Phenenyl Silicon Compounds

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New phenenyl silicon compounds containing three organosilyl groups attached to each benzene nucleus, $1\text{-}R_1\text{-}2,4,6\text{-}(R_2R_3R_4Si)_3C_6H_2$, have been prepared by an *in situ* Grignard reaction between *sym*-tribromobenzene of *sym*-tribromoanisole and organomonochlorosilanes. Careful hydrolysis of *sym*-tris(dimethylsilyl)benzene yielded *sym*-tris(dimethylhydroxysilyl)benzene. Structures were confirmed by nuclear magnetic resonance spectroscopy.

THE *in situ* Grignard technique (*1–5*) for the preparation of new phenenyl silicon compounds has been extended, Equations 1 and 2. The addition of a concentrated solution of *sym*-tribromobenzene in tetrahydrofuran (THF) to a stirred mixture of magnesium and monochlorosilane in tetrahydrofuran results in an exothermic reaction yielding the desired *sym*-tris(substituted silyl)benzene in fair to good yield. *Sym*-tribromoanisole when similarly treated yields the corresponding anisole derivative.

$$sym\text{-}C_6H_3Br_3 + R_1R_2R_3SiCl + 3\ Mg \xrightarrow{THF} sym\text{-}(R_1R_2R_3Si)_3C_6H_3 + 3\ MgClBr \qquad (1)$$

$$1\text{-}CH_3O\text{-}2,4,6\text{-}Br_3C_6H_2 + R_1R_2R_3SiCl + 3\ Mg \xrightarrow{THF} 1\text{-}CH_3O\text{-}2,4,6\text{-}(R_1R_2R_3Si)_3C_6H_2 + 3\ MgClBr \qquad (2)$$

Table I lists the compounds prepared and their physical properties. The use of *sym*-trichlorobenzene or a mixture of *sym*-trichlorobenzene and *sym*-tribromobenzene in place of *sym*-tribromobenzene gave mixtures that were very difficult to separate and purify. The trifunctional Grignard reagent was difficult to prepare in good yield from *sym*-tribromobenzene, its preparation being accompanied by

Table I. Phenenyl Silicon Compounds

Compd. No.	R_1	R_2	R_3	Yield %	B.P.[a] °C.	B.P.[a] mm. Hg	n_D^{25}	d^{25} g./ml.	R_D Found	R_D Calcd. (*6, 7*)	% Si Found	% Si Calcd.	% C Found	% C Calcd.	% H Found	% H Calcd.
							sym-$(R_1R_2R_3Si)_3C_6H_3$									
I	H	Me	Me	47	102–102. 5	2.4	1.4980	0.8694	0.3372	0.3355	33.5	33.4	57.3	57.1	9.8	9.6
II	Me	Me	Me	53	80–81	0.4	1.4828	0.8613	0.3311	0.3322	28.5	28.6	61.6	61.1	10.4	10.3
III	Me	Me	Ph	24	166–168	0.6	1.5713	1.009	0.3258	0.3276	17.3	17.5	74.3	74.9	7.6	7.6
IV	HO	Me	Me	66	173–174[b]	...	...	...	...	...	27.8	28.0	47.5	48.0	7.8	8.1
							$1\text{-}CH_3O\text{-}2,4,6\text{-}(R_1R_2R_3Si)_3C_6H_2$									
V	H	Me	Me	48	114	2.0	1.5042	0.9163	0.3235	0.3226	29.7	29.8	55.6	55.3	9.6	9.3
VI	Me	Me	Me	40	130	4.6	1.4937	0.9067	0.3209	0.3213	26.0	26.0	59.3	59.2	9.9	9.9

[a] Uncorrected. [b] Melting point, uncorrected, of white crystals on Fisher–Johns apparatus.

Table II. NMR Spectral Data[a]

Compound Number	Absorption, Γ[b]	Proton Ratios[c] Found	Proton Ratios[c] Calcd.
I[d]	H_{ar}[e], 2.36[f]; H_{Si}, 5.55[g]; H_{MeSi}, 9.67[h]	2.94:3.00:18.00	3.00:3.00:18.0
II[d]	H_{ar}, 2.45[f]; H_{MeSi}, 9.73[f]	2.98:27.0	3.00:27.0
III[d]	H_{ar}, 2.36[f]; H_{PhSi}, 2.75[i]; H_{MeSi}, 9.50[f]	3.08:15.4:18.0	3.00:15.0:18.0
IV[j]	H_{ar}, 2.11[f]; H_{HOSi}, 5.10[k]; H_{MeSi}, 9.68[f]	2.98:2.88:18.0	3.00:3.00:18.0
V[d]	H_{ar}, 2.40[f]; H_{Si}, 5.50[l]; H_{OCH_3}, 6.22; H_{MeSi}, ~9.65[m]	2.06:3.08:3.06:18.0	2.00:3.00:3.00:18.0
VI[d]	H_{ar}, 2.47[f]; H_{OCH_3}, 6.30[f]; H_{MeSi}, 9.67, 9.75	1.97:2.94:18.1:8.9	2.00:3.00:18.0:9.00
sym-$C_6H_3Br_3$[n]	H_{ar}, 2.40[f]		

[a] Using Varian Associates A–60 NMR spectrometer employing tetramethylsilane as internal standard. [b] Γ (p.p.m.) defined as 10 – [Δ(Me_4Si)·10^6/oscillator frequency (c/s)]. [c] Ratios of integrated band areas. [d] ~15% in CCl_4. [e] Denotes absorption of equivalent protons on central aromatic ring. [f] Singlet. [g] Seven line multiplet. [h] Doublet. [i] Multiplet. [j] Saturated solution in acetone. [k] Slightly broadened singlet. [l] Overlapping with 6.22Γ band. [m] Two sets of overlapping doublets. [n] ~10% in CCl_4.

undersirable coupling and side reactions characteristic of difunctional Grignard formation. The triol, *sym*-tris(dimethylhydroxysilyl)benzene (IV), was prepared by careful hydrolysis of I, following the procedure of Merker and Scott, (*3*). Similar treatment of V failed to give the corresponding pure anisole derivative.

The NMR data, Table II, establish the presence of symmetrical substitution in all cases. A 1,2,3 or 1,2,4 type of substitution would give rise to nonequivalent aromatic protons with a subsequent increase in the number of peaks in the spectrum. The sharp aromatic singlet at low field together with the proton ratios unequivocally point to 1,3,5 substitution for the benzene derivatives and to 2,4,6 substitution for the anisole derivatives. Infrared spectral analyses were consistent with proposed structures and showed all compounds to be free of siloxane except for a small amount in IV.

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Isatoic Anhydride

Reactions with Isocyanates, Isothiocyanates, and Schiff's Bases

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The reactions of isatoic anhydride with nucleophiles have been extended to include additional amines, alcohols, and mercaptans which yield respectively substituted o-amino benzamides, benzoates and thiobenzoates. The reaction of isatoic anhydride with isocyanates, isothiocyanates and Schiff's base is reported as yielding 2,4-dioxo-; 2-thiono-4-oxo-; and 4-oxo-1,2,3,4-tetrahydroquinazolines. Forty seven compounds of new composition are characterized.

REACTIONS OF ISATOIC ANHYDRIDE with ammonia, primary and secondary amines, amides, primary and secondary alcohols, mercaptans, phenols and thiophenols, and conditions of the reactions have previously been studied (*1, 4*). The present investigators have extended the reactions of isatoic anhydride to include isocyanates, isothiocyanates, and a Schiff's base forming 2,4-dioxo-1,2,3,4-tetrahydroquinazolines; 2-thiono-4-oxo-1,2,3,4-tetrahydroquinazolines; and 4-oxo-1,2,3,4-tetrahydroquinazoline, respectively.

The reactions of isatoic anhydride with isocyanates and isothiocyanates are carried out under anhydrous conditions using dimethylformamide (DMF) as solvent and catalyst. Upon cooling, the 2,4-dioxo-1,2,3,4-tetrahydroquinazolines and 2-thiono-4-oxo-1,2,3,4-tetrahydroquinazolines separate as crystalline precipitates in yields of 30 to 60% (Figure 1).

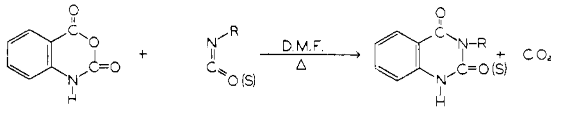

Figure 1. Reactions of isatoic anhydride with isocyanates and isothiocyanates

The nucleophilic nitrogen of the phenyl isocyanate attacks the number four carbon atom of isatoic anhydride, which is followed by loss of CO_2 and ring closure to the 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline. To establish the number three position as the point of substitution of the phenyl group, the 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline was formed by an alternate synthesis through the ψ-phenyl ureidobenzoic acid (*2*). The physical properties and infrared spectra of the products from the two syntheses were found to be identical (Figure 2).

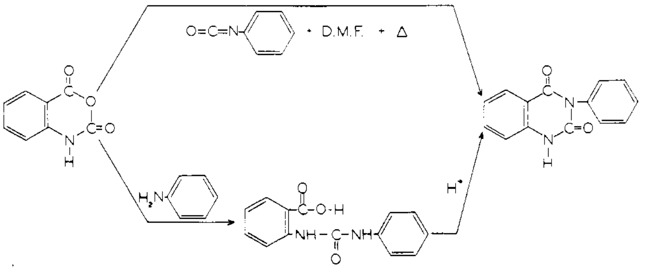

Figure 2. Synthesis of 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline