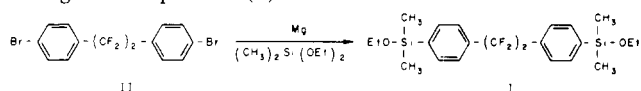


Synthesis

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):



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.

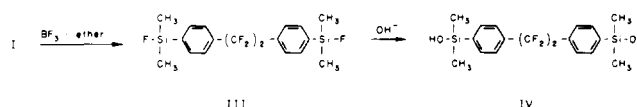


Table I. Preparation.

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. 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 nmoles); BF ₃ -etherate, 5.0 ml (40 nmoles).	Mixed at room temperature. The solid mass was dissolved in benzene and refluxed overnight.	100, crude
IV	III, 2.10 g.; ether, 100 ml. 40 ml of 1.5 <i>N</i> 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 ϕ , singlet	H ¹ , 2.42 (doublet, J, 8 cps, 4 protons) 2.53 (doublet, J, 8 cps, 4 protons) 6.35 (quartet, J, 7 cps, 4 protons) 8.84 (triplet, J, 7 cps, 6 protons) 9.65 (singlet, 12 protons)	...
Infrared	...	...	λ_{Nujol} 3.10 (SiOH), 11.5 (SiOH). No absorption at 10.55 (SiOC).

ACKNOWLEDGMENT

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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-dihydroisoquinaldamide (1). The structure was confirmed by reversion 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 distilla-

tion 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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