# Synthesis of 1,2-Bis[*p*-(Ethoxydimethylsilyl)-Phenyl]Tetrafluoroethane and of 1,2-Bis[*p*-(Hydroxydimethylsilyl)Phenyl]Tetrafluoroethane

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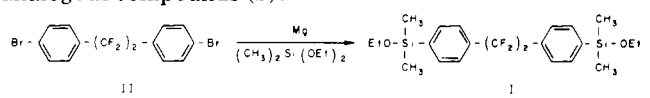
THE SYNTHESIS of 1,2-bis[*p*-(ethoxydimethylsilyl)-phenyl]tetrafluoroethane I was accomplished (in 55% yield) through a Grignard reaction, using excess diethoxydimethylsilane, from 1,2-bis(*p*-bromophenyl)tetrafluoroethane II; the procedure follows that developed for analogous compounds (*2*):

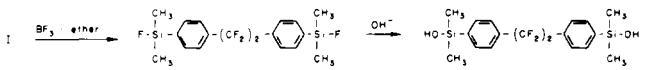


II I

Treatment of 4,4′-dibromobenzil (*1*) with sulfur hexafluoride by the method of Hasek, Smith, and Engelhardt (*3*) gave a 52% yield of 1,2-bis(*p*-bromophenyl)tetrafluoroethane II.

[1] Deceased.

Conversion of 1,2-bis[*p*-(ethoxydimethylsilyl)phenyl]-tetrafluoroethane I to 1,2-bis[*p*-(fluorodimethylsilyl)-phenyl]tetrafluoroethane III was accomplished with boron trifluoride-etherate by the method of Omietanski and Reid (*4*). Hydrolysis of the fluorosilane III by the method of Sveda (*5*) gave 1,2-bis[*p*-(hydroxydimethylsilyl)phenyl]-tetrafluoroethane IV.



III IV

Table I. Preparation.

| Compound | Starting Materials | Conditions | Yield % |
|---|---|---|---|
| II | 4,4′-Dibromobenzil (*1*), 202 g. (0.547 mole); Sulfur tetrafluoride (90%), 264 g. (2.2 moles). | 250° (1 hr.), 230–240° (16 hr.) | 55 |
| I | Mg turnings, sublimed (Dow), 4.86 g. (0.20 mole); II, 41.2 g. (0.10 mole); Tetrahydrofuran, 250 ml.<br><br>Diethoxydimethylsilane (Pensinsular Chemical), 600 g. (4.04 moles); Tetrahydrofuran, 500 ml. | Refluxed 2 hr. Added to refluxing diethoxydimethylsilane solution and refluxed 14 hr. | 55 |
| III | I, 2.35 g. (5.17 mmoles); $BF_3$-etherate, 5.0 ml (40 mmoles). | Mixed at room temperature. The solid mass was dissolved in benzene and refluxed overnight. | 100, crude |
| IV | III, 2.10 g.; ether, 100 ml.<br><br>40 ml of 1.5*N* sodium hydroxide. | Ether solution of III was added to stirred, cooled (ice bath) aqueous alkali. Stirred additional 5 minutes and separated. | 21 |

Table II. Physical Properties.

| | II | I | IV |
|---|---|---|---|
| Boiling point | 158–160°/2 mm. of Hg | 101°/$10^{-3}$ mm. of Hg | ... |
| Melting point | 98–99° (pentane) | ... | 171–172° ($CCl_4$) |
| Anal: Calcd. | C, 40.81; H, 1.96; Br, 38.79; F, 18.44 | C, 57.61; H, 6.59 | C, 53.71; H, 5.51 |
| Found | C, 40.60; H, 1.97; Br, 38.92; F, 17.99 | C, 57.50; H, 6.29 | C, 53.30; H, 5.75 |
| NMR | $F^{19}$. + 111.6 $\phi$, singlet | $H^1$. 2.42 (doublet, J, 8 cps, 4 protons)<br>2.53 (doublet, J, 8 cps, 4 protons)<br>6.35 (quartet, J, 7 cps, 4 protons)<br>8.84 (triplet, J, 7 cps, 6 protons)<br>9.65 (singlet, 12 protons) | |
| Infrared | ... | ... | $\lambda^{Nujol}$ 3.10 (SiOH), 11.5 (SiOH). No absorption at 10.55 (SiOC). |

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The NMR spectra were run by W.R. Anderson, Jr., Analytical Research Department, Stanford Research Institute.

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# 2-Benzoyl-1,2-dihydroisoquinaldamide

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WHILE INVESTIGATING the chemistry of Reissert compounds, it became necessary to prepare 2-benzoyl-1,2-dihydroisoquinaldamide. This was accomplished by treating 2-benzoyl-1,2-dihydroisoquinaldonitrile with 30% hydrogen peroxide. The reaction was analogous to that used by Cobb and McEwen to prepare 1-benzoyl-1,2-dihydroquinaldamide (*1*). The structure was confirmed by reconversion of the amide to the starting material by dehydration with phosphorus pentoxide.

## EXPERIMENTAL

**2-Benzoyl-1,2-dihydroisoquinaldamide.** To a solution of 10.0 grams (0.038 mole) of 2-benzoyl-1,2-dihydroisoquinaldonitrile in 250 ml. of acetone was added 4.0 grams of sodium bicarbonate. This was cooled in a water bath and stirred while 150 ml. of 30% hydrogen peroxide was added over a period of two hours; then six ml. of 5% sodium bicarbonate solution was added. The mixture was stirred for an additional two hours and allowed to stand overnight. The mixture was concentrated to about 150 ml. by distillation and 400 ml. of water added. A tan solid precipitated upon cooling in an ice bath. The solid was filtered, washed with water and dried to yield 3.0 grams (28.3%). Several recrystallizations from ethanol gave a sample of m.p. 232–234°.

ANAL. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.03; N, 10.07. Found: C, 73.57; H, 5.12; N, 9.68.

ACKNOWLEDGMENT

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