

The perfluoroketone readily yielded a semicarbazone from a concentrated aqueous solution, which, on recrystallization from a benzene alcohol mixture and drying at 78° under reduced pressure, melted at 137–138° (dec.).

Anal. Calcd. for $C_8H_3N_3OF_8$: F, 55.6. Found: F, 55.6.

The C_4HOF_7 Fraction.—On redistillation this fraction yielded a small amount (1.5% of the total) of pure C_4HO-F_7 , b. p. 21°, mol. wt., 198 (see analysis above).

The $C_4H_2OF_6$ Fraction.—This portion on redistillation gave a considerable central cut (1.5% of the total), which was pure hexafluoromethyl ethyl ketone, $C_4H_2OF_6$ (mixture of isomers), b. p. 15° at 140 mm.

Anal. Calcd. for $C_4H_2OF_6$: F, 63.3; mol. wt., 180. Found: F, 63.5, 63.4; mol. wt., 179, 180.

The Second Transition.—This material contained a small amount of unstable product (1% of the total), b. p. 26° at 140 mm., mol. wt., 164, 162, which may have contained isomeric pentafluoromethyl ethyl ketones (calcd. mol. wt. 162).

The Direct Fluorination of Cyclopentanone.—This ketone was fluorinated as before at 0.05 mole (4.2 g.) per hr., saturator temperature 84°, reaction ratio 6:1:16, base temperature 127°, and equilibrium reaction temperature 178°. After processing in the usual way, the crude product in 5 hrs. of operation amounted to 28 cc., which was subsequently rectified. From this preliminary run, only one pure product could be isolated, which was perfluorocyclopentanone (1 cc.), a colorless liquid boiling at 24°.

Anal. Calcd. for C_5OF_8 : F, 66.6; mol. wt., 228. Found: F, 66.5, 66.8; mol. wt., 226, 228.

This perfluoroketone formed a semicarbazone which separated from water, and on recrystallization from a benzene-alcohol mixture, came down as white crystals of the monohydrate, m. p. 185–186° (dec.).

Anal. Calcd. for $C_6H_2N_3OF_8 \cdot H_2O$: F, 50.1. Found: F, 50.2, 50.3.

Summary

Acetone, methyl ethyl ketone and diethyl ketone have been fluorinated by cobaltic fluoride in a modified Fowler apparatus. The ketones were completely cleaved under the mildest conditions used, and it has been shown that acetone was split, in part at least, before any substitution had occurred.

In contrast, methylethyl ketone has been fluorinated by elementary fluorine, in a recently modified unit which is described in detail. Under these conditions the perfluoroketone $CF_3COCF_2CF_3$ was formed in significant yield, together with smaller amounts of the corresponding heptafluoro- and hexafluoroketones (isomeric mixtures), as well as a number of cleavage products, including CF_4 , C_2F_6 and CF_3COF .

The observed total cleavage by the milder reagent, and only partial fragmentation by the more vigorous reagent, has been attributed to the formation of transitional complex compounds between the ketones and the cobaltic fluoride, which would be expected to promote cleavage. Presumably such complexes would not be formed when elementary fluorine was used.

Certain related work has also been described, including the formation of perfluorocyclopentanone by the direct method, and the conversion of some fluoroethanes into one another in good yields by cobaltic fluoride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Substituted Naphthylsilanes

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Although a large number of alkyl- and aryl-silanes have been prepared, very few naphthylsilanes have been reported. The only compounds recorded in the literature are triethoxynaphthylsilanes and trichloro-1-naphthylsilane prepared, respectively, by the action of ethyl silicate and silicon tetrachloride upon the corresponding Grignard reagents.¹ Several di- and tri-naphthylsilanes have recently been prepared² in connection with a study of steric effects in silicon compounds.

We now wish to report the preparation and properties of several new naphthylsilanes which were needed for the synthesis of silicon-containing azo dyes.

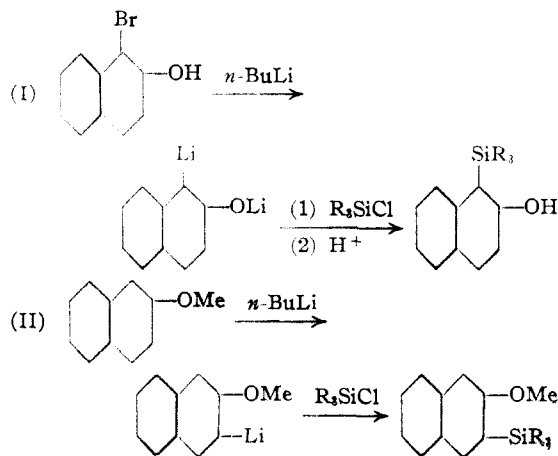
A convenient method for the preparation of organosilicon compounds is by the action of chlorosilanes upon organolithium compounds.³ Tri-

(1) Khotinsky and Seregenkoff, *Ber.*, **41**, 2952 (1908); Melzer, *ibid.*, **41**, 3394 (1908); Andrianov, *J. Gen. Chem. (U. S. S. R.)*, **16**, 487 (1946) [*C. A.*, **41**, 701 (1947)].

(2) Unpublished studies of Cecil G. Brannen.

(3) (a) Fleming, U. S. Patent 2,386,452 (1945) [*C. A.*, **40**, 603 (1946)]; (b) Gilman and Clark, *THIS JOURNAL*, **68**, 1675 (1946); (c) *ibid.*, **69**, 1499 (1947); (d) Tyler, Sommer and Whitmore, *ibid.*, **70**, 2876 (1948).

kylsilyl- and triarylsilyl-naphthols were compounds of choice for our work. Therefore, trimethyl- and triphenylchlorosilanes were used to react with the lithium compounds of naphthols and their methyl ethers. The lithium compounds of methoxynaphthalenes were prepared both by



direct metalation with *n*-butyllithium and by the halogen-metal interconversion reaction with their bromo derivatives. The latter reaction was employed exclusively with the hydroxy compounds. The metalation of 1- and 2-methoxynaphthalene gave 2-lithio-1-methoxynaphthalene and 3-lithio-2-methoxynaphthalene, respectively, because the acids obtained by carbonation and subsequent hydrolysis of the lithium compounds were 1-methoxy-2-naphthoic acid and 2-methoxy-3-naphthoic acid. Similarly, the identification of the acids obtained from the lithium compounds of naphthalene, prepared by the halogen-metal interconversion reactions, confirmed that the bromine-lithium interconversions involve no rearrangements.⁴

The silicon-containing naphthols did not give a color reaction with ferric chloride but could be converted to methyl ethers using dimethyl sulfate. Furthermore, the compounds coupled readily with the diazonium salts to give azo dyes.

In general, the preparation of hydroxynaphthylsilanes presents much more difficulty than the preparation of the methoxy compounds. The reaction of chlorosilanes with the lithium compounds of naphthols, therefore, had to be carried out with special precautions. After preliminary experiments, it was found that the best yields were obtained when the chlorosilanes were added gradually to the lithium compounds and the reaction mixtures were hydrolyzed when Color Test I⁵ was negative. The use of an excess of trimethylchlorosilane was also found to increase the over-all yield. Triphenylchlorosilane reacted much more slowly than trimethylchlorosilane and prolonged stirring at reflux temperature was frequently necessary to effect complete reaction. This was, perhaps, to be expected from steric considerations.^{3c,3d,6} Further evidence of the importance of steric effects is found in the relative reactivities of 1-lithio-2-hydroxynaphthalene, 4-lithio-1-hydroxynaphthalene and 6-lithio-2-hydroxynaphthalene⁷ toward chlorosilanes. The 6-lithio compound reacted smoothly with both silanes giving good yields of the expected products. The 1-isomer, in which steric hindrance to the reaction of trialkyl- and triarylchlorosilane is at a maximum, reacted promptly with trimethylchlorosilane but did not give the expected compound when reacting with triphenylchlorosilane. 2-Hydroxynaphthalene and triphenylsilanol were isolated from the reaction mixture when the reaction of triphenylchlorosilane with 1-lithio-2-hydroxynaphthalene was carried out at ether reflux temperature for twenty-four hours. Also, when the reaction was repeated under forced conditions in refluxing benzene for several hours, only gums

were obtained which gave, when distilled under reduced pressure, the same two compounds. That steric effects are not the only important considerations is demonstrated by the smooth reaction of 1-lithio-2-methoxynaphthalene with triphenylchlorosilane to give the desired silicon compound.

In the case of 4-lithio-1-hydroxynaphthalene, however, the results were quite unexpected. Following the addition of the lithium compound a reaction occurred, as evidenced by the formation of a white precipitate (probably of the lithium salt) and disappearance of types which give a positive Color Test I. However, subsequent to hydrolysis either with water, ammonium chloride solution, or a solution of ammonium hydroxide and ammonium acetate, the only compounds isolated were 1-naphthol, 4-bromo-1-hydroxynaphthalene and triphenylsilanol (when triphenylchlorosilane was used). It is possible that the silicon compounds are formed but the products are cleaved when the reaction mixtures are hydrolyzed. The susceptibility to hydrolytic cleavage of these compounds may be due to the activating influence of the hydroxyl group in the 1-position.

The preparation of methoxy-naphthylsilanes had a double purpose. First, the direct metalation of the 1- and 2-methoxynaphthalenes gave ortho lithio derivatives and facilitated the introduction of trialkyl- and triarylsilyl groups in 2- and 3-positions in the naphthalene ring. Second, the hydrolysis of the methoxynaphthylsilanes offered a possible route to the 2-trialkylsilyl- and triarylsilyl-1-naphthol and 3-trialkylsilyl- and triarylsilyl-2-naphthol which are not readily obtainable by the usual procedure because of the inaccessibility of the corresponding bromonaphthols.

However, the demethylation of 3-triphenylsilyl-2-methoxynaphthalene did not take place when this compound was refluxed with hydriodic acid (d. 1.5) for two hours, but when the refluxing was continued for six hours, 2-naphthol, along with a material, probably polymeric in nature, which did not melt up to 300°, was isolated. Similar results were obtained when the demethylation was carried out in glacial acetic acid. Apparently both the cleavage and the polymerization of the silane are caused by the action of hydriodic acid. Meads and Kipping⁸ have shown that the action of hydriodic acid on the silicon ethers also gives polymeric compounds.

Next, the action of acidic and alkaline cleaving agents on the silicon-containing naphthols was examined. 1-Trimethylsilyl-2-hydroxynaphthalene was cleaved readily when refluxed for a few hours with 20% hydrochloric acid and also when its acetone solution was refluxed with 20% aqueous potassium hydroxide. 6-Trimethylsilyl-2-hydroxynaphthalene, however, was cleaved by hy-

(4) The experimental details will be reported later.

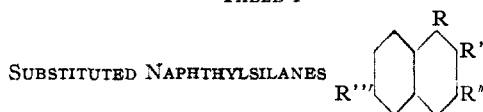
(5) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

(6) Whitmore and Sommer, *ibid.*, **68**, 481 (1946); Price, *ibid.*, **69**, 2600 (1947).

(7) Since the active hydrogens of the phenolic groups react first, the true products are the -OLi salts of the organolithium compounds.

(8) Meads and Kipping, *J. Chem. Soc.*, **105**, 679 (1914); **107**, 459 (1915).

TABLE I



No.	R	R'	R''	R'''	Method	Yield, %	M. p., ^a °C.	Formula	Calcd.	Silicon, % ^b Found
1	(CH ₃) ₃ Si	OH	H	H	I	53	^c	C ₁₃ H ₁₄ OSi	12.96	12.9 12.8
2	H	OH	H	(CH ₃) ₃ Si	I	48	107-108 ^d	C ₁₃ H ₁₆ OSi	12.96	12.7 12.85
3	H	OH	H	(C ₆ H ₅) ₃ Si	I	51	139-140	C ₂₉ H ₂₂ OSi	6.96	6.80 6.96
4	H	OCH ₃	H	(C ₆ H ₅) ₃ Si	I	24	168 ^e	C ₂₉ H ₂₄ OSi	6.73
5	H	OCH ₃	H	(CH ₃) ₃ Si	I	20	77-78 ^f	C ₁₄ H ₁₈ OSi	12.15	12.40
6	OCH ₃	(CH ₃) ₃ Si	H	H	II	18	^g	C ₁₄ H ₁₈ OSi	12.15	11.90
7	OCH ₃	(C ₆ H ₅) ₃ Si	H	H	II	10	176-177 ^h	C ₂₉ H ₂₄ OSi	6.73	6.60
8	(CH ₃) ₃ Si	OCH ₃	H	H	I	35	ⁱ	C ₁₄ H ₁₈ OSi	12.15	11.70
9	(C ₆ H ₅) ₃ Si	OCH ₃	H	H	I	15	165-166 ^j	C ₂₉ H ₂₄ OSi	6.73	6.77 6.75
10	H	OCH ₃	(CH ₃) ₃ Si	H	II	51	59 ^k	C ₁₄ H ₁₈ OSi	12.15	12.40
11	H	OCH ₃	(C ₆ H ₅) ₃ Si	H	II	40	131-132 ^{l,m}	C ₂₉ H ₂₄ OSi	6.73	6.83 6.85

^a All melting and boiling points are uncorrected. ^b Parr bomb and sulfuric acid methods were used for the silicon analysis in trimethyl- and triphenylsilyl derivatives, respectively. ^c B. p. 126-127° (0.5 mm.); d_{20}^{20} , 1.002; n_D^{20} , 1.5569; MR_D , 69.4 (calcd. MR_D , 68.9). ^d Crystallized from petroleum ether (b. p. 30-40°). ^e Alternatively this compound was prepared by methylating compound no. 3, dispersed in dilute potassium hydroxide solution, with dimethyl sulfate. The product was crystallized from ethanol; m. p. 168-169°, not depressed when mixed with the compound no. 4. *Anal.* Calcd. for C₂₉H₂₄OSi: Si, 6.73. Found: Si, 6.71. ^f Crystallized from methanol. Mixed m. p. with the product, obtained by methylating compound No. 2 with dimethyl sulfate, was 77-78°. ^g B. p. 99-100° (0.4 mm.); d_{20}^{20} , 1.034; n_D^{20} , 1.5802; MR_D , 74.0 (calcd. MR_D , 73.8). ^h Crystallized from acetone. ⁱ B. p. 108-109° (0.4 mm.); d_{20}^{20} , 1.030; n_D^{20} , 1.5850; MR_D , 74.7 (calcd. MR_D , 73.8). ^j Crystallization solvent was ethanol. ^k Crystallized from dilute ethanol. ^l Crystallized from petroleum ether (b. p. 90-100°). ^m Two grams of this compound was refluxed with hydriodic acid (d. 1.5) for six hours. The alkali soluble portion of the product, 0.2 g. (30%) was identified as 2-naphthol by mixed m. p.; the alkali insoluble compound did not melt up to 300°. *Anal.* Found: Si, 20.1.

drochloric acid, but was unaffected when treated with potassium hydroxide solution. Similarly, 6-triphenylsilyl-2-hydroxynaphthalene was unaffected by the alkaline cleaving agent, but it was cleaved when dry hydrogen chloride⁹ was passed into its solution in refluxing glacial acetic acid for twenty-four hours. 2-Naphthol, in addition to a polymeric product, was isolated from the acid solution.

Experimental

General Procedure.—*n*-Butyllithium in ether was added to the ether solutions of bromo derivatives of naphthols or of methoxynaphthalenes and the mixtures were stirred at room temperature for appropriate times.⁴ The solutions of the required amounts of the chlorosilanes in ether were added and the mixtures were refluxed with stirring until Color Test I was negative. The reaction mixtures were hydrolyzed with ammonium chloride solutions. The ether layers were separated and dried over anhydrous sodium sulfate. Ether was removed by distillation. The liquid compounds were purified by careful fractionation to remove the persistent impurity of naphthols or methoxynaphthalenes. In the case of triphenylsilyl derivatives, the residues obtained from ether were oils from which solid products separated when kept below a gentle stream of air for several hours. The metalation of the methoxynaphthalenes was carried out by refluxing their ethereal solutions with *n*-butyllithium for twenty-four hours. The yields and properties of the compounds are listed in Table I. The following are typical experiments.

1-Trimethylsilyl-2-hydroxynaphthalene (Method I).—To a solution of 16.7 g. (0.075 mole) of 1-bromo-2-naphthol in 75 ml. of ether was added a solution of 0.15 mole of *n*-butyllithium in 100 ml. of ether in a nitrogen atmosphere. The mixture was stirred at room temperature for one hour. To the resulting aryllithium compound was added drop-

wise a solution of 8.1 g. (0.075 mole) of trimethylchlorosilane in 50 ml. of ether and the mixture was refluxed for three hours. Since Color Test I was positive, 8.1 g. (0.075 mole) more of the silane was added and the mixture was refluxed for one and one-half hours. Subsequent to hydrolysis with ammonium chloride solution, the ether layer was separated and dried over anhydrous sodium sulfate. After removal of ether by distillation, the liquid was fractionated under reduced pressure.

6-Triphenylsilyl-2-hydroxynaphthalene.—To the organolithium compound prepared from 24.5 g. (0.11 mole) of 6-bromo-2-naphthol and (0.22 mole) of *n*-butyllithium was added a solution of 25 g. (0.085 mole) of triphenylchlorosilane in 100 ml. of ether. The mixture was stirred overnight at room temperature and then refluxed for one hour to complete the reaction. Subsequent to hydrolysis by water, the ether layer was separated, washed with dilute hydrochloric acid, then with water and dried. After the removal of ether by distillation, the oily product (36 g.) solidified slowly when kept below a gentle stream of air for several hours. It was extracted with petroleum ether (b. p. 30-40°), to remove the contaminating oils; and then dissolved in hot ethanol and reprecipitated by diluting with water and stirring the mixture vigorously. The crude product was crystallized from dilute ethanol. The yield was 15 g. (33%), m. p. 132-136°. After repeated crystallizations, the compound melted at 139-140° with decomposition. On acidifying the aqueous portion, 14 g. of the product was obtained. On crystallization from dilute ethanol, the product, 8 g. (18%), melted at 130-134°. Recrystallization from ethanol raised the melting point to 139-140°. The combined yield was 18 g. (51%).

2-Trimethylsilyl-1-methoxynaphthalene (Method II).—A solution of 0.075 mole of *n*-butyllithium in 90 ml. of ether was added to a solution of 11.8 g. (0.075 mole) of 1-methoxynaphthalene in 75 ml. of ether. The mixture was refluxed with stirring for twenty-four hours. After about ten hours, a copious precipitate separated and the color of the solution changed from brown-red to pink. A solution of 8 g. (0.074 mole) of trimethylchlorosilane in 50 ml. of ether was added and the mixture was refluxed for two hours. Subsequent to hydrolysis with water the ether layer was separated and dried. After the removal of

(9) Gilman and Marshall, *THIS JOURNAL*, **71**, 2066 (1949). See this paper for other references on the cleavage of organosilicon compounds.

ether, the liquid residue was fractionated to give 3 g. (17.4%) of 2-trimethylsilyl-1-methoxynaphthalene.

Cleavage of 1-Trimethylsilyl-2-hydroxynaphthalene (A) Acid Cleavage.—To 0.6 g. (0.0028 mole) of the silane was added 50 ml. of 20% hydrochloric acid and the mixture was refluxed for eight hours. It was then diluted with water and, after cooling, was extracted with ether. The residue from ether was crystallized from water, 0.4 g. (100%), m. p. 120–121°, which was not depressed when mixed with 2-naphthol.

(B) **Alkali Cleavage.**—A solution of 0.6 g. (0.0028 mole) of the silane in 25 ml. of acetone was added to 50 ml. of 20% aqueous solution of potassium hydroxide and the mixture was refluxed for twelve hours. Acetone was removed by distillation and the solution was acidified with dilute hydrochloric acid. The acidic mixture was extracted with ether. The residue from ether, 0.3 g. (75%), was identified as 2-naphthol by mixed m. p.

Cleavage of 6-Trimethylsilyl-2-hydroxynaphthalene (A).—Five-tenths gram (0.0023 mole) of the silane was added to 50 ml. of 20% hydrochloric acid and the mixture was refluxed for eight hours. It was diluted with water and the mixture was extracted with ether. The residue obtained from ether was extracted with 10 ml. of petroleum ether (b. p. 30–40°) to remove the starting material and the residue was crystallized from dilute methanol. The product, 0.25 g. (76%) melted at 120–121°, which was not depressed when mixed with 2-naphthol.

(B).—When the solution of 1 g. (0.0046 mole) of the silane in 25 ml. of acetone was refluxed with 20% aqueous potassium hydroxide for twelve hours, the silane was un-

affected and the starting material, 1 g., was recovered from the basic solution.

Cleavage of 6-Triphenylsilyl-2-hydroxynaphthalene (A).—Dry hydrogen chloride gas was passed into a stirred refluxing solution of 2 g. (0.005 mole) of the silane in 100 ml. of glacial acetic acid for twenty-four hours. The reaction mixture was diluted with 200 ml. of water and filtered. The filtrate was made basic with sodium bicarbonate solution and the resulting mixture was extracted with ether. Removal of ether left a viscous oil, which on crystallization from water gave a product, 0.4 g. (56%) of melting point 120–121°, which was not depressed when mixed with 2-naphthol. The residue, a sticky material, not melting up to 300°, was probably some polymeric compound.

Summary

Several hydroxy- and methoxy-naphthylsilanes have been prepared by the action of chlorosilanes on the corresponding naphthyllithium compounds.

An examination has been made of the cleavage of 1-trimethylsilyl-2-hydroxynaphthalene, 6-trimethylsilyl-2-hydroxynaphthalene, and 6-triphenylsilyl-2-hydroxynaphthalene by acids and by bases. An attempted demethylation of 3-triphenylsilyl-2-methoxynaphthalene by hydriodic acid gave 2-naphthol.

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Quinazolines. IX. A Study of an Unusual Reaction of 5-Diazoacetyl-1,3-dimethyl-2,4-quinazolinedione¹

By C. H. WANG, T. C. FENG AND BERT E. CHRISTENSEN

In the course of synthesizing certain amino alcohols with a quinazoline nucleus an unusual side reaction as observed, namely, the loss of a methyl substituent upon the conversion of 5-diazoacetyl-1,3-dimethyl-2,4-quinazolinedione to the corresponding bromomethyl ketone.² Oxidation of this ketone, followed by decarboxylation of the acid yielded supposedly 1-(or 3)-methyl-2,4-quinazolinedione, whose m. p. 198° does not agree with either the 3-methyl-2,4-quinazolinedione m. p. 234° reported by Abt³ and Bogert⁴ as resulting from cyclization and methylation experiments, respectively, or for the 1-methyl isomer m. p. 265° reported by Sentara Mayeda⁵ or 147° m. p. product reported by Abt,³ resulting from the cyclization of N-methylantranilamide.

The preparation of the 3-methyl-2,4-quinazolinedione by the method of Abt and the 1-methyl isomer by the method of Sentara Mayeda were confirmed in this Laboratory. However, repeated attempts to prepare the 1-methyl isomer

m. p. 147° using two procedures suggested by Abt were unsuccessful. Although this Laboratory obtained a crude cyclization product with a melting point of approximately 147°, this material was easily resolved on basis of acid solubility into two fractions, one melting at 265°, and the other the starting product. From this work it would appear that Abt's cyclization was only partially complete and his product largely starting material contaminated with the 1-methyl-2,4-quinazolinedione, m. p. 265°. This opinion finds additional support in the fact that the m. p. 147° is far out of line for compounds of this type.

In the search for an explanation of this puzzling question (the existence of what appears to be three compounds which are either 1- or 3-methyl substituted 2,4-quinazolinedione) attention turned to the 5-substituted carboxylic acid intermediate to determine if the same anomaly existed among the 1- and 3-methyl-2,4-quinazolinedione-5-carboxylic acids.

Both the 1-methyl-2,4-quinazolinedione-5-carboxylic acid, m. p. 320°, and the 3-methyl isomer, m. p. 332°, were synthesized in this Laboratory by methods which should leave little doubt as to the position of the methyl substituents. The 3-methyl-2,4-quinazolinedione-5-carboxylic acid

(1) The work described in this paper was made possible by a grant-in-aid from the Research Corporation. Published with the approval of the Monograph Publications Committee, Oregon State College, as a Research Paper, School of Science, Department of Chemistry.

(2) Wang and Christensen, *THIS JOURNAL*, **71**, 1440 (1949).

(3) Abt, *J. prakt. Chem.*, [2] **39**, 148 (1889).

(4) Bogert and Scatchard, *THIS JOURNAL*, **41**, 2062 (1919).

(5) Sentara Mayeda, *C. A.*, **11**, 578 (1916).