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Thermolysis of Hexakis(trifluoromethyl)benzene

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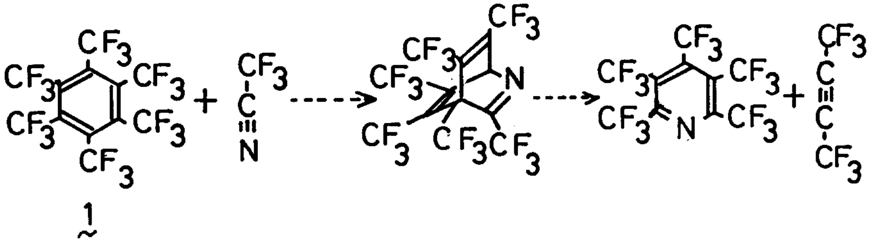
SUMMARY

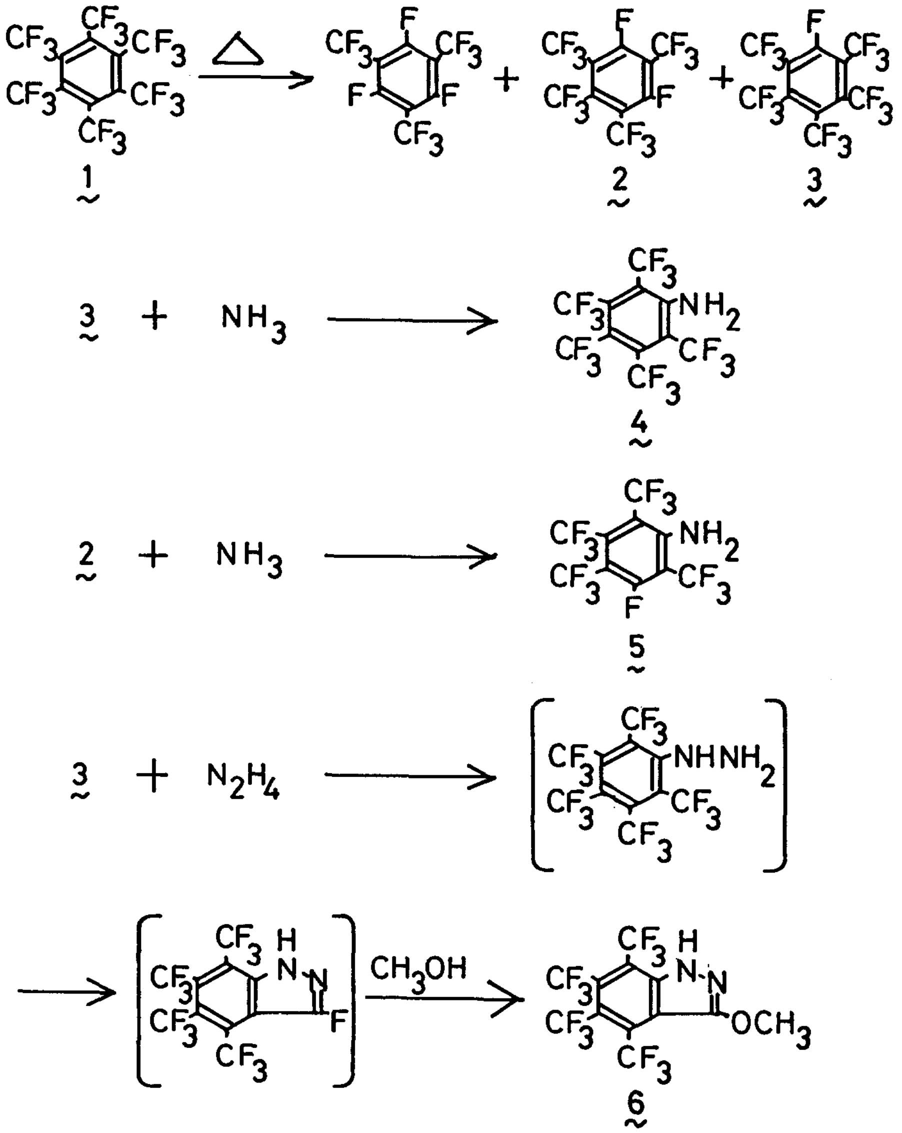
Hexakis(trifluoromethyl)benzene gave perfluoro-(pentamethylbenzene), -(1,2,3,5-tetramethylbenzene), and -(1,3,5-trimethylbenzene) on thermolysis in the presence of trifluoroacetonitrile.

In the course of our study on the valence-bond isomers of aromatic compounds stabilized with trifluoromethyl groups [1], we attempted to synthesize pentakis(trifluoromethyl)-pyridine from hexakis(trifluoromethyl)benzene (1) by the route shown below.



However, pentakis(trifluoromethyl)pyridine was not obtained, and a new elimination reaction of difluoromethylene units occurred. Equimolar amounts of 1 and trifluoroacetonitrile were heated in an autoclave of stainless steel at 550°C under autogenous pressure of 280 atm for 48 hr. After extrusion of gaseous products at room temperature, the mixture was extracted with methylene chloride. About 30% of 1 was recovered as an insoluble fraction. The solvent was removed by a fractional distillation and the products were separated by a preparative g.l.c: column DEGS 3m; column temp. 70°; carrier N_2. The first fraction was a trace of 1,3,5-trifluoro-2,4,6-tris(trifluoromethyl)benzene; colourless oil; M^+ 336 [2]; ^{19}F-NMR δ($CDCl_3$) [3], -58.5 (9F, t, J=25.4 Hz), -103.0 (3F, m). The second was 1,3-difluoro-2,4,5,6-tetrakis-(trifluoromethyl)benzene (**2**); yield 15-20%; colourless oil, which solidified on ice-cooling; M^+ 386; ^{19}F-NMR δ($CDCl_3$) -55.0 (3F, sept, J=14.2 Hz), -57.0 (6F, m), -58.8 (3F, t, J= 24.8 Hz), -101.2 (2F, broad sept, J=24.8 Hz). The third was perfluoropentamethylbenzene (**3**); yield 15-20%; colourless oil, which solidified on cooling; mp 43-5°C; M^+ 436; ^{19}F-NMR δ ($CDCl_3$) -53.0 (3F, sept, J=15.8 Hz), -55.0 (6F, sept, J=15.8 Hz), -58.2 (6F, d-q, J=32.0 Hz, J=15.8 Hz), -98.0 (1F, sept, J=32.0 Hz). Thus, CF_2 units from the 1-, 3-, and 5-positions were eliminated stepwise on the thermolysis of **1**. Since only quite low yields of **2** and **3** were obtained in the absence of trifluoroacetonitrile, the presence of CF_3CN was essential. We did not examined the structures of the gaseous products and could not tell the fate of the CF_2 units.

Treatment of **3** with concentrated ammonia in ethanol under ice-cooling gave pentakis(trifluoromethyl)aniline (**4**) in a few minutes. **4**; yield 87%; mp 111°C (EtOH); M^+ 433; ^{19}F-NMR δ ($CDCl_3$) -49.8 (3F, sept, J=17.1 Hz), -52.2 (6F, sept, J=17.1 Hz), -57.6 (6F, q, J=17.1 Hz). The similar reaction of **2** gave a monoamino compound (**5**); yield 82%; yellow oil after purification through SiO_2 in benzene; M^+ 383; ^{19}F-NMR δ($CDCl_3$) -53.0 (3F, sept, J=14.7 Hz), -54.6 (3F, m), -55.2 (3F, d, J=31.5 Hz) -55.7 (3F, q, J=14.7 Hz), -103.5 (1F, sept, J=31.5 Hz). These results show that one fluorine atom of **2** or **3** is very reactive towards a nucleophile, but the second one of **2** becomes much less reactive. Treatment of **3** with an excess of hydrazine hydrate in methanol gave 3-methoxy-4,5,6,7-tetrakis(trifluoromethyl)indazole (**6**); yield 35%; colourless needles; mp 147-50 °C(C_6H_6); M^+ 420; ^{19}F-NMR δ($CDCl_3$) -49.1 (3F, sept, J=14.5 Hz) -51.6 (3F, sept, J=14.5 Hz), -54.2 (3F, q, J=14.5 Hz), -55.5 (3F, q, J=14.5 Hz). This reaction shows that a trifluoro-



methyl group in an α-position to an electron donating group is reactive for a nucleophile [4].

The amino group of 4 was highly hindered sterically and deactivated electronically by the trifluoromethyl groups. Acetylation of 4 with acetic anhydride was unsuccessful, while heating the solution of 4 and acetic anhydride in pyridine gave pentakis(trifluoromethyl)acetanilide.

REFERENCES AND NOTES

1 Y. Kobayashi and I. Kumadaki, Accounts Chem. Research, 14, (1981) 76, and references there in.

2 High resolution mass spectra of all the products were consistent with those calculated from the structures.

3 From $CFCl_3$: Lower field is shown positive.

4 Y. Kobayashi and I. Kumadaki, Accounts Chem. Research, 11, (1978), 197.