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September 2014: The paragraphs above replace the section “Handling and Disposal of Hazardous Chemicals” in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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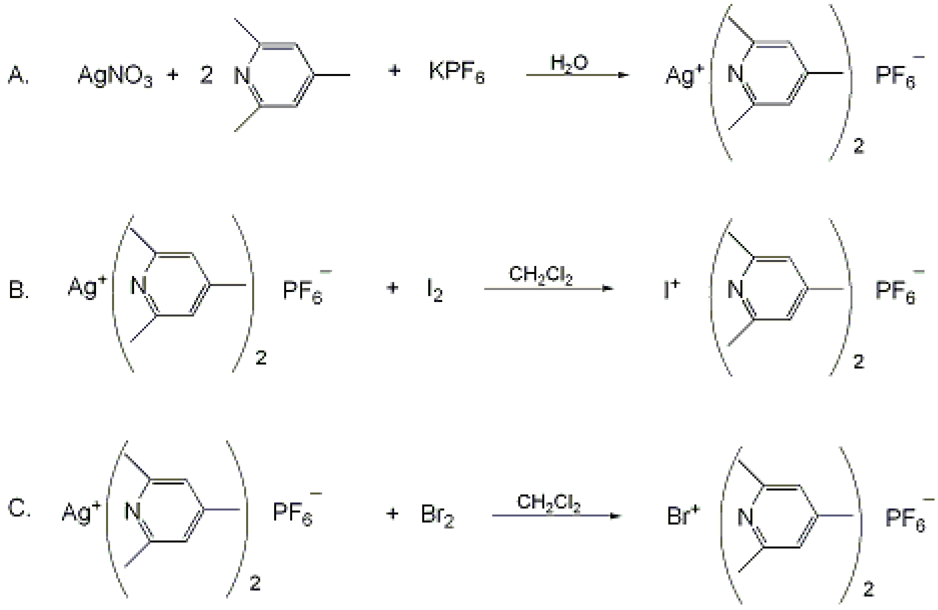
PREPARATION OF BIS(2,4,6-TRIMETHYLPYRIDINE)IODINE(I) HEXAFLUOROPHOSPHATE AND BIS(2,4,6-TRIMETHYLPYRIDINE) BROMINE(I) HEXAFLUOROPHOSPHATE

[Iodine(1+), bis(2,4,6-trimethylpyridine)-, hexafluorophosphate(1−), and Bromine (1+), bis(2,4,6-trimethylpyridine)-, hexafluorophosphate(1−)]



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1. Procedure

Caution! These procedures should be conducted in an efficient fume hood because of the toxicity of iodine and bromine.

A. Bis(2,4,6-trimethylpyridine)silver(I) hexafluorophosphate . A 2-L, three-necked, round-bottomed flask is equipped with a mechanical stirrer and a 250-mL pressure-equalizing dropping funnel. The flask is charged with 1 L of distilled water, 100 g of silver nitrate (0.588 mol) and 109.3 g of potassium hexafluorophosphate (0.594 mol) (Note 1). When all the solids are dissolved, 221 mL of 2,4,6-collidine (1.67 mol) is added over 10 min while stirring (Note 2), (Note 3). A slight exothermic reaction is observed, corresponding to the formation of a white solid. The mixture is stirred for 1 hr at room temperature, the solid is suction filtered, and the filtercake is washed with 1 L of water. The solid is dried in the dark in a desiccator under high vacuum over phosphorus pentoxide (P_2O_5) for 1 week, to afford 262-291 g (90-99%) of silver salt as a white-gray solid, mp 210°C (Note 4), (Note 5).

B. Bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate . A 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, condenser topped with a drying tube containing calcium chloride, and a stopper is charged with 500 mL of dry methylene chloride (Note 6), 82.5 g of bis(trimethylpyridine)silver(I) hexafluorophosphate (0.166 mol), and 41.9 g of iodine (0.165 mol). The mixture is stirred until all the iodine is consumed (1 hr - 2 hr) (Note 7). The resulting yellow solid (silver iodide) is suction filtered, and washed with 100 mL of dry methylene chloride . The filtrate is concentrated on a rotary evaporator at a maximum bath temperature of 30°C to give 68-76 g (80-88%) of yellowish solid bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate (mp 132-133°C) (Note 8), (Note 9), and (Note 10). This product is suitable for reactions without further purification.

C. Bis(2,4,6-trimethylpyridine)bromine(I) hexafluorophosphate . A 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, 50-mL pressure-equalizing addition funnel, and a drying tube containing calcium chloride is charged with 500 mL of dry methylene chloride (Note 6), and 82.5 g of bis(trimethylpyridine)silver(I) hexafluorophosphate (0.166 mol). Then 8.3 mL of bromine (0.161 mol) is added in 10 min. The mixture is stirred until all the bromine is consumed (1 hr) (Note 11). The resulting yellowish solid (silver bromide) is suction filtered and washed with 100 mL of dried methylene chloride . The filtrate is concentrated on a rotary evaporator at a maximum bath temperature of 30°C to give 65-74 g (83-95%) of bis(2,4,6-trimethylpyridine)bromine(I) hexafluorophosphate (mp 127-128°C) as a white solid (Note 9), (Note 12), and (Note 13). This product is suitable for reactions without further purification.

2. Notes

1. Silver nitrate was obtained from ACROS and potassium hexafluorophosphate from Aldrich Chemical Company, Inc.
2. Collidine (99% grade) from Aldrich Chemical Company, Inc. was used. Technical grade (from ACROS) can be used after purification by distillation from calcium hydride (CaH_2).
3. The checkers always observed a small amount of undissolved solid and began the addition of collidine when dissolution appeared to cease.
4. The range of melting is 210°-253°C. At 253°C the submitters observe solid decomposition. The checkers observed an mp range of 222-238°C (dec.).
5. The NMR spectrum was as follows: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.40 (s, 6 H), 2.78 (s, 12 H), 7.11 (s, 4 H) . ^{13}C NMR (63 MHz, CD_2Cl_2) δ: 21.6, 28.0, 124.4, 153.9, 158.2 . Anal. Calcd for $C_{16}H_{22}AgF_6N_2P$: C, 38.81; H, 4.48; N, 5.66. Found: C, 38.73; H, 4.36; N, 5.59.
6. Methylene chloride was dried by distillation over CaH_2.
7. It is important that all the iodine reacts with the silver salt. After concentration, the presence of iodine can catalyze the decomposition of bis(trimethylpyridine)iodine(I) hexafluorophosphate. If necessary a small amount of silver salt can be added.
8. The submitters note that after recrystallization from methylene chloride a white solid is obtained [mp 131-132°C (dec)]. No difference in reactivity is observed compared with the crude product.
9. This solid must be stored in the dark at 0°C. In these conditions it can be kept for several years, or for several months at room temperature.
10. The following spectra were obtained: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.41 (s, 3 H), 2.43 (s, 3 H), 2.65 (s, 6 H), 2.85 (s, 6 H), 7.11 (s, 2 H), 7.17 (s, 2 H) ; ^{13}C NMR (63 MHz, CD_2Cl_2) δ: 21.5, 29.9, 125.9, 155.0, 158.3 ; IR (KBr) cm^{-1}: 2989 (vs), 1618 (s), 1461 (s), 1384 (s), 1312 (s), 1031 (s), 1003 (s), 829 (br) . Anal. Calcd for $C_{16}H_{22}F_6IN_2P$: C, 37.37; H, 4.31; N, 5.45. Found: C, 37.45; H, 4.36; N, 5.42.
11. All the bromine should have reacted before removal of the solvent. See (Note 7).
12. The submitters indicate that after recrystallization from methylene chloride the mp is 125°C (decomposition). No difference in reactivity is observed compared with the crude product.
13. The following spectra were obtained: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.43 (s, 6 H), 2.78 (s, 12 H), 7.16 (s, 4 H) ; ^{13}C NMR (63 MHz, CD_2Cl_2) δ: 21.6, 25.9, 126.3, 154.9, 156.4 ; IR (KBr) cm^{-1}: 2990 (vs), 1618, (s), 1463 (s), 1386 (s), 1313 (s), 1030 (s), 1005 (s), 828 (br) .

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

These preparations of bis(2,4,6-trimethylpyridine)iodine(I) and bromine(I) hexafluorophosphate are adaptations of methods previously reported for obtaining the corresponding perchlorates.[2]

The advantages of the hexafluorophosphate salts compared to the perchlorate salts are the safety of preparation, ease of use, and their low hygroscopicities. This method of preparation can be applied to a large variety of mono aromatic amines (pyridine, chloropyridine, 2-methoxypyridine, etc.); however, in the reactions that the submitters have examined these salts are less reactive than the parent collidine salts. Bis(2,4,6-trimethylpyridine)iodine(I) and -bromine(I) hexafluorophosphate have been used for specific electrophilic halogenations, such as the preparation of 7-membered ring lactones[3] and ethers,[4] medium ring lactones,[3,5] halogenation of phenols,[6] pyridinols[7] and acetylenic compounds.[8] Most of these reactions are impossible or difficult with other known halogenation reagents.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate:
Iodine(1+) bis(2,4,6-trimethylpyridine)-, hexafluorophosphate(1−) (12); (113119-46-3)

Bis(2,4,6-trimethylpyridine)bromine(I) hexafluorophosphate:
Bromine(1+) bis(2,4,6-trimethylpyridine)-, hexafluorophosphate(1−) (14); (188944-77-6)

Silver(I)nitrate:
Nitric acid silver(1+) salt (8,9); (7761-88-8)

Potassium hexafluorophosphate.
Phosphate(1−), hexafluoro, potassium (8,9); (17084-13-8)

2,4,6-Collidine:
Pyridine, 2,4,6-trimethyl- (8,9); (108-75-8)

Iodine (8,9); (7553-56-2)

Bromine (8,9); (7726-95-6)