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Reaction of Triphenylsilyllithium with Halogenated Heterocycles

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The reaction of triphenylsilyllithium with halogenated heterocycles was investigated employing different heterocycles and varying the halogen, solvent, and time of reaction. The results indicate that the reaction of triphenylsilyllithium with Ar-X compounds varies appreciably with the nature of the halogen and solvent. The triphenylsilyl group was introduced into the various nuclear positions of 10-ethylphenothiazine. Several other new derivatives of 10-ethylphenothiazine were also synthesized.

The versatility of silylmetallics as a useful tool in the synthesis of silicon-containing compounds has been well established.[1] During a study on the reactivity of silylmetallics, it became of interest to investigate the reaction of triphenylsilyllithium with various halogenated heterocycles.

There have been several reported instances of reactions between silylmetallic compounds and organic halides. During the investigation of the properties of triphenylsilylpotassium, it was found that this silylmetallic reagent could be conveniently derivatized with bromobenzene to yield tetraphenylsilane.[2-4] It was demonstrated that the order of decreasing activity with various phenyl halides was: iodobenzene, bromobenzene, chlorobenzene, and fluorobenzene.[5] A different order of reactivity was obtained using triphenylsilyllithium with halobenzenes.[6]

The reaction of a silylmetallic reagent with an organic halide can take three courses: (1) primary coupling; (2) secondary coupling as a result of halogen-metal interconversions; and (3) dehydrohalogenation. The reaction between triphenylsilyllithium and an organic halide to give a tetrasubstituted silane is generally considered the

$$(C_6H_5)_3SiLi + RX \longrightarrow (C_6H_5)_3SiR + LiX$$

primary coupling reaction. This reaction has been extensively employed for the preparation of organopolysilanes.[7]

However, in the attempted preparation of triphenylmethyltriphenylsilane from the reaction of triphenylsilylpotassium and triphenylchloromethane, the only products realized were hexaphenyldisilane and hexaphenylethane.[8] It was suggested that triphenylsilylpotassium underwent a halogen-metal interconversion[9] with triphenylchloromethane to give triphenylchlorosilane and triphenylmethyl potassium. A secondary coupling reaction between the triphenylchlorosilane and triphenylsilylpotassium would yield the observed hexaphenyldisilane.

$$(C_6H_5)_3SiK + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3SiCl + (C_6H_5)_3CK$$
$$(C_6H_5)_3SiCl + (C_6H_5)_3SiK \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3$$

Other halogen-metal interconversion reactions have been reported in silylmetallic studies.[10-12] Halogen-metal interconversion was found to be a predominant reaction between triphenylsilyllithium and alkyl or aryl bromides.[13] For example, triphenylsilyllithium and *n*-butyl bromide gave a 60% yield of hexaphenyldisilane and a 10% yield of *n*-butyltriphenylsilane. A study of the reaction of triphenylsilyllithium with epichlorohydrin and epibromohydrin has given related results.[14]

The third possible reaction that has been observed is dehydrohalogenation. When triphenylsilyllithium reacted with *t*-butyl chloride, triphenylsilane was isolated in good yield; however, hexaphenyldisilane was the principal product of a reaction between triphenylsilyllithium and *t*-butyl bromide.[6]

The principal reaction which occurred when triphenylsilyllithium reacted with halogenated heterocycles was that of halogen-metal interconversion and, to a lesser extent, primary coupling. Triphenylsilyllithium underwent reaction with 3-bromo-9-ethylcarbazole in tetrahydrofuran to yield 57.7% of the secondary coupling product, hexa-

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[1] D. Wittenberg and H. Gilman, *Quart. Rev.* (*London*), **13**, 116 (1959).

[2] R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951).

[3] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951).

[4] R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 648 (1952).

[5] H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

[6] G. Dappen, unpublished studies.

[7] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *J. Am. Chem. Soc.*, **74**, 561 (1952)

[8] A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953).

[9] The halogen-metal interconversion reaction has been well-established in organic chemical systems. See R. G. Jones and H. Gilman in *Org. Reactions*, **6**, 339 (1951).

[10] A. G. Brook and S. Wolfe, *J. Am. Chem. Soc.*, **79**, 1431 (1957).

[11] D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

[12] H. Gilman and D. Miles, *J. Am. Chem. Soc.*, **80**, 611 (1958).

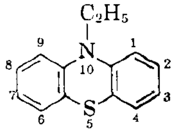
[13] H. Gilman and D. Aoki, *J. Org. Chem.*, **24**, 426 (1959).

[14] H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 1107 (1959).

phenyldisilane, and a 27.5% yield of the primary coupling product, 3-triphenylsilyl-9-ethylcarbazole. The use of ether as the solvent for the 3-bromo-9-ethylcarbazole altered the yields to 44.3% hexaphenyldisilane and 40.7% of the primary coupling product. Previously[15] 3-triphenylsilyl-9-ethylcarbazole was prepared by treating 3-bromo-9-ethylcarbazole with an ethereal suspension of triphenylsilylpotassium. Apparently the solvent exerted some influence on the extent to which halogen-metal interconversion occurs in reactions between silylmetallics and organic halides. Only trace quantities of hexaphenyldisilane were isolated from the reaction of triphenylsilylpotassium with bromobenzene in ether,[10] yet the same reaction employing triphenylsilyllithium in tetrahydrofuran gave hexaphenyldisilane as the principal product.[6]

2-Triphenylsilyldibenzofuran has been prepared by the reaction of either triphenylsilylpotassium with 2-bromodibenzofuran or by treating 2-lithiodibenzofuran with triphenylchlorosilane.[15] We have found that this coupling product can also be synthesized using triphenylsilyllithium with 2-chloro- or 2-bromodibenzofuran, the chloro compound affording a higher yield.

It was of interest in connection with other studies to investigate one particular heterocycle, namely, 10-ethylphenothiazine (A), and attempt to incorporate the triphenylsilyl grouping in as many different positions as possible. In order to prepare the requisite halogenated 10-ethylphenothiazine derivatives, it was necessary to synthesize several oxide and dioxide derivatives (see Experimental and Table II).



A

2-Triphenylsilyl-10-ethylphenothiazine and 10-(β-triphenylsilylethyl)phenothiazine were prepared by the reaction of triphenylsilyllithium with 2-chloro-10-ethylphenothiazine and 10-(β-chloroethyl)phenothiazine, respectively. An attempt to prepare 10-triphenylsilylphenothiazine by interaction of triphenylchlorosilane with 10-lithiophenothiazine was unsuccessful. Other workers have been unable to prepare certain silylamines if the nitrogen were attached to an aromatic system.[16] It is possible that the phenyl group withdraws electrons from the nitrogen-lithium salt, consequently decreasing its nucleophilic ability to the extent that reaction does not occur appreciably with the silicon-chlorine bond. However, the probability of steric factors must not be discounted since no silylamine was isolated by the treatment of dicyclohexylamine with triphenylsilyllithium.

Ranck[17] treated 3-bromo-10-ethylphenothiazine with triphenylsilyllithium in an attempt to synthesize the primary coupling product. 3-Triphenylsilyl-10-ethylphenothiazine has now been prepared by the reaction of triphenylsilyllithium with either 3-chloro- or 3-bromo-10-ethylphenothiazine; the chloro compound giving a slightly better yield of the primary coupling product. Treatment of 3-lithio-10-ethylphenothiazine, obtained *via* the halogen-metal interconversion of 3-bromo-10-ethylphenothiazine, with triphenylchlorosilane also afforded 3-triphenylsilyl-10-ethylphenothiazine. The melting point range of the latter compound was 184.5–186°, which is in fair agreement to that of the amorphous solid obtained by Ranck.[17]

4-Triphenylsilyl-10-ethylphenothiazine was obtained in a 14.8% yield by the interaction of triphenylsilyllithium with 4-iodo-10-ethylphenothiazine. This primary coupling reaction appeared to be the only route not previously attempted. Champaigne[18] had treated triphenylchlorosilane with 4-lithio-10-ethylphenothiazine and Ranck[17] carried out several modifications of the same reaction, yet neither was able to isolate any pure product. The reaction of the 4-iodo derivative with triphenylsilyllithium was run in mixed solvents to increase the formation of the primary coupling product.

The lower melting point of the 4-triphenylsilyl compound is in keeping with previous comparisons of the melting points of the various ring derivatives of phenothiazine. It has been found that the 1- and 4-substituted phenothiazine derivatives have low melting points while those of the 2- and 3-substituted derivatives are relatively high.[19] The 2-triphenylsilyl- and 3-triphenylsilyl-10-ethylphenothiazine compounds melted about 20° higher than the corresponding 4-triphenylsilyl derivative.

In order to prepare 3,7-bis(triphenylsilyl)-10-ethylphenothiazine, it was necessary to synthesize a 3,7 - dihalogenated - 10 - ethylphenothiazine derivative. 3-Bromo-10-ethylphenothiazine was converted to the sulfoxide, and this latter compound was reductively halogenated with aqueous hydrobromic acid to give crude 3,7-dibromo-10-ethylphenothiazine which as an oil, was oxidized to the corresponding sulfone. 3,7-Dichloro-10-ethylphenothiazine-5,5-dioxide was prepared in an analogous manner. The position that the second halogen took in the reductive halogenation step was not rigorously established, but it was believed to be the 7-position by analogy with the mechanism proposed for the formation of the monohalogenated deriva-

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(16) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(17) R. Ranck, Ph.D. Thesis, Iowa State University of Science and Technology, Ames, Iowa (1957).

(18) J. F. Champaigne, Jr., M.S. Thesis, Iowa State University of Science and Technology, Ames, Iowa (1952).

(19) S. P. Massie and P. K. Kadaba, *J. Org. Chem.*, **21**, 347 (1956).

TABLE I

REACTION OF TRIPHENYLSILYLLITHIUM WITH HALOGENATED 10-ETHYLPHENOTHIAZINE DERIVATIVES

Reactant: 10-Ethylphenothiazine Derivative	Mole	Solvent	Yield (%) $Ph_3SiSiPh_3$	Yield (%) Coupled Product	M.P.	Silicon	
						Calcd.	Found
2-Chloro-	0.018	Ether/THF	57.6	28.0	187–189°	5.78	5.55, 5.67
3-Chloro-	0.040	Ether/THF	53.8	27.8	184.5–186°	5.78	5.72, 5.76
4-Iodo-	0.0135	Ether/THF	46.3	14.8	166.5–168°	5.78	5.88, 5.98
β-Chloro-	0.040	Ether/THF	58.6	32.9	176–177°	5.78	5.72, 5.84
3,7-Dibromo-5,5-dioxide	0.0150	Ether/THF	64.2	19.0	271–276.5°	7.21	6.09, 6.14
3-Bromo-	0.040	Ether/THF	58.0	23.7	180–185°	..[a]	....
3,7-Dichloro-5,5-dioxide	0.02	Ether/THF	44.2	17.5	270–275°	..[a]	....

[a] Identified by the method of mixture melting points with an authentic sample.

TABLE II

REACTION OF TRIPHENYLSILYLLITHIUM WITH HALOGENATED 9-ETHYLCARBAZOLE AND DIBENZOFURAN DERIVATIVES

Reactant	Mole	Solvent	Yield (%) $Ph_3SiSiPh_3$	Yield (%) Coupling Product	M.P.	Recovery of Starting Material (%)
3-Bromo-9-ethylcarbazole	0.02	THF	57.7	27.5	213–216°	..
3-Bromo-9-ethylcarbazole	0.02	THF/ether	44.3	40.7	217–219°	..
2-Bromodibenzofuran	0.02	THF	53.8	..	......	45.4
2-Bromodibenzofuran	0.02	THF/ether	54.0	11.8	136–138°	30.2
2-Chlorodibenzofuran	0.02	THF	44.3	19.0	136–138°	30.0

tive.[20] This orientation into the 3- and 7- positions parallels that observed in formylation.[21] Reaction of either 3,7-dibromo- or 3,7-dichloro-10-ethylphenothazine-5,5-dioxide with two equivalents of triphenylsilyllithium yielded material with a wide melting range which could not be adequately purified but is thought to be 3,7-bis (triphenylsilyl)-10-ethylphenothiazine-5,5-dioxide.

A summary of the reactions of triphenylsilyllithium with halogenated 10-ethylphenothiazine derivatives is presented in Table I.

EXPERIMENTAL[22]

Reactions of triphenylsilyllithium with halogenated 9-ethylcarbazole and dibenzofuran derivatives. (*a*) *3-Triphenylsilyl-9-ethylcarbazole.* Triphenylsilyllithium,[23] prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane, was added slowly to a stirred solution of 5.48 g. (0.02 mole) of 3-bromo-9-ethylcarbazole[24] in 30 ml. of tetrahydrofuran (THF). The reaction was slightly exothermic and Color Test I[25] was negative shortly after complete addition. The mixture was hydrolyzed, filtered, and the residue washed carefully with ether to leave 3.0 g. (57.7%) of hexaphenyldisilane, m.p. 358–361° (mixture melting point).

The organic layer was separated, dried, and concentrated to yield a green oil. The oil was treated with 5 ml. of hot benzene and 20 ml. of ethanol to give 2.5 g. (27.5%) of 3-triphenylsilyl-9-ethylcarbazole,[15] m.p. 213–216°.

(*b*) *Reaction of triphenylsilyllithium with halogenated 9-ethylcarbazole and dibenzofuran derivatives.* Several other experiments were conducted in essential accordance with the above procedure making variations only in the halogenated heterocycle and the solvent. The results of these experiments are given in Table II.

Preparation of some 10-ethylphenothiazine derivatives. (*a*) *3-Bromo-10-ethylphenothiazine-5-oxide.* Thirty grams (0.098 mole) of 3-bromo-10-ethylphenothiazine[20] was dissolved in 660 ml. of refluxing absolute ethanol in a nitrogen atmosphere. To this solution was added 34 ml. of 30% hydrogen peroxide, and stirring was continued at reflux for 5 hr. Four hundred forty milliliters of the solvent was then removed by distillation and the remaining portion was poured into 1200 ml. of water which had been heated previously to 80°. Upon cooling, 29.8 g. (94.6%) of a greenish white solid melting at 124–127° crystallized. Two recrystallizations from ethanol (Norit) gave 25.7 g. (81.4%) of white 3-bromo-10-ethylphenothiazine-5-oxide, m.p. 126–127.5°. The infrared spectrum showed the characteristic sulfoxide absorption band.

Anal. Calcd. for $C_{14}H_{12}BrNOS$: S, 9.95. Found: S, 10.11, 10.23.

(*b*) *3-Bromo-10-ethylphenothiazine-5,5-dioxide.* Three grams (0.0098 mole) of 3-bromo-10-ethylphenothiazine was dissolved in 60 ml. of glacial acetic acid at 70°. To this solution was added 5 ml. of 30% hydrogen peroxide, and the resulting solution was heated for 2 hr. at 80°. Thirty milliliters of the solvent was then removed by distillation and, after the undistilled portion had cooled, 3.0 g. (90.4%) of a pink solid (m.p. 165–168°) separated. Recrystallization from an acetone-petroleum ether (b.p. 60–70°) mixture gave 2.3 g. (69.4%) of white 3-bromo-10-ethylphenothiazine-5,5-dioxide, m.p. 167.5–169°. The infrared spectrum showed an absorption band characteristic of the sulfone.

Anal. Calcd. for $C_{14}H_{12}BrNO_2S$: S, 9.48. Found: S, 9.41, 9.35.

(*c*) *Some 10-ethylphenothiazine-5,5-dioxides.* Several other 10-ethylphenothiazine-5,5-dioxide compounds were prepared from the corresponding sulfides essentially in accord-

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[20] H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

[21] N. P. Buu-Hoï and N. Hoán, *J. Chem. Soc.*, 1834 (1951).

[22] All melting points are uncorrected. Reactions involving silylmetallics were conducted in an oxygen-free, nitrogen atmosphere.

[23] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

[24] N. G. Buu-Hoï and R. Royer, *Rec. trav. chim.*, **66**, 533 (1947).

[25] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

TABLE III

10-ETHYLPHENOTHIAZINE-5,5-DIOXIDE COMPOUNDS FROM CORRESPONDING SULFIDES

Compound Oxidized	M.P. of Dioxide	Moles	30% H_2O_2, Ml.	Solvent (HOAc), Ml.	Yield, %	Sulfur Calcd.	Sulfur Found
3-Bromo-7-nitro-	201–202.5°[a]	0.10	30	200	98	8.36	8.23, 8.27
2-Chloro-	165–166.5°	0.0115	5	60	89	10.88	10.98, 10.78
3,7-Dibromo-	217–219°	0.040	15	80	73	7.68	7.71, 7.62
2,7-Dichloro-	213–215°	0.0325	10	60	52	9.78	9.72, 9.87
3,7-Dichloro-	203–204.5°	0.0096[b]	5	60	82	9.78	9.80, 9.79

[a] Also prepared in a 67.3% yield from 3-bromo-7-nitro-10-ethylphenothiazine-5-oxide. [b] Starting material was 3,7-dichloro-10-ethylphenothiazine-5-oxide.

ance with the above procedure. The results of these preparations are given in Table III.

(*d*) *2-Chloro-10-ethylphenothiazine.* Methyllithium was added over a 1-hr. period to an ethereal solution of 58.5 g. (0.25 mole) of 2-chlorophenothiazine[26] at ice-bath temperature until Color Test I[25] was positive. To the orange reaction mixture was added 43 g. (0.28 mole) of freshly distilled diethyl sulfate in 200 ml. of tetrahydrofuran. The ether was stripped off and the resulting solution gently refluxed overnight. The cooled solution was hydrolyzed, the water layer was washed with some ether and discarded. The combined organic layers were dried over sodium sulfate and the solvents removed by distillation to give 51.0 g. (78.2%) of crude 2-chloro-10-ethylphenothiazine, m.p. 116–118.5°. Recrystallization from ethanol raised the melting point to 119–120.5°. The infrared spectrum showed the absence of the N—H band.

Anal. Calcd. for $C_{14}H_{12}ClNS$: C, 64.30; H, 4.58. Found: C, 64.17, 64.07; H, 4.75, 4.71.

Preparation of 2-chloro-10-ethylphenothiazine *via* the "no-solvent" technique[27] was unsuccessful as only starting material was isolated.

An attempt to prepare a Grignard reagent of 2-chloro-10-ethylphenothiazine with magnesium turnings in refluxing tetrahydrofuran was not successful for subsequent carbonation of the reaction mass failed to yield any of the known 2-carboxy-10-ethylphenothiazine.[28]

(*e*) *2-Chloro-10-ethylphenothiazine-5-oxide.* Ten grams (0.0383 mole) of 2-chloro-10-ethylphenothiazine, dissolved in 250 ml. of refluxing absolute ethanol was oxidized with 13 ml. of 30% hydrogen peroxide in essential accordance with the procedure described previously. There was obtained 10.0 g. (94.3%) of a light pink solid melting at 169.5–171°. Recrystallization from methanol gave 9.0 g. (84.8%) of white 2-chloro-10-ethylphenothiazine-5-oxide, m.p. 170–171.5°. The infrared spectrum showed the characteristic sulfoxide absorption band.

Anal. Calcd. for $C_{14}H_{12}ClNOS$: S, 11.53. Found: S, 11.47, 11.47.

(*f*) *3-Bromo-7-nitro-10-ethylphenothiazine.* A mixture of 57.6 g. (0.2 mole) of 7-nitro-10-ethylphenothiazine-5-oxide, 100 ml. of water and 100 ml. of 48% hydrobromic acid (0.89 mole) was stirred at room temperature for 1 hr. and then at reflux for 1 hr. The dark red solid was collected and recrystallized from ethanol (Norit) to give 42.5 g. (60.6%) of red 3-bromo-7-nitro-10-ethylphenothiazine, m.p. 124.5–126°. The infrared spectrum showed the absence of the sulfoxide absorption band.

Anal. Calcd. for $C_{14}H_{11}BrN_2O_2S$: S, 9.12. Found: S, 8.97, 9.08.

(*g*) *3-Bromo-7-nitro-10-ethylphenothiazine-5-oxide.* Ten grams (0.0326 mole) of 3-bromo-10-ethylphenothiazine was dissolved in 250 ml. of glacial acetic acid; 10 ml. of concd. nitric acid in 40 ml. of acetic acid was added over a period of 30 min. The solution was allowed to stand for 2 days, then poured into water. The precipitated yellow solid was recrystallized from acetic acid to give 11.0 g. (91.6%) of bright yellow 3-bromo-7-nitro-10-ethylphenothiazine-5-oxide, m.p. 246.5–248°.

Anal. Calcd. for $C_{14}H_{11}BrN_2O_3S$: S, 8.73. Found: S, 8.62, 8.68.

(*h*) *3-Bromo-7-amino-10-ethylphenothiazine-5,5-dioxide.* A solution of 80 g. (0.42 mole) of anhydrous tin (II) chloride in 50 ml. of concd. hydrochloric acid was added slowly to a hot solution of 34.5 g. (0.09 mole) of 3-bromo-7-nitro-10-ethylphenothiazine-5,5-dioxide in 300 ml. of glacial acetic acid. The resulting yellow solution was stirred at 110–115° for 5 hr., at which time the yellow color had disappeared. The cooled mixture which contained a pale yellow precipitate, was made strongly basic with aqueous sodium hydroxide and filtered. Recrystallization of the crude material from chloroform gave 18.0 g. (57%) of 3-bromo-7-amino-10-ethylphenothiazine-5,5-dioxide, m.p. 230–231°. The absorption band characteristic of the nitro group was not present in the infrared spectrum.

Anal. Calcd. for $C_{14}H_{13}BrN_2O_2S$: S, 9.08. Found: S, 9.12, 9.16.

A solution of 1.0 g. (0.00283 mole) of 3-bromo-7-amino-10-ethylphenothiazine-5,5-dioxide in 20 ml. of benzene was treated with 1.0 g. (0.019 mole) of acetic anhydride and the solution refluxed for 2 hr. Cooling and filtering gave 0.7 g. (63%) of a white solid, m.p. 245–247°. Recrystallization from ethanol afforded 3-bromo-7-acetamino-10-ethylphenothiazine-5,5-dioxide, m.p. 246–247°.

Anal. Calcd. for $C_{16}H_{15}BrN_2O_3S$: S, 8.11. Found: S, 8.10, 7.88.

3,7-Dibromo-10-ethylphenothiazine-5,5-dioxide. (*a*) *By reductive bromination of 3-bromo-10-ethylphenothiazine-5-oxide followed by oxidation.* A mixture of 12.9 g. (0.04 mole) of 3-bromo-10-ethylphenothiazine-5-oxide, 17 ml. of water and 33 ml. of 48% hydrobromic acid was stirred at room temperature for 1 hr. and then at reflux for 1 hr. A viscous red oil remained. Extraction with ether, washing of the ether extracts with dilute sodium hydroxide, washing with water, drying and concentration gave a red gum. All attempts to crystallize this material were unsuccessful. The crude, impure 3,7-dibromo-10-ethylphenothiazine was converted to the corresponding sulfone in a 73% yield. The results of this experiment are listed in Table II. The pure, 3,7-dibromo-10-ethylphenothiazine-5,5-dioxide melted at 217–219°.

(*b*) *Diazotization of 3-bromo-7-amino-10-ethylphenothiazine-5,5-dioxide.* A solution of 4.0 g. (0.0113 mole) of 3-bromo-7-amino-10-ethylphenothiazine-5,5-dioxide in 5 ml. of glacial acetic acid, cooled to 18°, was diazotized with 0.2 mole of nitrosylsulfuric acid.[29] The resulting mixture was stirred for 0.5 hr. and then added at 0–5° to a hydrobromic acid solution of freshly prepared copper (I) bromide. The mixture was heated to 80°, diluted with water, and filtered.

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[26] Generously donated by Parke, Davis and Co., Detroit, Mich.

[27] H. Gilman and D. Shirley, *J. Am. Chem. Soc.*, **66**, 888 (1944).

[28] R. Baltzby, M. Harfenist, and F. J. Webb, *J. Am. Chem. Soc.*, **68**, 2673 (1946).

[29] K. H. Saunders, *The Aromatic Diazo Compounds*, Edward Arnold and Co., London, 1949, p. 13.

The crude material after chromatographic purification weighed 1.2 g. (25.5%), m.p. 208–215°. Two recrystallizations from acetic acid (Norit) gave 3,7-dibromo-10-ethylphenothiazine-5,5-dioxide, m.p. 215–218° [mixture melting point with the material described in part (a)].

(*c*) *3,7-Dichloro-10-ethylphenothiazine-5-oxide.* A mixture of 27.8 g. (0.1 mole) of 3-chloro-10-ethylphenothiazine,[30] 100 ml. of water, and 100 ml. of concd. hydrochloric acid was stirred at room temperature for 1 hr. and then at reflux for 1 hr. At the end of this time a viscous red oil remained and all attempts to induce crystallization were unsuccessful. The infrared spectrum of the oil indicated the absence of the sulfoxide grouping.

The oil was taken up in 150 ml. of absolute ethanol and to this solution was added 25 ml. of 30% hydrogen peroxide. The resulting solution was refluxed for 5 hr., then cooled to room temperature and filtered to give 23.4 g. (75%) of 3,7-dichloro-10-ethylphenothiazine-5-oxide, m.p. 183–187°. Two recrystallizations from ethanol (Norit) gave 15.5 g. (49.7%) of white needles, m.p. 187–188.5°. The infrared spectrum indicated the presence of the sulfoxide absorption band.

Anal. Calcd. for $C_{14}H_{11}Cl_2NOS$: S, 10.50. Found: S, 10.36, 10.38.

10-Triphenylsilylphenothiazine (*attempted*). 10-Lithiophenothiazine was prepared by the action of methyllithium on 17 g. (0.0858 mole) of phenothiazine suspended in 150 ml. of ether. Twenty-five grams (0.0858 mole) of triphenylchlorosilane in 200 ml. of ether was added, and the reaction mixture was stirred overnight at room temperature. After hydrolysis, chromatographic purification on alumina gave a 60% recovery of phenothiazine and a 50% yield of triphenylsilanol (mixture melting points). None of the desired 10-triphenylsilylphenothiazine was isolated.

N-Triphenylsilyldicyclohexylamine (*attempted*). Triphenylsilyllithium (0.04 mole) was added cautiously to 7.25 g. (0.04 mole) of dicyclohexylamine in 50 ml. of tetrahydrofuran. The reaction mixture was stirred at room temperature for 24 hr. The dark reaction mass was hydrolyzed with dilute ammonium hydroxide. A trace of solid, identified as impure hexaphenyldisilane, was obtained by filtration.

The light green organic layer was washed, dried with sodium sulfate, and concentrated to yield a green oil. Chromatography on alumina afforded on a 15% yield of triphenylsilane and a 31% yield of triphenylsilanol. None of the desired *N*-triphenylsilyldicyclohexylamine has been isolated.

In a second experiment, the green oil was distilled to give a 76.3% recovery of dicyclohexylamine.

1-Triphenylsilylphenothiazine (*attempted*). 1,10-Dilithiophenothiazine[31] was prepared by the reaction of two equivalents of *n*-butyllithium with 30.5 g. (0.151 mole) of phenothiazine suspended in 800 ml. of ether. To the above brown ethereal solution was added 89 g. (0.302 mole) of triphenylchlorosilane in 450 ml. of ether at such a rate as to maintain gentle reflux. After refluxing overnight, Color Test I[25] was slightly positive, and the light orange mixture was hydrolyzed. The layers were separated, the ether layer dried with sodium sulfate, and then concentrated to give a green-brown sticky solid. Chromatography on alumina gave 67% recovery of phenothiazine, a 70% yield of triphenylsilanol, and a 5% yield of hexaphenyldisiloxane, each identified by mixed melting points with authentic samples. None of the desired 1-triphenylsilylphenothiazine was obtained.

2-Triphenylsilyl-10-ethylphenothiazine. To a stirred suspension of 4.7 g. (0.018 mole) of 2-chloro-10-ethylphenothiazine in 30 ml. of ether was slowly added 100 ml. of a tetrahydrofuran solution of triphenylsilyllithium (0.018 mole). The reaction was slightly exothermic and Color Test I[25] was negative shortly after complete addition. The mixture was hydrolyzed, filtered, and the residue washed carefully with ether to leave 2.7 g. (57.6%) of hexaphenyldisilane, m.p. 358–360° (mixed melting point).

Work-up of the organic layer left a viscous brown residue. Boiling with a benzene-ethanol mixture gave 2.5 g. (28%) of brown 2-triphenylsilyl-10-ethylphenothiazine, m.p. 180–186°. Recrystallization from a benzene-ethanol mixture raised the melting range to 187–189°. The infrared spectrum showed the presence of the silicon-phenyl absorption band.

Anal. Calcd. for $C_{32}H_{27}NSSi$: Si, 5.78. Found: Si, 5.55, 5.67.

10-(β-Triphenylsilylethyl)phenothiazine. Triphenylsilyllithium (0.04 mole) was added slowly to a stirred solution of 10.47 g. (0.04 mole) of 10-(β-chloroethyl)phenothiazine[27] in 70 ml. of ether. After stirring at room temperature for 30 hr., Color Test I[25] was slightly positive. The mixture was hydrolyzed, filtered, and the residue washed carefully with ether leaving 6.1 g. (58.6%) of hexaphenyldisilane, m.p. 356–358° (mixed melting point).

Work-up of the organic layer left a viscous yellow oil. Boiling with ethanol and decanting gave 6.4 g. (32.9%) of 10-(β-triphenylsilylethyl)phenothiazine, m.p. 169–174°. Two recrystallizations from ethyl acetate raised the melting point to 176–177°. The infrared spectrum showed the presence of the silicon-phenyl absorption band.

Anal. Calcd. for $C_{32}H_{27}NSSi$: Si, 5.78. Found: Si, 5.72, 5.84.

3-Triphenylsilyl-10-ethylphenothiazine. To a stirred suspension of 10.47 g. (0.04 mole) of 3-chloro-10-ethylphenothiazine in 60 ml. of ether was added 0.04 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran. After stirring overnight, the color of the mixture was dark red. Some suspended white solid was noted in the reaction mass. Color Test I was negative and, subsequent to hydrolysis, 5.6 g. (53.8%) of hexaphenyldisilane, m.p. 360–363°, was separated by filtration.

The usual work-up of the organic layer left a brown oil which, subsequent to boiling with a benzene-ethanol mixture and chromatography of this mixture on alumina, gave 5.4 g. (27.8%) of crude 3-triphenylsilyl-10-ethylphenothiazine, m.p. 183–186°. A mixture melting point of this material with 3-triphenylsilyl-10-ethylphenothiazine, prepared by the reaction of triphenylchlorosilane with 3-lithio-10-ethylphenothiazine, was undepressed. Recrystallization from a 2:1 mixture of ethanol-benzene raised the melting point range to 184.5–186°. The infrared spectrum showed the presence of the silicon-phenyl absorption band in the molecule.

Anal. Calcd. for $C_{32}H_{27}NSSi$: Si, 5.78. Found: Si, 5.72, 5.76.

Reaction of triphenylsilyllithium with 3-bromo-10-ethylphenothiazine gave a 58.0% yield of hexaphenyldisilane and a 23.7% yield of coupled product, m.p. 180–185°.

Attempted oxidation of 3-triphenylsilyl-10-ethylphenothiazine to the corresponding sulfone by 30% hydrogen peroxide in glacial acetic acid failed to give any identifiable products.

3,7-Bis(triphenylsilyl)-10-ethylphenothiazine-5,5-dioxide. Triphenylsilyllithium (0.030 mole) was added to 6.25 g. (0.015 mole) of 3,7-dibromo-10-ethylphenothiazine-5,5-dioxide suspended in 60 ml. of ether. After stirring for 12 hr., Color Test I was weakly positive. Subsequent to hydrolysis, 5.0 g. (64.2%) of hexaphenyldisilane, m.p. 359–362°, was separated by filtration.

The tan organic layer was separated, dried, and the solvents were concentrated to give a viscous brown oil. Chromatographic purification on alumina using benzene as the eluent gave 2.2 g. (19%) of solid, melting over the range 235–250°. Recrystallization from benzene gave material melting at 271–276.5°; repeated recrystallizations of the compound failed to decrease the melting point range.

The infrared spectrum showed the silicon-phenyl, sulfone, and 1,2,4-trisubstitution absorption bands. The wide melting point range indicates an impure 3,7-bis(triphenylsilyl)-10-ethylphenothiazine-5,5-dioxide.

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[30] H. Gilman, R. K. Ingham, J. F. Champaigne, J. W. Diehl, and R. O. Ranck, *J. Org. Chem.*, **19**, 560 (1954).

[31] H. Gilman, D. Shirley, and P. R. Van Ess, *J. Am. Chem. Soc.*, **66**, 626 (1944).

Anal. Calcd. for $C_{50}H_{41}NO_2SSi_2$: Si, 7.21. Found: Si, 6.09, 6.14. An attempt to prepare this material by the reaction of triphenylchlorosilane with 3,7-dilithio-10-ethylphenothiazine-5,5-dioxide gave essentially the same results.

Reaction of triphenylsilyllithium with 3,7-dichloro 10-ethylphenothiazine-5,5-dioxide in ether gave a 44.2% yield of hexaphenyldisilane and 17.5% yield of coupled product, slightly impure, m.p. 270–275°.

4-Triphenylsilyl-10-ethylphenothiazine. Triphenylsilyllithium (0.0135 mole) was added cautiously to 5 g. (0.0135 mole) of 4-iodo-10-ethylphenothiazine[30] in 50 ml. of ether over a period of 1 hr. Color Test I was strongly positive after the addition was completed. After stirring for 24 hr., Color Test I was negative. Subsequent to hydrolysis, 1.8 g. (46.3%) of hexaphenyldisilane, m.p. 358–360°, was separated by filtration.

The yellow organic layer was separated, dried, and the solvents were removed to leave a viscous light yellow oil. Chromatographing on alumina of the yellow oil obtained subsequent to evaporation of the organic layer gave 2.3 g. (46%) of recovered starting material, identified by the method of mixture melting points; and 0.5 g. (14.8%) of 4-triphenylsilyl-10-ethylphenothiazine, m.p. 164–166°. Recrystallization from ethanol raised the melting point to 166.5–168°. The infrared spectrum showed the presence of the silicon-phenyl absorption band and 1,2,3-trisubstitution.

Anal. Calcd. for $C_{32}H_{27}NSSi$: Si, 5.78. Found: Si, 5.88, 5.98.

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Fluoroalkyl- and 3-(Fluoroalkoxy)propylpolysiloxanes

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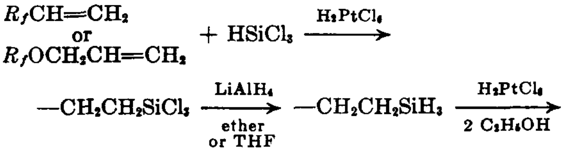
The synthesis of seven fluoroalkyl- and 3-(fluoroalkoxy)propylpolysiloxanes is reported. The intermediates obtained were also characterized. An attempt to synthesize β-cyanoethylpolysiloxane was not successful.

This paper describes a convenient laboratory method for the preparation of fluoroalkyl- and 3-(fluoroalkoxy)propylpolysiloxanes.

Fluoroalkylpolysiloxanes have been prepared previously by alternate routes. Holbrook[1] obtained small yields of 1H,1H,2H,2H-perfluoroalkyldichlorosilanes by heating 1H,1H,2H-perfluoro-1-alkenes with dichlorosilane in an autoclave at 250°. Extensive disproportionation of the dichlorosilane was observed. Hydrolysis of the fluoroalkyldichlorosilanes gave the corresponding fluoroalkylpolysiloxanes. Geyer *et al.*[2] reported the addition of 3,3,3-trifluoropropene to dichlorosilane using ultraviolet light to yield 3,3,3-trifluoropropyldichlorosilane which would give 3,3,3-trifluoropropylpolysiloxane on hydrolysis. The above addition was slow and gave only a moderate yield. Dichlorosilane is difficult to obtain and hard to handle in large quantities.

RESULTS AND DISCUSSION

The general synthetic method is given below:



$$\begin{matrix} R_fCH{=}CH_2 \\ \text{or} \\ R_fOCH_2CH{=}CH_2 \end{matrix} + HSiCl_3 \xrightarrow{H_2PtCl_6}$$

$$—CH_2CH_2SiCl_3 \xrightarrow[\text{ether or THF}]{LiAlH_4} —CH_2CH_2SiH_3 \xrightarrow[2\ C_2H_5OH]{H_2PtCl_6}$$

$$—CH_2CH_2Si(H)(OC_2H_5)_2 \xrightarrow{0.01N\ HCl} [—CH_2CH_2Si(H)O]_n \quad R_f = \text{fluoroalkyl}$$

The allyl αH,αH,ωH-perfluoroalkyl ethers and the allyl αH,αH-perfluoroalkyl ethers have not been previously reported. They were synthesized by three variations of the Williamson ether synthesis: (1) addition of the allyl halogenide to the sodium fluoroalkoxide in dimethyl carbitol followed by distillation of the allyl fluoroalkyl ether directly from the reaction mixture; (2) addition of the allyl halogenide to the sodium fluoroalkoxide in ether followed by hydrolysis; (3) refluxing a mixture of allyl bromide, the fluoro alcohol and anhydrous potassium carbonate in a ketone solvent followed by hydrolysis.

In general, the yields of the allyl fluoroalkyl ethers (21–67%) were lower than would be expected for two reasons. The boiling points of the starting alcohols and the ethers are very close, particularly in the first member of each series (allyl 2,2,2-trifluoroethyl ether and allyl 2,2,3,3-tetrafluoropropyl ether). To prepare these two ethers in a pure state, it was necessary to use Method 1 in which the unchanged alcohol remains in the flask as the sodium salt. With the long chain fluoro alcohols, preparation of the sodium salt was difficult and heating caused decomposition.[3,4]

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[1] G. W. Holbrook, private communication.

[2] A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 4472 (1957).

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[4] E. T. McBee, C. R. Roberts, and G. W. Wilson, Jr., *J. Am. Chem. Soc.*, 80, 1721 (1958).