SYNLETT Spotlight 34

2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate

Compiled by Diego Peña

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

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Introduction: Although benzyne (**4**) has been widely used in organic synthesis, there are relatively few ways of generating it under mild conditions from readily available chemicals. Subjecting 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**3**) to fluoride-induced 1,2-elimination generates benzyne conveniently at room temperature without the use of strong bases or oxidants.

Preparation: The benzyne precursor **3** was first reported by Himeshima, Sonoda and Kobayashi in 1983.¹ It is commercially supplied by Aldrich and can easily be obtained in high yield from 2-bromophenol (**1**).²

Abstracts

(1) The formation of benzyne (**4**) from triflate **3** was exploited in an usual aryne reaction by trapping benzyne with furan to afford **5**.¹ This mild method of generating benzyne has proved to be more powerful in some cases than classical methods.³

(2) Slow generation of benzyne by treatment of triflate **3** with CsF, in the presence of catalytic amounts of Pd(0), afforded triphenylene (**6**) as a result of the cyclotrimerization of benzyne.⁴ The cocyclization of alkynes with benzyne can also be catalyzed by palladium complexes: in this case phenanthrene **7** and naphthalene **8** were obtained.⁵ The course of the reaction can be controlled by the choice of catalyst.

(3) The palladium-catalyzed reaction of allyl chloride (**9**) with the benzyne precursor **3** produced phenanthrene **10** in good yield.⁶ This reaction is assumed to proceed by insertion of benzyne into the π -allylpalladium intermediate.⁷

References and Notes

- (1) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.
- (2) D. Peña, Ph.D. thesis.
- (3) (a) Constable, K. P.; Blough, B. E.; Carroll, F. I. *Chem. Commun.* **1996**, 717. (b) Cobas, A.; Guitián, E.; Castedo, L. *J. Org. Chem.* **1997**, 62, 4896.
- (4) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem. Int. Ed.* **1998**, 37, 2659.
- (5) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827.
- (6) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem. Int. Ed.* **2000**, 39, 173.
- (7) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, 122, 7280.