α-alanine (XXVI), 17 g. of *p*-toluenesulfonyl chloride and 170 ml. of 4% sodium hydroxide solution was shaken for 24 hr. The reddish-black solution was filtered and acidified with 10% hydrochloric acid. The gummy precipitate solidified when the mixture was heated on a steam-bath for 30 minutes and was filtered.

β-(2-Methyl-3,4-dimethoxyphenyl)-N-methyl-N-*p*-tosyl-α-alanine.—To a stirred solution of 19.6 g. of β-(2-methyl-3,4-dimethoxyphenyl)-N-*p*-tosyl-α-alanine in 100 ml. of 10% sodium hydroxide solution was added 20 ml. of dimethyl sulfate, at room temperature. After 10 minutes, the mixture was made alkaline by adding 10% sodium hydroxide solution, diluted with 2 l. of water and heated on a steam-bath until solution was complete. After treatment with Darco the solution was acidified with dilute hydrochloric acid. The gummy solid became crystalline after standing for several hours.

β-(2-Methyl-3,4-dihydroxyphenyl)-N-methyl-α-alanine (XXIV).—A mixture of 2 g. of β-(2-methyl-3,4-dimethoxyphenyl)-N-methyl-N-*p*-tosyl-α-alanine and 17 ml. of 57% hydriodic acid was heated under reflux for 4 hr. The dark brown reaction mixture was concentrated under reduced pressure, the residue suspended in 20 ml. of water and extracted continuously with ether for 5 days. The clear aqueous layer was separated and concentrated to dryness under reduced pressure. When the residue was dissolved in 4 ml. of water and adjusted to *p*H 5–6, colorless crystals appeared.

5-Methylveratric Acid.—5-Methylvanillin[25] was methylated with dimethyl sulfate and 10% sodium hydroxide solution, as described for an analogous case,[26] and the crude oily 5-methylveratraldehyde was oxidized with alkaline potassium permanganate solution under the conditions used in the oxidation of 2-methylveratryl chloride.[11] Recrystallization from 50% aqueous ethanol gave colorless needles, m.p. 146–148°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.87; H, 5.91.

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(25) J. Koetschet and P. Koetschet, *Helv. Chim. Acta*, **13**, 476 (1930).

(26) H. Decker and O. Koch, *Ber.*, **40**, 4794 (1907).

CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The $BF_3\cdot N_2O_3$ Complex. Its Use in Diazotization and Nitration[1]

BY G. BRYANT BACHMAN AND TAKEO HOKAMA

RECEIVED JANUARY 2, 1957

Boron trifluoride reacts with nitrogen trioxide to form a stable, white, solid complex, $BF_3\cdot N_2O_3$. Physical and chemical properties suggest that the structure is best represented as $(F_3B \leftarrow NO_2)^-(NO)^+$. The complex is a weak nitrating agent but a powerful diazotizing agent in the aromatic series.

It was reported recently that boron trifluoride forms a 1:1 addition complex with dinitrogen tetroxide[2] which is an excellent nitrating agent. It has now been found that boron trifluoride also forms a similar complex with dinitrogen trioxide. The combining ratio was determined gravimetrically to be 1:1. The complex is a white, stable solid, insoluble in all solvents with which it does not react, including alkanes, nitroalkanes and polychlorinated alkanes. It sublimes at room temperatures and does not melt in a sealed tube below 300°. Above this temperature, the very dark color of the dissociation products (especially NO_2) prevents observation of the remaining solid. These properties suggest that the complex is ionic in character and is formed as illustrated in equation 1 or 2

$$F_3B + ON\,\vdots{:}NO_2 \longrightarrow \underset{A}{(F_3B \leftarrow NO_2)^-(NO)^+} \qquad (1)$$

$$F_3B + O_2N\,\vdots{:}NO \longrightarrow \underset{B}{(F_3B \leftarrow NO)^-(NO_2)^+} \qquad (2)$$

That the preferred one of the above two formulations is A is probable on the basis of the chemical properties described below.

The $BF_3\cdot N_2O_3$ complex reacts rapidly with substances with which BF_3 and N_2O_3 react separately, including water, alcohols, ethers, ketones, carboxylic acids, amines and pyridine. However, under rather vigorous conditions it will introduce an NO_2 group into aromatic nuclei. If benzene is refluxed over the complex in a glass fiber thimble in a Soxhlet extractor for 42 hr., a 5–6% yield of nitrobenzene is obtained. Under the same conditions, toluene yields a red-black tar, but in the solvent nitroethane at 60–65° for 3 days, toluene gives a 56% yield of *o*-nitrotoluene. Other nitration results are shown in Table I. It will be noted that the complex produces a different ratio of isomers than is reported for nitric acid nitrations of toluene, 1-nitronaphthalene and chlorobenzene. This apparently is the result of its mild nitrating action since the isomer distribution obtained represents increased amounts of the principal isomer produced in nitric acid nitrations. Powerful reagents favor a more nearly statistical distribution of isomers in aromatic substitution.

The nitrating action of the complex suggests structure B but does not preclude structure A since it has been shown by Ingold[3] that primary attack by a nitrosonium ion is probably a factor in the nitration of *p*-nitrophenol and *p*-chloroanisole. Furthermore it has been shown that nitrogen trioxide produces nitrosonium cations in the presence of another strong acid, namely, sulfuric acid.[4,5] In addition there remains the possibility that oxidation by air occurs during the nitration and converts the nitroso product to a nitro product or converts the complex $BF_3\cdot N_2O_3$ to $BF_3\cdot N_2O_4$ a known nitrating agent.[2] To test this, naphthalene was nitrated at 25° in three different ways: under air, under nitrogen, and with oxygen bubbling through the mixture. The second of these produced a low yield (14%) of 1-nitronaphthalene and

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(1) From the M.S. Thesis of Takeo Hokama, Purdue University, January, 1956.

(2) G. B. Bachman, H. Feuer, B. R. Bluestein and C. M. Vogt, THIS JOURNAL, **77**, 6188 (1955).

(3) C. K. Ingold, C. A. Bunton, E. D. Hughes, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff and R. I. Reed, *J. Chem. Soc.*, 2628 (1950).

(4) C. K. Ingold and E. D. Hughes, *et al.*, *ibid.*, 2504 (1950).

(5) J. D. S. Goulden and D. J. Millen, *ibid.*, 2620 (1950).

TABLE I

NITRATIONS WITH $BF_3N_2O_3$

Substance	Products	Yields,[e] %	Time, hr.	Temp., °C.	Solvent
Benzene	Nitrobenzene	5	42	45	None
Toluene[a]	*o*-Nitrotoluene	56	72	60–65	Nitroethane
	p-Nitrotoluene	1			
	2,4-Dinitrotoluene	3			
o-Nitrotoluene[b]	2,4-Dinitrotoluene	40	12	85–90	Nitroethane
Naphthalene (air)	1-Nitronaphthalene	67	24	25	2-Nitropropane
Naphthalene (oxygen)	1-Nitronaphthalene	62	24	25	2-Nitropropane
	Dinitronaphthalene	13			
Naphthalene (nitrogen)	1-Nitronaphthalene	14	24	25	2-Nitropropane
1-Nitronaphthalene[c]	1,5-Dinitronaphthalene	14	24	60–70	Nitroethane
	1,8-Dinitronaphthalene	36			
Chlorobenzene[d]	2-Nitrochlorobenzene	12	24	85–95	Nitroethane
	4-Nitrochlorobenzene	50			
Cyclohexane	No reaction	..	4	*ca.* 80	Nitroethane

[a] An *ortho–para* ratio of 60:40 in the mononitration of toluene with mixed acids has been reported by A. F. Holleman, J. Vermeulen and W. J. deMooy, *Rec. trav. chim.*, **33**, 1 (1914). [b] In the nitration of *o*-nitrotoluene with mixed acids, a 91% yield of dinitrotoluene with a 66:34 ratio of 2,4- to 2,6-dinitrotoluene was obtained by W. H. Gibson, R. Deuckham and R. Fairbairns, *J. Chem. Soc.*, **121**, 270 (1922). [c] A 1:2 ratio of 1,5- and 1,8-dinitronaphthalene was obtained in the nitration of 1-nitronaphthalene with mixed acids by H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, 202 (1945). [d] An *ortho–para* ratio of 30:70 in the nearly quantitative mononitration of chlorobenzene by mixed acids was obtained by A. F. Holleman and B. R. deBruyn, *Rec. trav. chim.*, **19**, 189 (1900). [e] No attempt was made to determine isomer distributions by highly refined techniques, such as infrared analyses. The results are believed, however, to be accurate enough to indicate marked differences between the nitrating actions of the complex and nitric acid.

much tar. The first and third produced good yields of 1-nitronaphthalene (>60%). The oxygen experiment also gave a considerable amount (13%) of mixed dinitronaphthalenes. We conclude that the nitrating action of the complex is negligible in the absence of oxidizing agents such as air or pure oxygen, and that the structure B for the complex is therefore unlikely.

The $BF_3 \cdot N_2O_3$ complex is a powerful diazotizing agent in inert (non-aqueous) solvents and will convert weak aromatic amines such as 2,4-dinitroaniline into diazonium salts in a few minutes at room temperatures or below. The diazonium salts formed are generally insoluble in the reaction medium and may be isolated readily in a pure, stable form by filtration. If heated, these salts decompose to form fluoro derivatives of the starting aromatic nucleus (Schiemann reaction). Thus, fluorobenzene is prepared readily in 56% yield by diazotizing aniline with the complex in nitrobenzene and then raising the temperature gradually to about 85° when nitrogen is smoothly evolved and fluorobenzene distills.

Another reaction which can be accomplished satisfactorily in non-aqueous solvents is the Gomberg–Bachmann reaction.[6] Thus, if the diazotization is carried out in benzene solution and then sodium acetate is added, nitrogen is evolved and the corresponding biphenyl derivative is formed. The yields of 2,4-dinitrobiphenyl and 4-chlorobiphenyl by this method were better than those reported by Hey.[7]

Alternatively, the isolated diazonium salt may be coupled with phenols or otherwise treated in aqueous solution in the customary manner. Table II shows some of the results obtained with a series of aromatic amines, most of which were selected because of their weak basicity and corresponding troublesomeness in ordinary diazotization procedures. It will be noted that the results were uniformly excellent except for the tetrazotizations of the *p*-phenylenediamines. Apparently the complex is not effective in preventing coupling between the diazotized intermediates and the unreacted diamine.

A study of the nitrosating action of the complex was made with diethyl malonate at −40° in nitroethane. A 39% yield of diethyl oximinomalonate and a 28% yield of diethyl mesoxalate were obtained, results which are comparable to those resulting by the action of N_2O_3 alone on diethyl malonate.[8] Ethyl propionate did not react with the complex in 12 hr. at its reflux temperature.

An addition reaction was attempted with the complex and cyclohexene in chloroform of 0°. A thick dark oil was obtained which decomposed on attempted vacuum distillation. Steam distillation produced very little volatile material and a non-volatile tar. The isolation procedures[9] used successfully in working up the reaction products of cyclohexene and N_2O_4 failed to yield identifiable products in this case.

Conclusions.—The complex $BF_3 \cdot N_2O_3$ is prepared readily and serves as a useful reagent in mild nitrations of aromatic compounds. It produces the usual isomers in different ratios than are normally obtained with nitric acid and absorbs oxygen (from the air) in the process. The complex is a powerful nitrosating agent and is especially useful and convenient in diazotizing weakly basic aromatic amines in non-aqueous solvents and in preparing pure, dry, stabilized diazonium salts. Decomposition of these diazonium salts by heat leads to the corresponding fluoro compounds

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(6) M. Gomberg and W. E. Bachmann, THIS JOURNAL, **46**, 3339 (1924).

(7) D. H. Hey, J. W. Haworth and J. Elks, *J. Chem. Soc.*, 1284 (1940); D. H. Hey, H. France and I. M. Heilbron, *ibid.*, 369 (1940).

(8) V. Cerchez and R. Locquin, *Bull. soc. chim. France*, [4] **47**, 1279 (1930).

(9) H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

TABLE II

DIAZOTIZATION WITH $BF_3 \cdot N_2O_3$

Aromatic amine	Reactant	Product	M.p., °C.	Yield, % Present	Yield, % Lit.
Aniline	Heat	Fluorobenzene		56	Quant.[a]
	2-Naphthol	Azo dye	133–134	85	Quant.[b]
4-Chloroaniline	Benzene + Na acetate	4-Chlorobiphenyl	76–77	47	40[c]
4-Nitroaniline	Heat	4-Nitrofluorobenzene	26–27	43.5	50–60[d]
sym-Tribromoaniline	2-Naphthol	Azo dye	173–174	98	Quant.[e]
2,6-Dibromo-4-nitroaniline	2-Naphthol	Azo dye	222–223	98	Quant.[f]
2,4-Dinitroaniline	2-Naphthol, benzene +	Azo dye	305–306	98	Quant.[f]
	Na acetate	2,4-Dinitrobiphenyl	109–110	25	10[c]
2,4-Dinitro-1-naphthylamine	KI	Iodide	182–183	80	60–85[g]
Picramide	No reaction	. . .	. . . . .	. . .	Quant.[f]
2-Nitro-*p*-phenylenediamine	KI	Diiodide	108–110	Trace	. . . . .[f]
p-Phenylenediamine	KI	Diiodide	127–128	Trace	Quant.[f]

[a] G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927). [b] C. Liebermann, *ibid.*, **16**, 2860 (1883). [c] *Cf.* reference 7. [d] G. Schiemann and R. Pillarsky, *Ber.*, **62**, 3035 (1929). [e] K. J. P. Orton, *J. Chem. Soc.*, **83**, 808 (1903). [f] H. A. J. Schoutissen, THIS JOURNAL, **55**, 4531 (1933). [g] H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1620 (1933).

(Schiemann reaction). Isolation by filtration and reaction in aqueous media leads to the usual replacement reactions.

Experimental

Preparation of $BF_3 \cdot N_2O_3$.—Dry nitroethane (300 ml.) was placed in a 3-necked flask fitted with a stirrer, a reflux condenser having a calcium chloride drying tube at the top and a gas inlet tube extending below the surface of the liquid. The flask and contents were cooled to −20° with a Dry Ice–trichloroethylene bath and previously collected, dry, liquid nitrogen tetroxide,[2] 23 g. (0.5 mole), was added. Then dry nitric oxide gas was bubbled slowly into the solution while the bath temperature was lowered quickly to −70°. A low temperature is used to minimize the dissociation of N_2O_3 and to avoid the formation of $BF_3 \cdot 2NO_2$. Abel and Proisl[10] report that N_2O_3 is 90% dissociated at 25°, while Berl and Winnacker[11] report that it is not over 6% dissociated at −50°. Good cooling is essential since the complex formation is exothermic. When brown fumes began to be emitted from the condenser as a result of unabsorbed nitric oxide being oxidized to nitrogen dioxide by the air, the nitric oxide flow was stopped and a dry, gaseous, flow of boron trifluoride was started. This was continued until the blue color of the dinitrogen trioxide disappeared and white fumes of boron trifluoride appeared at the end of the condenser. The flask now contained a suspension of the white, solid complex in nitroethane. It could be used as such or the complex could be filtered off under anhydrous conditions, washed with an inert solvent and stored in stoppered bottles or suspended in another inert liquid medium.

In a series of five experiments, the combining mole ratios by weight of the reactants were determined in the absence of solvents. The results are shown in Table III. In order to be sure that the complex was not a mixture of the two complexes, $BF_3 \cdot 2NO$ and $BF_3 \cdot 2NO_2$, an attempt was made to form a complex between boron trifluoride and nitric oxide alone but without success. Furthermore no gas, including nitric oxide, was evolved during the addition of the boron trifluoride. Any evolution of nitric oxide would have led to the formation of $BF_3 \cdot 2NO_2$. Hence it may be concluded that the reactants combine in a 1:1 ratio and that the correct formula for the complex is $BF_3 \cdot N_2O_3$.

TABLE III

COMPOSITION OF THE COMPLEX BY COMBINING WEIGHTS

Expt.	Dinitrogen trioxide Gram	Dinitrogen trioxide Mmoles	Boron trifluoride Gram	Boron trifluoride Mmoles	Mole ratio N_2O_3/BF_3
1	0.3785	4.98	0.3302	4.87	1.02
2	.2567	3.37	.2306	3.40	0.99
3	.1837	2.42	.1650	2.43	0.99
4	.2014	2.68	.1803	2.66	0.99
5	.3432	4.51	.3016	4.51	1.00
Av.	.2727	3.59	.2415	3.57	1.00

Nitration Procedure.—The complex was prepared in one of the lower nitroalkanes, and the material to be nitrated was added in about an equimolar amount. The temperature of mixing was adjusted to the expected reactivity of the aromatic compound, being about 0° for a substance such as naphthalene and room temperature for a substance such as *o*-nitrotoluene. The reaction mixture was allowed to stand or, if reaction was slow, it was heated until the insoluble complex disappeared. Boron trifluoride and oxides of nitrogen were evolved during the reaction. Eventually, the mixture was cooled, poured into water, the organic layer separated, dried and distilled or steam distilled. In some cases (*e.g.*, dinitronaphthalene), the product separated as a solid during the reaction. In such cases the solid was filtered off, washed with water and recrystallized.

The isomeric ratio of dinitronaphthalenes (1,5- and 1,8-) formed was determined by the method of Hodgson and Walker.[12] The ratio for the nitrochlorobenzenes and the nitrotoluenes (*o*- and *p*-) was determined by separating the isomers in part by distillation and in part by recrystallization from alcohol.

Diazotization Procedure.—The aromatic amine was added with stirring to a suspension of a 10% molar excess of the complex in dry chloroform at 0–5°. After 30 minutes, 20 ml. of ether was added to destroy the excess complex. The precipitated diazonium salt was filtered off and used as such.

Thermal Decomposition of Diazonium Salts.—The diazonium salt of aniline was prepared as described above except that the solvent was nitrobenzene instead of chloroform. After diazotization was complete the temperature was raised until nitrogen evolution began and fluorobenzene distilled; yield 56%, b.p. 84–85°.

The diazonium salt of *p*-nitroaniline was prepared in chloroform, isolated by filtration and decomposed by heating in the absence of solvent. The yield of *p*-nitrofluorobenzene was 43%, m.p. 26–27°, b.p. 203–205°.

p-Nitroaniline was diazotized in dibutyl phthalate, and the diazonium salt was decomposed by heating. The *p*-nitrofluorobenzene distilled from the reaction mixture amounted to a 5% yield.

Coupling Procedure.—The isolated diazonium salt was added with stirring to a solution of 2-naphthol in 10% sodium hydroxide. The precipitated azo dye was filtered off, washed with water and dried and recrystallized.

Replacement Reactions. (a) ***In Aqueous Solvent.***—The isolated diazonium salt was added to a solution of potassium iodide in 50% phosphoric acid and allowed to stand overnight to obtain the corresponding iodide. (b) ***In Non-aqueous Solvents* (Gomberg–Bachmann Reaction).**—The diazonium salt was prepared in benzene, and 10% molar excess of sodium acetate and 2 ml. of acetic anhydride were added. The reaction mixture was heated with stirring until the evolution of nitrogen ceased and the benzene solution

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(10) E. Abel and J. Proisl, *Z. Elektrochem.*, **35**, 712 (1929).

(11) E. Berl and K. Winnacker, *Z. anorg. Chem.*, **212**, 123 (1933).

(12) H. H. Hodgson and T. Walker, *J. Chem. Soc.*, 1346 (1933).

was filtered. The solid obtained by removal of the benzene was purified according to the methods utilized in the literature references (*cf.* Table II).

Nitrosation Procedure.—Diethyl malonate, 55.0 g. (0.32 mole), was added dropwise at −40° to a suspension of 72.0 g. (0.45 mole) of complex in 300 ml. of nitroethane in a 500-ml. flask equipped with a dropping funnel, stirrer and reflux condenser. After 45 minutes the blue-colored mixture was allowed to warm to room temperature whereupon an exothermic reaction occurred which required cooling to maintain the temperature below 35°. When the reaction subsided, the mixture was washed with 5% sodium carbonate solution and water, dried and distilled. There were obtained: (a) diethyl mesoxalate, 11 g. (28%), b.p. 95–115° (18 mm.), hydrate m.p. 56°; (b) diethyl oximinomalonate, 25 g. (39%), b.p. 170–180° (18 mm.).

A 90% yield of diethyl mesoxalate was obtained by Curtiss[13] using gaseous N_2O_3 on diethyl malonate in the absence of solvent while Cerchez[6] reported a 50–90% yield of diethyl oximinomalonate using N_2O_3 and sodium ethoxide.

Dimethylaniline, 1.2 g., dissolved in 30 ml. of nitroethane, was added to a suspension of complex in nitroethane at 0–2°. The nitroethane was boiled off after washing with 5% sodium carbonate solution giving 1.5 g. of *p*-nitrosodimethylaniline, m.p. 84°.

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(13) R. S. Curtiss, *Am. Chem. J.*, **35**, 482 (1906).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Triphenylsilyl Phenyl Ketone

BY A. G. BROOK

RECEIVED APRIL 1, 1957

Triphenylsilyl phenyl ketone, the first reported α-silyl ketone, has been prepared. Although not susceptible to thermal rearrangement, it is readily decomposed by base to triphenylsilanol and benzaldehyde. It reacts abnormally with phenylmagnesium bromide and phenyllithium.

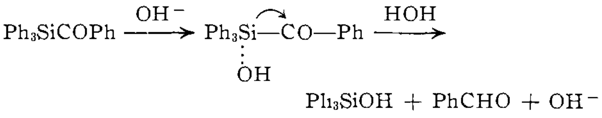
The abnormal behavior of substituents (especially halogen) attached to carbon alpha to a silicon atom has been referred to as the "α-silicon effect."[1,2] It is also apparent that functional groups located alpha to a silicon atom display unusual reactivity: the susceptibility of α-silanecarboxylic acids and their esters both to thermal rearrangement and to base-catalyzed decomposition have been reported recently from this Laboratory.[2] It seemed of interest to see whether this enhanced reactivity was present in other α-silylcarbonyl compounds, to which end the ketone, triphenylsilyl phenyl ketone, has been prepared. No α-silyl ketones have previously been reported in the literature, although indirect evidence for the formation of an α-silylaldehyde has been reported.[3]

Triphenylsilyl phenyl ketone was best prepared from triphenylbenzylsilane. Neither permanganate oxidation nor chromic acid oxidation yielded the desired compound, probably because of its instability, and only triphenylsilanol was isolated. Treatment with two equivalents of N-bromsuccinimide led to triphenylsilyl-α,α-dibromobenzylsilane. This compound was converted readily with silver acetate in an acetone–ethanol–water medium to the yellow ketone, m.p. 102–104°, in good yield. A phenylhydrazone derivative was prepared; attempts to prepare the oxime led to the formation of triphenylsilanol and benzaldehyde.

The ketone was also prepared, but in poor yield, by treatment of benzoyl chloride with an ethereal suspension of triphenylsilylpotassium: attempts to prepare it from triphenylsilane and benzoyl chloride using pyridine, aluminum chloride or boron fluoride as catalysts failed, and only tars or starting materials were isolated.

That the ketone is colored is of interest since organosilicon compounds are generally colorless, a fact generally attributed to the failure of silicon to participate significantly in resonance hybridization.[4] In the present case the color is even more unusual since the carbon analog, β-benzopinacolone, is colorless. The infrared spectrum of the ketone shows apparently normal absorption for the benzoyl group at about 1575 and 1610 cm.$^{-1}$.

The ketone does not rearrange thermally. When heated to 250°, it was recovered almost quantitatively, and when heated to 365°, although some decomposition occurred, no carbon monoxide was eliminated, and 70% of the material was recovered unchanged. However, the compound is extremely labile in basic medium. If a dilute ethanol solution is treated at room temperature with a few drops of aqueous alkali, the yellow color disappears in a few minutes and triphenylsilanol and benzaldehyde are formed. The same reaction occurs when the compound is chromatographed on activated alumina, although it may be recovered by elution from acid-washed alumina. This decomposition is evidently analogous to the base-catalyzed decomposition of triphenylsilanecarboxylic acid and its esters.



$$\mathrm{Ph_3SiCOPh} \xrightarrow{\mathrm{OH^-}} \mathrm{Ph_3}\underset{\underset{\mathrm{OH}}{\vdots}}{\mathrm{Si}}\text{—}\overset{\curvearrowright}{\mathrm{CO}}\text{—}\mathrm{Ph} \xrightarrow{\mathrm{HOH}} \mathrm{Ph_3SiOH} + \mathrm{PhCHO} + \mathrm{OH^-}$$

When triphenylsilyl phenyl ketone was treated with phenylmagnesium bromide, the expected product of addition to the carbonyl group, triphenylsilyldiphenylcarbinol, was not isolated. Instead, the only product isolated was tetraphenylsilane (5%), other than some recovered ketone and triphenylsilanol, presumably formed by decomposition of the ketone when the reaction mixture

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(1) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946).

(2) A. G. Brook and H. Gilman, *ibid.*, **77**, 2322, 4827 (1955); A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(3) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, *ibid.*, **76**, 1613 (1954).

(4) For a summary of pertinent evidence and references see H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).