Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 1325–1326

Synthesis of 2-pentafluorosulfanylnaphthalene

William R. Dolbier, Jr.,* Akira Mitani and Robin D. Warren

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611, United States

Received 15 August 2006; revised 19 December 2006; accepted 20 December 2006
Available online 23 December 2006

Abstract—A three step synthesis of 2-pentafluorosulfanylnaphthalene is reported. Initial addition of SF_5Cl to benzobarralene was followed by elimination to form 2-pentafluorosulfanylbenzobarralene. Heating of this compound with 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine led to elimination of the ethylene bridge via a sequence of cycloadditions and retro-cycloadditions to form the title compound.

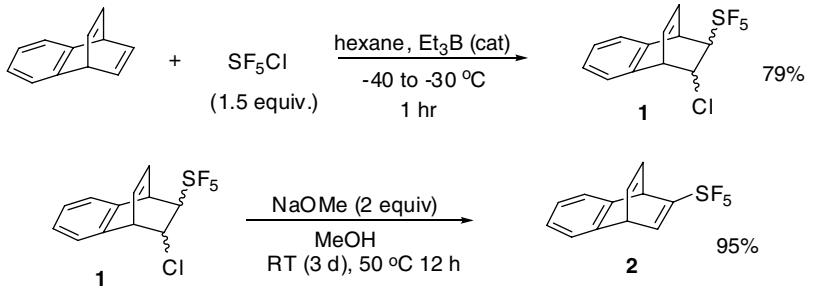
In recent years interest in pentafluorosulfanyl aromatics with respect to their unique potential in materials, pharmaceutical and agrochemical applications has followed the development of new and useful methods for their synthesis.

There have been two main approaches utilized for the synthesis of SF_5-aromatics, one based on direct fluorination of highly electron deficient aryl disulfides,[1] and the other based upon the free radical chain addition of SF_5Cl or SF_5Br to unsaturated cyclohexane derivatives followed by conversion of such adducts to SF_5–benzene.[2,3]

Thus far, there has been no mention in the literature of any pentafluorosulfanyl naphthalene derivatives[4,5] In this Letter we would like to report an efficient synthesis of 2-pentafluorosulfanylnaphthalene.

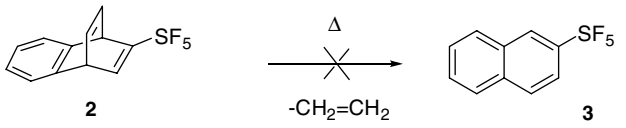
Benzobarralene[6–8] underwent clean mono-addition of SF_5Cl (1.5 equiv) to one of its double bonds using our convenient low temperature, Et_3B-initiated procedure.[9] Adduct **1** was formed in 79% yield, appearing on the basis of its ^{19}F NMR to consist of one major isomer.[10] Without further purification, it was subjected to elimination by excess methoxide in methanol at 50 °C to form 2-pentafluorosulfanylbenzobarralene (**2**).[11]

It was hoped that a simple thermal retro-Diels–Alder reaction of **2** would eliminate ethylene to form the desired 2-pentafluorosulfanylnaphthalene. However, **2** proved to be quite stable thermally, being completely recovered after 15 min at 250 °C, whereas heating at 350 °C led to decomposition, with none of the desired product being evident in the mixture.

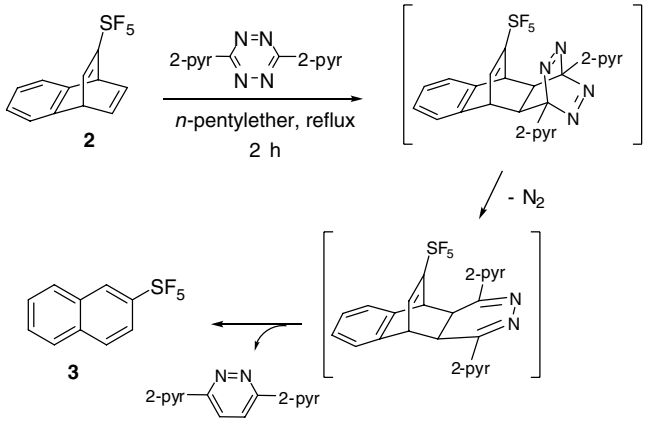


Keywords: SF_5 Group; Pentafluorosulfanyl group; Naphthalene; SF_5Cl.
* Corresponding author. Tel.: +1 352 392 0591; fax: +1 352 846 1962; e-mail: wrd@chem.ufl.edu

0040-4039/$ - see front matter
doi:10.1016/j.tetlet.2006.12.123



The desired net elimination of ethylene could be accomplished indirectly by the reaction of **2** with 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine via the tandem cycloaddition, N_2 elimination, and retrocycloaddition process as shown below.[12] The yield of 2-pentafluorosulfanylnaphthalene from this process was 65%.[13]



If SF_5-napthalene is to be used as a building block, it must be further substituted. Thus, the electrophilic aromatic substitution chemistry of 2-pentafluorosulfanylnaphthalene is currently being examined, and the results will be reported in due course.

Acknowledgements

Support of this research in part by the National Science Foundation is acknowledged with thanks. This research was also generously supported by Nippon Soda Co., Inc. in the form of a fellowship to A.M.

References and notes

1. Bowden, R. D.; Comina, P. J.; Greenhall, M. P.; Kariuki, B. M.; Loveday, A.; Philp, D. *Tetrahedron* **2000**, *56*, 3399–3408.
2. Sergeeva, T. A.; Dolbier, W. R., Jr. *Org. Lett.* **2004**, *6*, 1417–1419.
3. Winter, R. W.; Gard, G. L. *J. Fluorine Chem.* **2004**, *125*, 549–552.
4. A recent US Patent Application Publication[5] which describes an alternative three step synthesis of the title compound has been brought to our attention. The sequence involves initial addition of SF_5Br or SF_5Cl to 1,4-dihydronaphthalene, followed by elimination and aromatization steps.
5. Lal, G. S.; Minnich, K. E. US Patent Application Publication No. 2006/0069285 A1.
6. Benzobarralene was prepared by the known procedure of Jefford and co-workers.[7] Its ^{1}H NMR spectrum was consistent with the little data reported in the literature:[8] ^{1}H NMR, d 4.92 (m, 2H), 6.87 (m, 4H), 6.89 (m, 2H), 7.16 (m, 2H); ^{13}C NMR, d 31.4, 49.6, 122.6, 123.8, 140.1.
7. Johnson, R. P.; Exarchou, A.; Jefford, C. W.; Hahn, R. C. *J. Org. Chem.* **1977**, *42*, 3758–3759.
8. Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798–1800.
9. Ait-Mohand, S.; Dolbier, W. R., Jr. *Org. Lett.* **2002**, *4*, 3013–3015.
10. ^{1}H NMR, d 3.9–4.2 (m, 2H), 4.51 (m, 1H), 4.68 (s, 1H), 6.61 (t, $J = 6$–7 Hz, 1H), 6.69 (t, $J = 6$–7 Hz, 1H), 7.1–7.4 (m, 4H); ^{19}F NMR, d +60.2 (d, $J = 153$ Hz, 4F), +84.4 (pent, $J = 153$ Hz, 1F).
11. *Experimental procedure*: To a solution of **1** (1.1 g, 3.47 mmol) in MeOH (10 mL) was added NaOMe (0.37 g, 6.94 mmol) at rt. The mixture was was stirred for 2 h at RT, after which 3 more equivalents of NaOMe were added, and the mixture stirred for an additional 48 h and then refluxed for 2 h. The mixture was then poured into ice-water and neutralized with 2 N HCl, extracted twice with ether, the organic layers combined and washed with water and brine, and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (elution with *n*-hexane/ethyl acetate = 9/1) to obtain 0.92 g of **2** (95%), which contained only a small amount of impurity. This product was used in the next reaction without further purification. ^{1}H NMR, d 4.98 (br s, 1H), 5.26 (m, 1H), 6.97 (m, 4H), 7.22–7.29 (m, 3H); ^{19}F NMR, d 62.2 (d, $J = 161$ Hz, 4F), 84.4 (pent, $J = 161$ Hz, 1F); ^{13}C NMR, 134.1, 132.2, 129.45, 128.83, 128.79, 127.83, 127.69, 126.61 (pent, $J = 4.6$ Hz), 122.50 (pent, $J = 4.4$ Hz).
12. Zhai, Y.-A.; Ghiviriga, I.; Battiste, M. A.; Dolbier, W. R., Jr. *Synthesis* **2004**, 2747–2750.
13. ^{1}H NMR, ä 7.62 (m, 2H), 7.80 (dd, $J = 9.0$, 2.1 Hz, 1H), 7.92 (m, 3H), 8.28 (d, $J = 2.1$ Hz, 1H); ^{19}F NMR, ä +63.0 (d, $J = 160$ Hz, 4F), +84.4 (pent, $J = 160$ Hz, 1F); ^{13}C NMR, ä 122.5 (pent, $J = 2.8$ Hz), 126.6 (pent, $J = 4.6$ Hz), 127.7, 127.8, 128.78, 128.82, 129.4, 132.2, 134.1, 151.5 (t, $J = 17$ Hz); Anal. Calcd for $C_{10}H_7F_5S$: C, 47.25; H, 2.78. Found: C, 46.98; H, 2.57.