Tetrahedron Letters,Vol.30,No.10,pp 1271-1272,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

FREEZE-DRIED POTASSIUM FLUORIDE: SYNTHETIC UTILITY AS A FLUORINATING AGENT

Yoshikazu Kimura* and Hiroshi Suzuki

Research and Development Department, Ihara Chemical Industry Co., Ltd.

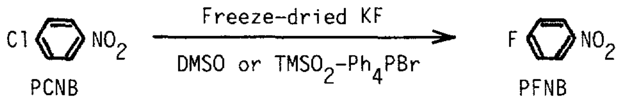
Fujikawa-cho, Ihara-gun, Shizuoka 421-33, Japan

Summary: The title reagent was found to be more effective fluorinating agent than calcine-dried potassium fluoride on a halogen-exchange fluorination. The fluorinating abilities of potassium fluoride depended strongly upon a concentration of aqueous solution to be lyophilized.

In 1980, Ishikawa and coworkers[1] have reported that freeze-dried potassium fluoride had no effect for the fluorination of activated chlorine compounds, for example, only a trace of benzoyl fluoride was given by the 3 h's reaction of benzoyl chloride with freeze-dried potassium fluoride in acetonitrile at room temperature in the presence of polyethylene glycol. No further examination has been reported for the halogen-exchange fluorination of activated chlorine compound by freeze-dried potassium fluoride.

In the course of our synthetic studies on aromatic fluoride derivatives,[2] we have reexamined a fluorinating ability of freeze-dried potassium fluoride (FD-KF). Surprisingly, we have now found that FD-KF can be utilized as an excellent fluorinating agent.

In a typical example, commercial potassium fluoride (25 g) was dissolved in water (500 mL) in 1-L round-bottomed flask. The solution was frozen completely, and then lyophilized under vacuum for 3 days at room temperature, affording cotton like fine powdered 5% FD-KF.[3] As the fluorinating ability of this fine FD-KF could be tested, the reaction with 4-chloronitrobenzene (PCNB) in dimethylsulfoxide (DMSO) was first attempted. Thus, a mixture of PCNB (15.8 g, 0.10 mol) and 5% FD-KF[3] (8.7 g, 0.15 mol) in anhydrous DMSO (48.4 g) was heated at reflux with stirring for 5 h. GLC analysis of this sample revealed a 97.5% conversion (Fig. 1).[4] In the



case of using calcine-dried potassium fluoride (CD-KF), 4-fluoronitrobenzene (PFNB) was only obtained in 64% yield after 5 h.

In order to rigorously confirm the reactivity on fluorination reaction of FD-KF, several types of FD-KF were prepared from different concentrations of aqueous potassium fluoride, having the physical properties summarized in Table 1. The FD-KF prepared from diluted potassium fluoride solution has a small particle size and a large surface area.

With various types of FD-KF shown in Table 1 in hand, the halogen-exchange fluorination reactions PCNB with FD-KF were next examined in sulfolane ($TMSO_2$). The reactions were performed in the presence of tetraphenylphosphonium bromide (Ph_4PBr).[5] The results are given in Fig. 2. As expected, by the use of FD-KF prepared from low concentration of aqueous solution, a dramatic rate enhancement was observed. The obtained results are in good accordance with the assumption that super fined potassium fluoride crystals having large specific surface area show a high reactivity. The reactivity of 5% FD-KF[3] on PCNB fluorination was

Table 1. The Physical Properties of Freeze-dried Potassium Fluorides

	Calcine-Dried KF	Freeze-dried KF (Concn of aqueous soln/%)				
		1	5	10	20	40
Particle size (μm)[a]	200-300[c]	31.9	37.6	34.7	56.6	58.0
Specific surface[b] area (m^2/g)	0.1[c] 0.13	0.78	0.72	0.62	0.39	0.39
Bulk density (g/ml)	1.14	0.13	0.24	0.39	0.85	1.00

a) Average value of particle size distributions determined by Coulter Counter TA-II. b) By Micrometric Flow Sorb II 2300 (Shimadzu). c) N. Ishikawa et al., Chem. Lett., 1981, 761.

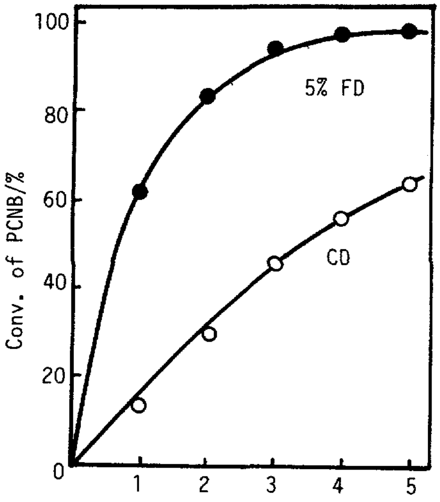


Fig. 1. Fluorination of PCNB in DMSO. (see text)

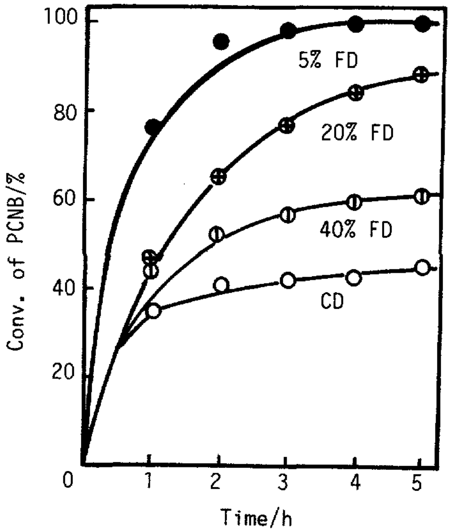


Fig. 2. Fluorination of PCNB in $TMSO_2$.

PCNB(0.10 mol), FD-KF(0.15 mol), Ph_4PBr (5 mmol), $TMSO_2$(60 g); 180°C

almost equal or a little greater than that of spray-dried potassium fluoride.

Based on these studies, it was finally established that a freeze-dried potassium fluoride has a powerful fluorinating ability on the halogen-exchange reactions of activated chlorine aromatic compounds.

Curiously, the methylation of phenol with methyl iodide was unsuccessful and the fluorination of benzoyl chloride gave benzoyl fluoride in a quantitative yield by 40% FD-KF[3] under the reported conditions.[1] Though the result is opposite to the reported one, the reason is quite obscure now.

Acknowledgment The authors are grateful to Messrs K. Nakamura and S. Fujita, Kumiai Chemical Co., Ltd. for measurements of particle size and specific surface area.

References and Notes

1. N. Ishikawa, T. Kitazume, and M. Nakabayashi, Chem. Lett., 1980, 1089.
2. Y. Yoshida and Y. Kimura, Chem. Lett., 1988, 1355.
3. It means freeze-dried potassium fluoride prepared from 5% aqueous solution. The following abbreviations are the same as above.
4. After removal of inorganic substances by filtration, PFNB was distilled out under reduced pressure (12.0 g, 85% yield). This sample was identified with the authentic sample.
5. J.H. Clark and D.J. Macquarrie, Tetrahedron Lett., 28, 111 (1987).

(Received in Japan 7 December 1988)