  | 83 |
| 7 | " | Recovered **2** | " | " | " | " | 24 |
| 8 | " | none | " | " | 6 | " | 11 |

a) GLC yields. Numbers in parentheses refer to isolated products. b) 3,4-Difluoronitrobenzene was obtained in 12% yield. c) 4-Chlorobenzoyl fluoride was obtained in 37% yield.

## References

1) J.H. Clark and D.J. Macquarrie, Tetrahedron Lett., **28**, 111 (1987); S. Kumai, Y. Furukawa, M. Sasabe, and M. Matsuo, 11th Symposium of Fluorine Chemistry, Nagoya, October 1986, Abstr. No. 2E07; Y. Yoshida and Y. Kimura, Chem. Lett., **1988**, 1355; Y. Yoshida and Y. Kimura, J. Fluorine Chem., **44**, 291 (1989); N. Yazawa, H. Suzuki, Y. Yoshida, O. Furusawa, and Y. Kimura, Chem. Lett., **1989**, 2213.
2) Y. Yoshida, Y. Kimura, and M. Tomoi, Tetrahedron Lett., **30**, 7199 (1989).
3) M.J. Farrall and J.M.T. Frechet, J. Org. Chem., **41**, 3877 (1976).
4) Polymer **2** was prepared in the following method: To an organic mixture of styrene (39.5 g), 2-(4-chlorophenyl)propene (15.2 g), divinylbenzene (2.5 g), and 2,2'-azobis(isobutyronitrile) (1 g) was added 250 ml of aqueous solution adjusted to pH 9 by 25% NaOH containing gelatine (0.7 g), boric acid (2.6 g), polyamine sulfone A (Nitto Boseki Co.) (8 g), and sodium nitrite (0.1 g). The resulting mixture was polymerized at 70 °C for 16 h to give a styrene/2-(4-chlorophenyl)propene copolymer in 75% yield. Then a mixture of the copolymer (11.5 g), triphenylphosphine (26.4 g, 0.1 mol) and anhydrous nickel bromide (11.0 g, 0.05 mol) in benzonitrile (50 ml) was refluxed under stirring for 10 h. The polymer was removed by filtration, washed successively with dichloromethane, acetone, and water. The resin was further stirred in a mixture of 1mol·dm$^{-3}$ HCl (50 ml) and tetrahydrofuran (150 ml) for 0.5 h, and stood upon overnight. After filtration, the resin was successively washed with water and tetrahydrofuran, dried (50 °C, overnight then 80-90 °C in vacuo, 5.5 h) to yield 16.3 g of grafted copolymer having 1.19 mmol of phosphonium salts/g of dry polymer.[5)]
5) Phosphonium content was determined by using methods previously described: M. Tomoi and W.T. Ford, J. Am. Chem. Soc., **103**, 3821 (1981).

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