The purple-colored filtrate decomposed and deposited a dark solid which was insouble in the carbon tetrachloride. The residue could be extracted with chloroform to yield more purple solution, which also decomposed in a few minutes.

It was found possible to add sufficient chlorine to a sample of nickel α-benzildioxime to dissolve it completely, but this solution was also unstable.

Hydrolysis of α-Benzildioximonickelic(III) Bromide.—Approximately 1 g. of α-benzildioximonickelic(III) bromide was stirred in 50 ml. of cold concentrated ammonium hydroxide. A maroon-colored compound formed which was somewhat soluble in the ammonia solution. The product was filtered, washed with distilled water, and dried in a desiccator.

The product decomposes slowly to give nickel α-benzildioxime. It is slightly soluble in dioxane but insoluble in water and in organic liquids such as benzene, carbon tetrachloride, diethyl ether, ethanol and acetone.

Action of Bromine on Other Nickel-oximes.—Besides α-benzildioxime and dimethylglyoxime, other nickel-oxime derivatives were treated with bromine in carbon tetrachloride solution. These include α-furildioxime, cyclohexanedionedioxime, glyoxalglyoxime, diacetylmonoöxime monophenylhydrazide and ethylenediamine-bis-diacetyldioxime. The last of these gave a stable bromide and the glyoxalglyoxime gave an unstable derivative. The other compounds were decomposed by the bromine.

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RECEIVED MAY 26, 1950

The *p*-Phenylphenacyl Ester of Phenylacetic Acid

BY EDWIN ERICKSON AND I. MOYER HUNSBERGER

Drake and Sweeney[1] reported 63° (dec.) as the melting point of the *p*-phenylphenacyl ester of phenylacetic acid. In the course of undergraduate instruction we recently had occasion to prepare this ester and found it to melt at 88.2–88.8° (cor.). Five preparations[2] showed the same melting point.

Experimental

***p*-Phenylphenacyl Phenylacetate.**—This compound was prepared by the standard method.[3] The light tan crude product was recrystallized three times from ethanol (once with charcoal). The pure white analytical sample melted 88.2–88.8° (cor.) to a completely colorless melt.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.43; H, 5.60.

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(1) N. L. Drake and J. P. Sweeney, THIS JOURNAL, **54**, 2059 (1932).

(2) Two of these were performed by Mitzi Wheeler and Donald Granger.

(3) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 185.

DEPARTMENT OF CHEMISTRY
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The Dissociation Constant of Hypobromous Acid

BY LADISLAS FARKAS AND MENACHEM LEWIN[1]

In studying the decomposition of hypohalite solutions, it is necessary to know the composition of these solutions which depend on the dissociation constants of the acids. Since there is some controversy over this constant in the literature, we have redetermined this constant for hypobromous acid. Shilow and Gladchikova[2] found by electrometric titration that K_{HOBr} at 20° $= 2.06 \times 10^{-9}$ and according to the same method, K_{HOCl} at 20° $= 3.16 \times 10^{-8}$. While the latter value is in good agreement with the results of other investigators[3,4] and is also close to the figure obtained by Skrabal and Berger[5] from the kinetics of the hypochlorite decomposition (*viz.*, 5.6×10^{-8} at 25°), the correctness of the above value of K_{HOBr} was questioned by Skrabal.[6] He calculated from data on the rate of decomposition of hypobromite depending upon the *p*H, the much lower value of 2×10^{-11} at 25°.

The following method was used for the determination of the dissociation constant of the hypobromous acid: To a hypochlorite solution, kept at a *p*H approximately equal to its *pK*, the equivalent amount of bromide was quickly added and the change of the *p*H was accurately measured by means of a glass electrode. Since, upon the addition of the bromide, all the hypochlorite was converted to hypobromite,[7] the observed Δ*p*H according to the Henderson–Hasselbach formula was in good approximation, equal to the Δ*pK* of hypochlorous and hypobromous acid.

In Table I, the results of a series of experiments are given. In these experiments, the solutions used were prepared by a method previously described.[8] The bromide was added to the hypochlorite solution while the electrodes were immersed in that solution. The final *p*H was established within a few seconds after the addition of the bromide[7,9] and remained constant for more than 15 minutes. The solutions were analyzed for hypochlorite before, and for hypobromite immediately after, the addition of the bromide according to the method already described[8]; no change in the oxidation capacity was found, the hypochlorite being quantitatively converted to hypobromite.

TABLE I

Expt. no	Total hypohalite moles/liter	Init. *p*H	Final *p*H	Δ*p*H
9	0.00344	7.21	8.46	1.25
12	.00344	7.46	8.72	1.26
1	.0172	7.54	8.80	1.26
5	.00344	7.57	8.83	1.26
6	.00344	7.73	9.00	1.27
2	.0172	8.09	9.32	1.23

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(1) Research Council of Israel, Hakirya, Israel.

(2) Shilow and Gladchikova, THIS JOURNAL, **60**, 490 (1938).

(3) J. W. Ingham and J. Morrison, *J. Chem. Soc.*, 1200 (1933).

(4) Hagisawa, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **19**, 1220 (1940).

(5) A. Skrabal and A. Berger, *Monatsh.*, **70**, 163 (1937).

(6) A. Skrabal, *Z. Elektrochem.*, **48**, 314 (1942).

(7) L. Farkas, M. Lewin and R. Bloch, THIS JOURNAL, **71**, 1988 (1949).

(8) L. Farkas and M. Lewin, *Anal. Chem.*, **19**, 662 (1947).

(9) In case the initial *p*H of the hypochlorite solution is below 7 or above 8.2, the observed Δ*p*H is smaller than the above figure.

From the ΔpH given in Table I and using $pK_{\mathrm{HOCl}} = 7.45$[3] at 19, we obtain for $pK_{\mathrm{HOBr}} = 8.70$ in excellent agreement with Shilow and Gladchikova.[2]

DEPARTMENT OF PHYSICAL CHEMISTRY
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The Preparation of Some Triarylaminosilanes

BY HENRY GILMAN, BURT HOFFERTH, H. W. MELVIN AND G. E. DUNN

In connection with some proposed cleavage studies, it was desired to prepare a series of triarylaminosilanes. In accordance with general procedures reported in the literature,[1] the reaction of triphenylchlorosilane with diethylamine in refluxing ether was attempted. Only a trace of unidentified material melting at 78–80° was obtained, the principal product being triphenylsilanol. When triphenylchlorosilane was refluxed with hydrazine, alone or in benzene, no nitrogen-containing product was obtained, and triphenylchlorosilane was recovered in 58% yield after recrystallization.

Results were not significantly better when alkali metal amides were substituted for the amines. With lithium or sodium di-*n*-butylamide and triphenylchlorosilane at 200° only 10% yields of the desired triphenyl-(di-*n*-butylamino)-silane were obtained. Lithium hydrazide in ether apparently gave a small yield of a nitrogen-containing silicon compound which hydrolyzed upon brief exposure to air. When triphenylchlorosilane and N-lithiocarbazole were refluxed in ether for twenty hours, or heated at 270–280° for four hours, starting materials were recovered to the extent of 91 and 86%, respectively.

$$(C_6H_5)_3SiCl + LiN(C_4H_9)_2 \longrightarrow (C_6H_5)_3SiN(C_4H_9)_2 + LiCl$$

Next was attempted the reaction of triphenylsilanol with amines. Di-*n*-butylamine at 165° converted triphenylsilanol to hexaphenyldisiloxane in 54–94% yields. Aniline and diethylamine failed to give any reaction at their respective boiling points; however, diethylamine in a sealed tube at 180–195° gave a 91% conversion to the disiloxane. A catalytic amount of di-*n*-butylamine in boiling xylene did not cause any condensation. It is of interest to point out here the anomalous behavior of tris-(*p*-dimethylaminophenyl)-silanol, which reacts in the desired manner with di-*n*-butylamine to give tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane almost quantitatively.

$$2(C_6H_5)_3SiOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + H_2O$$

$$[p\text{-}(CH_3)_2NC_6H_4]_3SiOH + HN(C_4H_9)_2 \longrightarrow [p\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9)_2 + H_2O$$

Since it is well known that hydrogen can be displaced from silicon by strongly basic reagents, reactions were attempted between triphenylsilane and some lithium amides. Good yields of dimethyl-, diethyl- and di-*n*-butyl-aminotriphenylsilanes were obtained from the corresponding lithium amides, but lithium hydrazide gave a nitrogen-containing material which hydrolyzed to triphenylsilanol and hexaphenyldisiloxane on attempted purification. When the lithium salts of carbazole, N-methylaniline, diphenylamine, and 2,5-dimethylpyrrole were employed, triphenylsilane was recovered to the extent of 60–90%. It may be noted that, with the exception of N-methylaniline, these unreactive lithium salts did not give Color Test IV.[2]

$$(C_6H_5)_3SiH + LiNR_2 \longrightarrow (C_6H_5)_3SiNR_2 + LiH$$

Experimental

Table I reports the yields, physical constants and analyses of the four triarylaminosilanes prepared in this study. All melting points are uncorrected. Representative preparations and the standard procedure used in this Laboratory for the analysis of non-volatile organometallic compounds for silicon are described below.

Silicon Analysis.—From 0.1 to 0.2 g. of sample is weighed accurately into a previously ignited 15-ml. platinum crucible with cover. About 1 ml. of pure concentrated sulfuric acid is added cautiously to the sample in the partially covered crucible. It is essential that the sample be thoroughly wetted by the sulfuric acid before heating is begun. This may be facilitated in stubborn cases by previously wetting the sample with glacial acetic acid, or by adding two or three drops of concentrated nitric acid to the sulfuric acid and sample in the crucible. The partially covered crucible is then placed in the platinum wire support of a Rogers ring burner. The supporting structure of the burner is lowered so that the flame impinges on the crucible above the level of the acid. The flame is adjusted, and the crucible support is raised at such a rate that sulfuric acid fumes are continuously evolved. When all the acid has been vaporized, the crucible is ignited to constant weight at dull red heat.[3] The percentage silicon is calculated using the factor 0.4672 for conversion of SiO_2 to Si.

Triphenyl-(di-*n*-butylamino)-silane from Triphenylchlorosilane and Lithium Di-*n*-butylamide.—A solution of phenyllithium in ether was added under dry nitrogen to an ether solution of 0.0463 mole of silicon tetrachloride in the usual way.[4] The mixture was refluxed for one-half hour and the salts were allowed to settle. The ether solution was added to 0.171 mole of lithium di-*n*-butylamide in about 30 ml. of di-*n*-butylamine. The ether was removed over a steam-bath and the residue was heated at 200° for an hour. After cooling the flask, dry benzene was added and refluxed for an hour. Salts were filtered off under nitrogen and the solvent was evaporated. Distillation of the residue under reduced pressure gave a red-brown product which, after being washed with petroleum ether (b. p. 60–70°), melted at 62° and weighed 1.8 g. (10%).

Triphenyl-(di-*n*-butylamino)-silane from Triphenylsilane and Lithium Di-*n*-butylamide.—To 0.034 mole of *n*-butyllithium[5] was added 5 g. (0.039 mole) of di-*n*-butyl-

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(1) Kraus and Rosen, THIS JOURNAL, **47**, 2739 (1925); Reynolds, Bigelow and Kraus, *ibid.*, **51**, 3067 (1929); Sauer and Hasek, *ibid.*, **68**, 241 (1946).

(2) Gilman and Woods, *ibid.*, **65**, 33 (1943).

(3) Ignition at too high a temperature may produce silicon carbide instead of silica: see McHard, Servais, and Clark, *Anal. Chem.*, **20**, 325 (1948).

(4) Gilman and Clark, THIS JOURNAL, **68**, 1675 (1946).

(5) Gilman, Beel, Brannen, Bullock, Dunn and Miller, *ibid.*, **71**, 1499 (1949).