

Molecule of the Month

A 'Hexacationic' Benzene Derivative!

Uday Maitra

A stable hexacationic benzene derivative has been prepared by the displacement of all the fluorine atoms of hexafluorobenzene by six molecules of 4-dimethylaminopyridine.

The nucleophilic displacement of a halogen atom attached to an aromatic ring is not a very favourable process.¹ Polyfluorinated aromatics are interesting in this regard, since the fluorine atom can act as a leaving group, as well as an activating group. Hexafluorobenzene, therefore, has been a popular molecule to examine the displacement of all the fluorine atoms by nucleophiles.

Imagine the (hypothetical) displacement of the fluorine atom of fluorobenzene by 4-dimethylaminopyridine (DMAP). The product of this reaction is a cation (an *onium salt*), which of course is resonance stabilized as shown in *Figure 1*. If we try to extend this idea with hexafluorobenzene, we would expect a hexa(onio)substituted benzene! At first sight this would appear to be impossible because of the accumulation of like charges. However, German chemists Robert Weiss and coworkers have

Uday Maitra is a member of the Organic Chemistry Faculty at Indian Institute of Science.

¹Usually, aromatic compounds undergo *electrophilic* substitution reactions. Nucleophilic substitution on an aromatic ring requires electron withdrawing groups on the ring (or, special reaction conditions, as in a benzyne mechanism). Such 'activated' aromatic halides undergo nucleophilic substitution by an addition-elimination sequence. The negatively charged addition product is called a *Meisenheimer complex*.

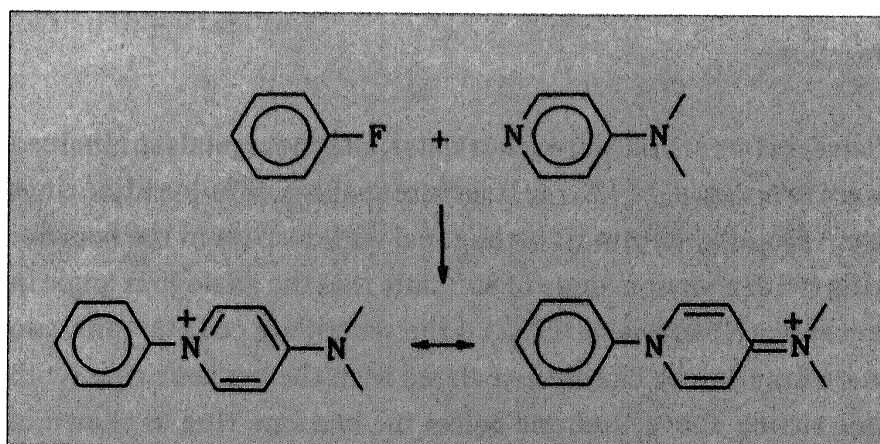
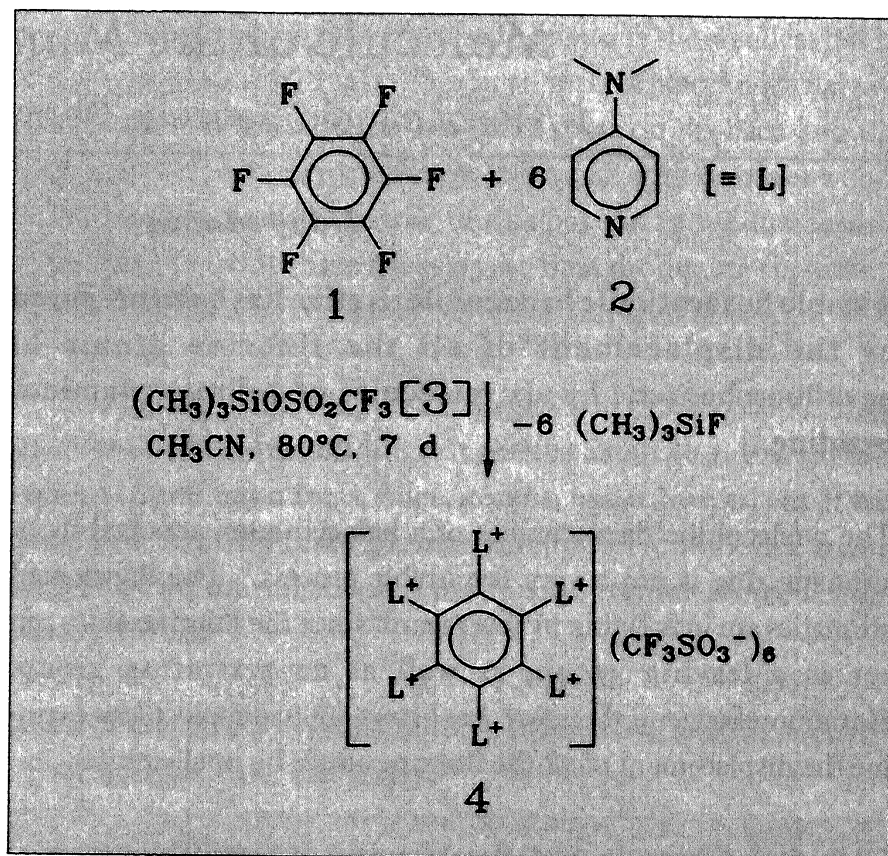


Figure 1 Resonance stabilization in N-phenyl-4-dimethylaminopyridinium salt.

Figure 2 Synthetic route to hexacationic benzene derivative 4.



² Per(onio) refers to the complete substitution of all displacable groups (F) by the cationic group. For example, perfluoroalkyl group refers to a $\text{C}_n\text{F}_{2n+1}$ unit.

recently shown that it is indeed possible (R. Weiss *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 1319). They simply reacted hexafluorobenzene (1) and DMAP (2) with trimethylsilyl trifluoromethanesulfonate (TMS-triflate, 3) in refluxing acetonitrile for seven days. What was formed in almost quantitative yield is the per(onio)² product 4, with six triflate counter ions (Figure 2). Clearly, the formation of this product is aided by the formation of strong Si-F bonds in the other product of the reaction.

Salt 4 was crystallized from hot water, and the crystals so obtained were investigated by X-ray structure analysis. The pyridine rings were found to be almost orthogonal with respect to the benzene ring (with a torsion angle of 80°; note that the analogous angle in hexaphenylbenzene is 65°). Of the six triflate counter ions, two were found to be closely associated with the benzene ring (with one sitting above, and one below the benzene ring as shown in

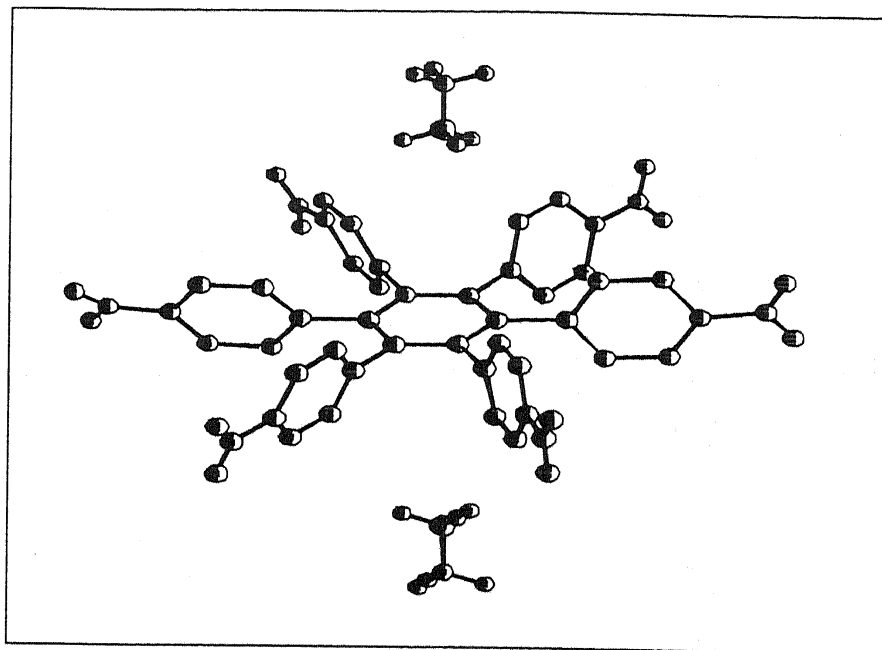
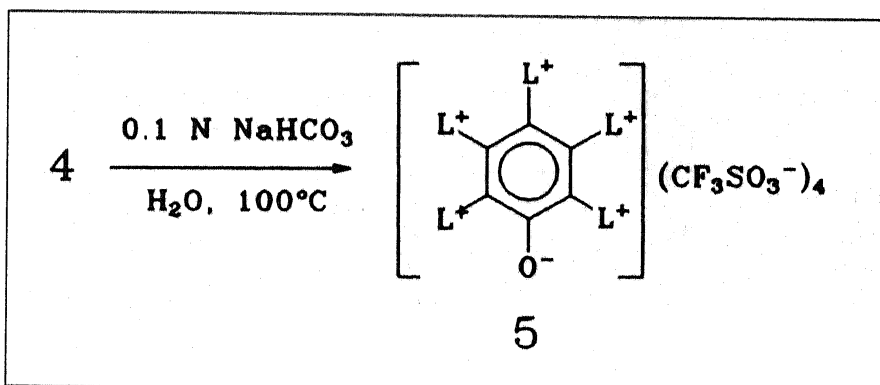


Figure 3 Approximate ball and stick model of the molecular structure of **4** in the solid state. Only the two closely associated triflate anions are shown. The hydrogen atoms are omitted for clarity.

Figure 3).

How would you expect the reactivity of **4** to be? Since it is substituted by six cationic units, one would certainly expect greatly facilitated nucleophilic substitutions. In fact, if **4** is simply boiled with dilute NaHCO_3 solution for 30 minutes, compound **5**, resulting from the displacement of one of the DMAP units, is formed (Figure 4). It is interesting to know that hexacyanobenzene also undergoes an analogous reaction under comparable conditions. The difference between **4** and hexacyanobenzene is that in **4** the activation is exclusively via electrostatic effects, whereas in hexacyanobenzene $-M$ effect³ plays an important role.



³The $-M$ effect refers to electron withdrawing ability through resonance (mesomeric effect). Electron donation through resonance is represented by $+M$.

Address for correspondence

Uday Maitra
Department of
Organic Chemistry,
Indian Institute of Science,
Bangalore 560 012, India.

Figure 4 Facile nucleophilic displacement of one ligand from **4**.