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2-Trimethylsilylcorannulenyl Trifluoromethanesulfonate: An Efficient Precursor for 1,2-Didehydrocorannulene

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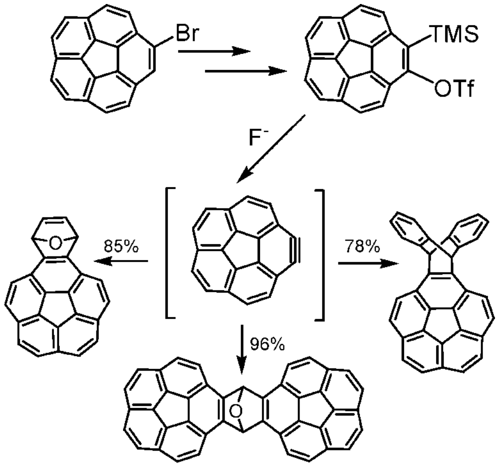
ABSTRACT



2-Trimethylsilylcorannulenyl trifluoromethanesulfonate, prepared from bromocorannulene, provides a means for generating of 1,2-didehydrocorannulene (corannulyne) under very mild conditions as demonstrated by the high-yield formation of its adducts with dienes.

We have been developing practical methodologies for the synthesis of buckybowls, i.e., polycyclic aromatic hydrocarbons with curved surfaces which are structurally related to fullerenes.[1] After discovering a gram-scale synthetic route to the smallest buckybowl, corannulene (**1**),[2] we have turned our attention to the larger molecular assemblies which incorporate corannulene subunits. Such assemblies can potentially act as host molecules in supramolecular complexes as we recently have shown in the case of bis-corannulene "buckycatcher" $C_{60}H_{28}$ which forms a stable $\pi-\pi$ bonded complex with C_{60} in the solid state as well as in solution.[3] Since Diels−Alder methodology is often applied to construct the large systems with corannulene subunits, we rely on the availability of the building blocks like 1,2-didehydrocorannulene (**2**) and/or corannulenoisofuran (**3**). In 2005, we reported that **2** can be generated by ortho-deprotonation of bromocorannulene (**4**) with sodium amide/potassium *tert*-butoxide mixture in THF.[4] Trapping **2** with dienes led to the formation of extended aromatic systems with an embedded corannulene subunit and subsequently, to the synthesis of isofuran **3**.[4,5] However, despite these successes, the very harsh conditions required for the genera-

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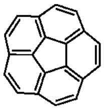
(1) For recent reviews see: (a) Wu, T.-Y.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (c) Sygula, A., Rabideau, P. W. In *Carbon Rich Compounds*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006; p 529.

(2) (a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323. (b) Sygula, A.; Xu, G.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron* **2001**, *57*, 3637.

(3) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3842.

10.1021/ol801581z CCC: $40.75

tion of **2** seriously limited the scope of this approach. Herein we report a synthetic route to 2-trimethylsilylcorannulenyl triflate (**5**) along with the experimental evidence for its efficiency in generation of **2** under very mild conditions.



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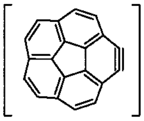

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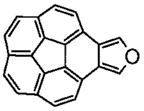
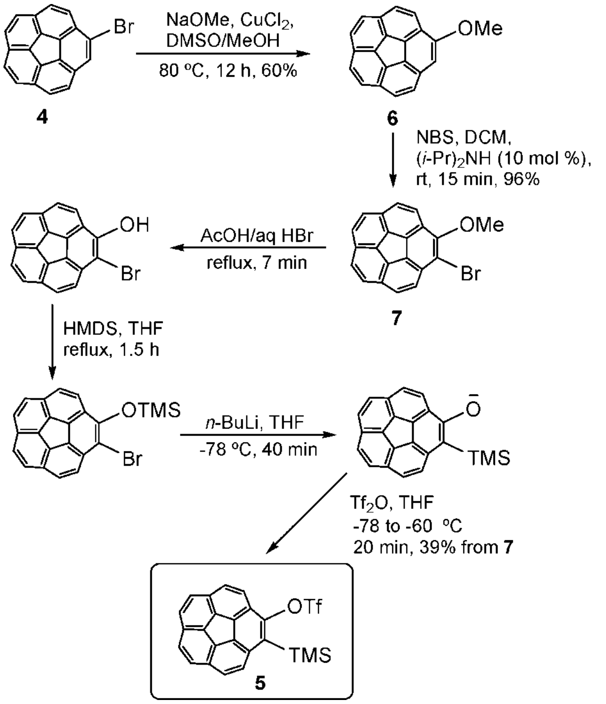


3

o-Trimethylsilylaryl triflates are attractive benzyne precursors since the ortho-elimination of the TMS and OTf groups can be promoted by fluoride anions.[6] In addition, efficient procedures have recently been developed for their synthesis usually starting from the appropriate phenols.[7] However, we have quickly learned that hydroxycorannulene is not stable enough to serve as a starting material in the synthesis of **5**.[8] After some experimentation, we have developed an alternative synthesis of 2-trimethylsilylcorannulene triflate (**5**) which is outlined in Scheme 1.

Scheme 1. Synthesis of **5**



Thus, copper-catalyzed etheration of easily accessible **4**[9] with NaOMe in MeOH/DMSO led to methoxycorannulene **6** with 60% yield.[10,11] **6** was then *o*-brominated by NBS in the presence of diisopropylamine providing **7** in a nearly quantitative yield.[12] Both **6** and **7** are stable compounds and were fully characterized. In contrast, all the other intermediates leading to **5** were rather unstable so they were not purified but quickly used in the subsequent steps. Conversion of **7** to the *o*-bromophenol was achieved by brief reflux in AcOH with aq HBr. The bromophenol was then treated with hexamethyldisilazine (HMDS), and the resulting crude *o*-bromo trimethylsilyl ether was metalated with *n*-butyllithium in THF at −78 °C and subsequently quenched with Tf_2O, producing **5** in a modest yield of 39% yield from **7**.

The *o*-TMS triflate **5** is stable enough to be stored for weeks without any evidence of decomposition. The most characteristic features of its ^{13}C NMR spectrum are the signals of the TMS group carbons at 2.75 ppm and a quartet of the CF_3 carbon atom at 119 ppm with the $^1J_{C-F}$ coupling constant of 320.3 Hz.[13]

The performance of **5** as a corannulyne precursor is outlined in Scheme 2. First, we tested **5** in the presence of furan as the aryne trapping agent with CsF as a fluorine anion source. It turned out that stirring of the reagents in acetonitrile at room temperature resulted in a rather slow formation of the known addition product **8**, presumably due to a limited solubility of CsF. On the other hand, sonication of the reaction mixture at slightly elevated temperatures of 40−45 °C resulted in a very fast and clean formation of the expected product. No starting material was detected in the reaction mixture after 1 h, and **8** was the only product formed with an excellent yield. For comparison, formation of side products like benzocorannulene and corannulene was observed when **8** was synthesized by trapping **2** formed by $NaNH_2$/tBuOK treatment of bromocorannulene.[4] Of course, for practical purposes the shorter route developed previously is clearly recommended if **8** is the intended synthetic target.

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(5) Sygula, A.; Sygula, R.; Rabideau, P. W. *Org. Lett.* **2006**, *8*, 5909.

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(7) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* **2002**, 1454.

(8) The instability of hydroxycorannulene has been noted before: Cheng, P.-G. Ph.D. Thesis, Boston College, Boston, MA, 1996.

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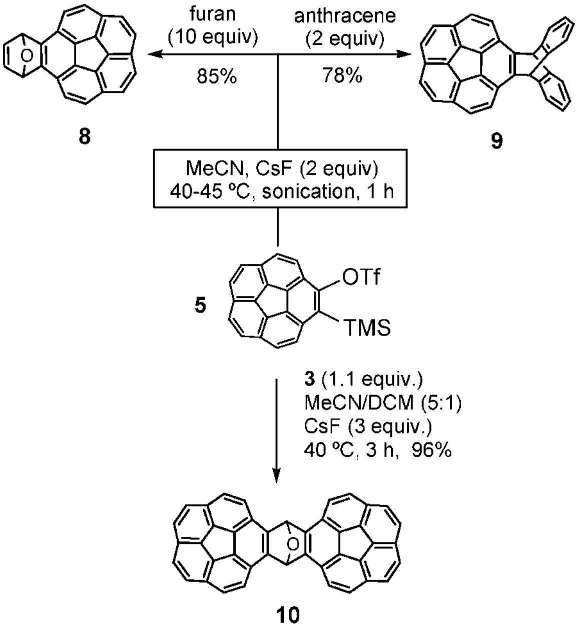
(10) **6**: white solid (from EtOH); mp 137−8 °C; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.08 (1H, d, $J = 8.7$ Hz), 7.83−7.76 (5H, m), 7.73 (1H, d, $J = 8.7$ Hz), 7.69 (1H, d, $J = 8.7$ Hz), 6.96 (1H, s), 4.06 (3H, s); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 158.77, 136.68, 136.58, 136.46, 135.19, 133.38, 131.55, 131.19, 131.13, 129.66, 127.62, 127.58, 127.24, 127.04, 126.91, 126.84, 126.02, 124.61, 123.92, 102.85, 56.25; MS *m/z* (rel intensity) 281 (24), 280 (100), 266 (20), 265 (87), 239 (21), 237 (76); HRMS (EI, 25 eV) calcd for $C_{21}H_{12}O$ 280.0888, found 280.0893.

(11) **6** was synthesized previously on a miligram scale by a different method (ref 9).

(12) **7**: light yellow solid (from EtOH/toluene); mp 159−60 °C; ^1H NMR ($CDCl_3$, 600 MHz) δ (concentration dependent) 7.90 (1H, d, $J = 8.7$ Hz), 7.88 (1H, d, $J = 8.8$ Hz), 7.80−7.73 (6H, m), 4.34 (3H, s); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 154.82, 136.31, 135.72, 135.50, 135.02, 132.43, 131.82, 131.21, 130.97, 130.47, 128.39, 127.74, 127.69, 127.25 (2), 126.84, 123.45, 112.75, 63.35; MS *m/z* (rel intensity) 360 (71), 358 (72), 346 (22), 245 (100), 344 (22), 343 (98), 317 (30), 315 (30), 236 (64), 235 (37); HRMS (EI, 25 eV) calcd for $C_{21}H_{11}OBr$ 357.9993, found 357.9994.

(13) **5**: white solid (from EtOH); mp 94−6 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ (strongly concentration dependent) 8.07 (1H, d, $J = 8.9$ Hz), 7.98 (1H, d, $J = 8.9$ Hz), 7.91 (1H, d, $J = 8.9$ Hz), 7.86 (1H, d, $J = 8.9$ Hz), 7.83 (1H, d, $J = 8.8$ Hz), 7.80−7.76 (3H, m), 0.76 (9H, s); ^{13}C NMR ($CDCl_3$, 75.5 MHz) d 148.02, 137.16, 136.74, 135.64, 135.09, 134.39, 134.38, 133.89, 131.26, 131.25, 130.86, 128.48, 128.15, 128.14, 127.75, 127.55, 127.28, 127.21, 123.78 (b), 123.61, 119.10 (q, $J = 320.3$ Hz), 2.75; MS *m/z* (rel intensity) 470 (6), 455 (49), 339 (24), 338 (74), 337 (53), 322 (27), 264 (26), 263 (100); HRMS (EI, 25 eV) calcd for $C_{24}H_{17}O_3F_3SiS$ 470.0619, found 470.0611.

Scheme 2



The remaining two reactions shown in Scheme 2 represent the examples of the processes we failed to complete previously with the base-promoted generation of corannulyne from **4**. However, treatment of **5** with CuF in acetonitrile in the presence of 2 equiv of anthracene led to a clean formation of the adduct **9** with a very good yield of 78%. Again, the expected adduct **9** was the only identifiable reaction product.

A successful Diels−Alder reaction between the dienophile **2** and a diene **3** leading to the bis-corannulene adduct **10** represents a powerful example of the versatility of *o*-TMS triflate **5** for the synthetically useful generation of corannulyne. Previously, we attempted the synthesis of **10** by the reaction of **3** with **4** in the presence of strong bases, but at low temperatures only starting materials were recovered while at the elevated temperatures we failed to isolate any identifiable products presumably due to decomposition of **3** caused by the harsh conditions required for the *o*-dehydrobromination of bromocorannulene.[5] In contrast, generation of corannulyne from **5** led to the clean formation of the expected adduct **10** even with essentially no excess of the trapping isofuran **3** (Scheme 2). Again, the mixture of **5** and **3** in MeCN/DCM was stirred at ca. 40 °C for 3 h with an excess of CsF resulting in a nearly quantitative formation of **10**.

In conclusion, we described a synthesis of 2-trimethylsilylcorannulenyl triflate **5** which efficiently generates 1,2-didehydrocorannulene under very mild conditions. The versatility of **5** as the corannulyne source was demonstrated by trapping experiments which led to the high-yield formation of adducts **8**−**10**. The successful syntheses of the latter two adducts illustrate the advantage of **5** as the corannulyne source over the previously reported alternative based on the base-promoted dehydrobromination of bromocorannulene. The availability of **5** opens several attractive possibilities for synthesis of novel systems with corannulene subunits not only by Diels−Alder methodology but also by [3 + 2] cycloaddition reactions with azides and diazo compounds[14] as well as palladium-catalyzed [2 + 2 + 2] cyclo- and/or cocyclotrimerization approaches.[15] We are currently exploring these possibilities.

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Supporting Information Available: Synthetic procedures and spectroscopic characterization of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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