

SYNLETT Spotlight 303

Triphenylcarbenium Tetrafluoroborate

Compiled by Huan Liang

Huan Liang was born in Tianjin, P. R. of China in 1980 and received his B.Sc. in Chemistry from Tianjin University in 2003. He is now pursuing his Ph.D. in the laboratory of Prof. Marco Ciufolini in the Department of Chemistry at the University of British Columbia. His research mainly focuses on the total synthesis of natural products with biological activities, and the development of new synthetic methodologies.

Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada
E-mail: lianghuan@chem.ubc.ca

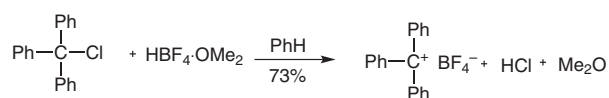


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Introduction

Triphenylcarbenium tetrafluoroborate, also called trityl fluoroborate, is widely applied in organic reactions,¹ such as dehydrogenation,² deprotection of ketone acetals,³ alkyl ethers,⁴ oxidation of silyl enol ethers,⁵ preparation of cationic organometallics⁶ or organic complexes,⁷ as a polymerization catalyst⁸ and as a Lewis acid catalyst.⁹ Trityl fluoroborate is a yellow solid (mp 200 °C dec.), which is soluble in most organic solvents, e.g., dichloromethane, tetrahydrofuran, and reacts with nucleophilic solvents, e.g., water. Several preparation methods were described

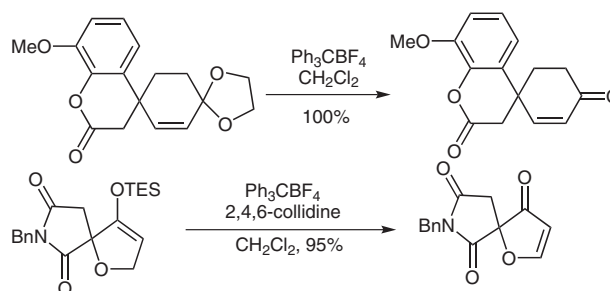
in the literature as early as the 1940s. Dauben et al. used triphenylcarbinol and 48% fluoroboric acid, while removing water from the reaction mixture by adding acetic anhydride.^{10a} In 1972, Olah et al. developed a more convenient and economical route using trityl chloride and anhydrous tetrafluoroboric acid dimethyl etherate in dry benzene.^{10b}



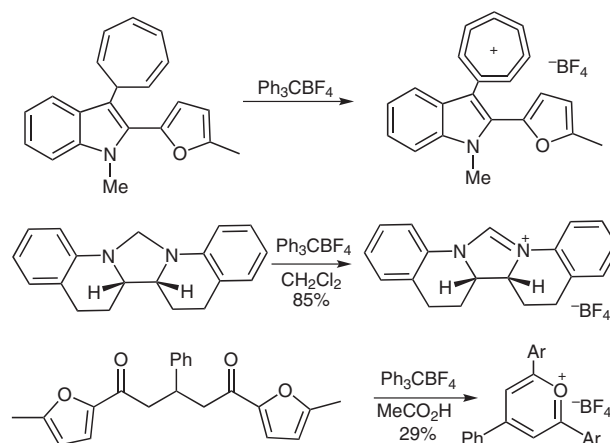
Scheme 1 Improved multi-gram preparation of trityl fluoroborate

Abstracts

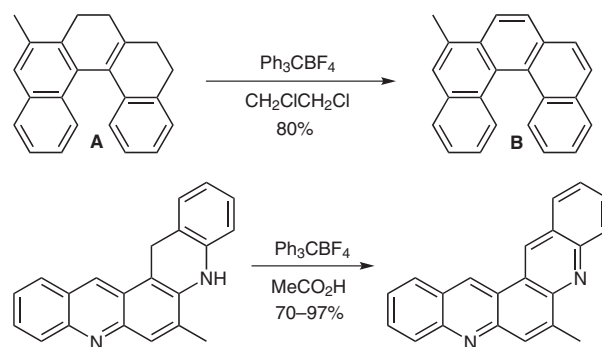
(A) Triphenylcarbenium tetrafluoroborate has been used to deprotect ketone acetals to ketones and change silyl enol ethers to α,β -unsaturated ketones. In the synthesis of (\pm)-codeine, Varin et al. employed this method to transform a dioxolane group into a ketone in quantitative yield.³ Another example was demonstrated in the synthesis of FD-838, featuring an asymmetric Stetter reaction, by the Rovis group in 2008.⁵ Oxidation of a silyl enol ether to a furanone by hydride transfer to the triphenylcarbenium ion gave 95% yield.



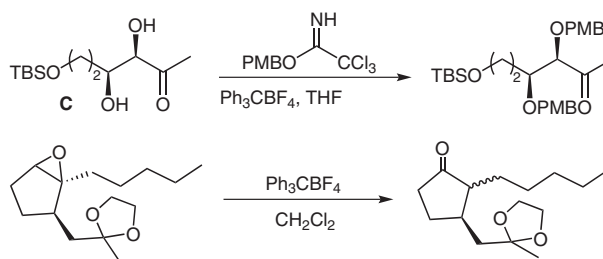
(B) Formation of carbo/heterocyclic cationic complexes is a major application of trityl fluoroborate by hydride abstraction. In 2006, the Yamamura group converted cycloheptatriene into the corresponding tropylium ion derivative in the study of lithiation of 2,3-dihalo-1-methylindoles.^{7a} Other analogues, i.e., imidazolium,^{7b} pyrylium^{7c} and selenopyrylium ions^{7d} were also formed by similar hydride abstractions.



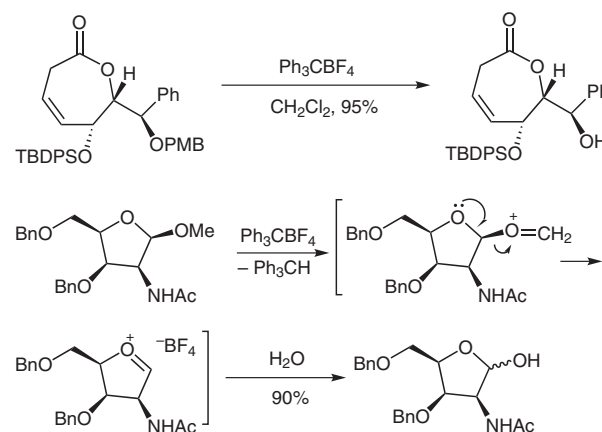
(C) Triphenylcarbenium tetrafluoroborate has been widely used in the dehydrogenation of polycyclic hydroaromatics. In one recent example from 2008, the Ichikawa group dehydrogenated pentacyclic compound **A** to [5]helicene **B** in 80% yield using trityl fluoroborate.^{2b} In 2005, in their improved synthesis of quinacridine derivatives, Lartia et al. applied the same reagent in acetic acid to oxidize the partially hydrogenated heterocycles in high yield.^{2c}



(D) Using trityl fluoroborate as a Lewis acid, the diol **C**, which was used in Paterson's work on the synthesis of brasilinolides, was converted into the corresponding bis-PMB ether by the *para*-methoxy benzyl ester of trichloroacetimidic acid.^{9a,b} Also, Helmchen and co-worker opened an epoxide to the corresponding ketone selectively in the enantioselective synthesis of isomers of magnolione®.^{9c}



(E) In the synthesis of (+)-goniopyprone, Yadav et al. employed Ph_3CBF_4 to remove a PMB protective group in the presence of TBDPS ether nearly instantaneously in 95% yield.⁴ Another application was developed by the Vankar group to deprotect anomeric *O*-methyl glycosides under mild and chemoselective conditions in 2008.¹¹ One plausible mechanism was also given to explain the loss of configuration of hemiacetals.



References

- (1) Jung, M. E. *Triphenylcarbenium Tetrafluoroborate* In *Encyclopedia of Reagents for Organic Synthesis*, Vol. 8; Parquette, L. A., Ed.; John Wiley & Sons: Chichester, **1995**, 5348–5350.
- (2) (a) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317. (b) Ichikawa, J.; Yokota, M.; Kudo, T.; Umezaki, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4870. (c) Lartia, R.; Bertrand, H.; Teulade-Fichou, M.-P. *Synlett* **2006**, 610.
- (3) Varin, M.; Barre, E.; Iorga, B.; Guillou, C. *Chem. Eur. J.* **2008**, *14*, 6606.
- (4) Yadav, V. K.; Agrawal, D. *Chem. Commun.* **2007**, 5232; and references therein.
- (5) Orellana, A.; Rovis, T. *Chem. Commun.* **2008**, 730.
- (6) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325.
- (7) (a) Ueda, I.; Nishiura, M.; Takahashi, T.; Eda, K.; Hashimoto, M.; Yamamura, K. *Tetrahedron Lett.* **2006**, *47*, 8535. (b) Vehlow, K.; Gessler, S.; Blechert, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 8082. (c) Ionkin, A. S.; Marshall, W. J. *Organometallics* **2004**, *23*, 3276. (d) Sashida, H.; Ohyanagi, K. *Chem. Pharm. Bull.* **2005**, *53*, 60.
- (8) Grazulevicius, J. V.; Strohrig, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297.
- (9) (a) Paterson, I.; Mühlthau, F. A.; Cordier, C. J.; Housden, M. P.; Burton, P. M.; Loiseleur, O. *Org. Lett.* **2009**, *11*, 353. (b) Paterson, I.; Coster, M. J.; Chen, D. Y.-K.; Acena, J. L.; Bach, J.; Keown, L.; Trieselmann, T. *Org. Biomol. Chem.* **2005**, *3*, 2420. (c) Stang, A. Q.; Helmchen, G. *Helv. Chim. Acta.* **2005**, *88*, 2738.
- (10) (a) Dauben, H. J. J. r.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442. (b) Olah, G. A.; Svoboda, J. J.; Olah, J. A. *Synthesis* **1972**, 544; and references therein.
- (11) Kumar, A.; Doddi, V. R.; Vankar, Y. D. *J. Org. Chem.* **2008**, *73*, 5993.