1959

Some organometallic reactions with heterocyclic compounds

Justin Ward Diehl
Iowa State University

Recommended Citation

Diehl, Justin Ward, "Some organometallic reactions with heterocyclic compounds " (1959). *Retrospective Theses and Dissertations*. 2574.
https://lib.dr.iastate.edu/rtd/2574

SOME ORGANOMETALLIC REACTIONS WITH HETEROCYCLIC COMPOUNDS

by

Justin Ward Diehl

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1959

TABLE OF CONTENTS

I. INTRODUCTION

The advent of accelerated silylmetallic research began with the development of tetrahydrofuran as a solvent for the lithium cleavage of hexaphenyldisilane.[1] Tetrahydrofuran had been previously recognized for its catalytic effect in the cleavage of silicon-silicon bonds[2] and for its favorable influence exerted on various organometallic reactions.[3,4] Thus a silylmetallic in tetrahydrofuran is a powerful tool in the synthesis of new organosilicon compounds. Monomeric organosilicon compounds usually possess admirable thermal stabilities and therefore offer promise for use as high temperature lubricants or in related applications.

Despite the ample publications on certain aspects of organosilicon chemistry,[5,6,7] the first comprehensive review

---

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

[2] H. Gilman, R. K. Ingham and A. G. Smith, J. Org. Chem., 18, 1743 (1953).

[3] H. Gilman and B. J. Gaj, ibid., 22, 447 (1957).

[4] H. Gilman and T. S. Soddy, ibid., 22, 1121 (1957).

[5] H. W. Post. Silicones and other organic silicon compounds. New York, N.Y., Reinhold Publishing Corp. 1949.

[6] E. G. Rochow. An introduction to the chemistry of silicones. 2nd ed. New York, N.Y., John Wiley and Sons, Inc. 1951.

[7] P. D. George, M. Prober and J. R. Elliot, Chem. Revs., 56, 1065 (1956).

of organosilylmetallic compounds has just recently appeared.[8] As a continuation of the research in determining the scope of silylmetallic chemistry, this investigation pursues the reactivity of organosilylmetallics, specifically, triphenylsilyllithium, with heterocycles. Initially, thiaxanthene was selected for study because, in spite of the considerable work done, the chemical knowledge of this system is fragmentary. Later, another heterocycle, namely, phenothiazine, was investigated and the preparation of some of its silicon derivatives was undertaken.

The purpose of this investigation has been: (1) to collect, systematize and extend the knowledge of the syntheses and orientation in thiaxanthene and related compounds; (2) to compare the effect of the solvent and the halogen on the reactivity of triphenylsilyllithium with mono-halogenated heterocycles; (3) to prepare several halogenated derivatives of 10-ethylphenothiazine and study their reaction with triphenylsilyllithium in the hope that some of these coupled compounds might manifest favorable thermal stabilities; (4) to ascertain the possible utilization of silicon hydrides as selective reagents for hydrogenations and hydrogenolyses.

The historical section has been developed so as to

---

[8] D. Wittenberg and H. Gilman, Quart. Revs. (London), June (1959).

present information which will be pertinent to the investigation described in the later parts of this dissertation.

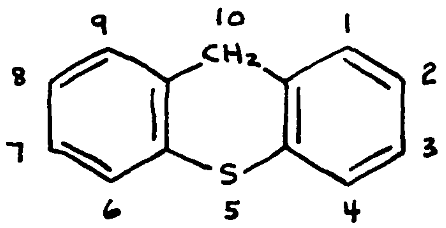
II. HISTORICAL

A. Thiaxanthene Chemistry

1. Introduction

Although thiaxanthene has been known for nearly seventy-five years there has been relatively little work reported during that period. Only one review on thiaxanthene and related compounds has appeared in the literature.[9]

Several names have been applied to the parent heterocyclic compound. Thiaxanthene is given as the preferred name by Patterson and Capell[10] and will be employed in this discussion. Other names often encountered in the literature are: thioxanthene; dibenzothiopyran; dibenzopenthiophene and diphenylenemethane sulfide. The preferred numbering of Patterson and Capell[10] as well as Chemical Abstracts is indicated in the following structural formula of thiaxanthene.



---

[9] D. S. Tarbell. Thiochromans and related compounds. In R. Elderfield, ed. Heterocyclic compounds. Vol. 2, pp. 533-550. New York, N.Y., John Wiley and Sons, Inc. 1951.

[10] A. M. Patterson and L. T. Capell. The ring index. No. 2019. New York, N.Y., Reinhold Publishing Corp. 1940.

There has been some interest in the preparation of complex thiaxanthene derivatives for anthelminthic drugs;[11] inhibitors for anterior pituitary secretions;[12] against bilharziasis[13] and as a chemotherapeutic agent for schistosomiasis.[14] Schönberg and Sidky[15] have recently synthesized a number of tetraarylethylenes in order to study thermochromism; several of these compounds were thiaxanthene derivatives. 10-Thiaxanthenol undergoes addition reactions with compounds which contain acidic hydrogens, for example, carbamates, mercaptans and β-diketone derivatives.[16] The diversity of the reactions in which the methylene group in thiaxanthene or the carbonyl group in 10-thiaxanthenone can participate prohibits a comprehensive review of the literature. Only the salient articles apropos to nuclear substitution in thiaxanthene and 10-thiaxanthenone will be presented here.

---

[11] W. P. Rogers, J. C. Craig and G. P. Warwick, <u>Brit. J. Pharmacol.</u>, <u>10</u>, 340 (1955).

[12] N. G. Buu-Hoï, E. Lescot, Jr. and N. D. Xuong, <u>J. Org. Chem.</u>, <u>22</u>, 1057 (1957).

[13] A. Mustafa, W. Asker and M. E. E. Sobhy, <u>J. Am. Chem. Soc.</u>, <u>77</u>, 5121 (1955).

[14] S. Archer and C. M. Suter, <u>ibid.</u>, <u>74</u>, 4296 (1952).

[15] A. Schönberg and M. M. Sidky, <u>ibid.</u>, <u>81</u>, 2259 (1959).

[16] E. Sawicki and V. T. Oliverio, <u>J. Org. Chem.</u>, <u>21</u>, 183 (1956).

2. Thiaxanthene

Graebe and Schulthess[17] originally synthesized thiaxanthene by the passage of phenyl *o*-tolyl sulfide through a hot tube. These workers then found that the reduction of 10-thiaxanthenone with hydrogen iodide and red phosphorus gave an improved yield of thiaxanthene.[17] A more convenient preparation of thiaxanthene is by the lithium aluminum hydride reduction of 10-thiaxanthenone.[18] Several other substituted 10-thiaxanthenone derivatives have been reduced to the corresponding thiaxanthenes using lithium aluminum hydride under forcing conditions.[19]

4-Nitro-2-(*p*-tolylthio)benzaldehyde dissolved in concentrated sulfuric acid gave equivalent quantities of the thiaxanthene and the 10-thiaxanthenone substitution products when treated with water.[20] Similar results were obtained with 5-nitro-2-(*p*-nitrothiophenoxy)benzaldehyde.[21]

The susceptibility of the 10-position to attack prevents

---

[17] C. Graebe and O. Schulthess, *Ann.*, *263*, 1 (1891).

[18] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1343 (1952).

[19] A. Mustafa and O. H. Hishmat, *J. Org. Chem.*, *22*, 1644 (1957).

[20] C. V. T. Campbell, A. Dick, J. Ferguson and J. D. Loudon, *J. Chem. Soc.*, 747 (1941).

[21] E. Amstutz and C. Neumoyer, *J. Am. Chem. Soc.*, *69*, 1925 (1947).

the ring from being substituted by the normal procedures. Metalation occurs readily with *n*-butyllithium in the 10-position; the lithium derivative can be carbonated to give the 10-acid, or coupled with alkyl halides.[22,23]

The conversion of the sulfur atom to the corresponding sulfoxide or sulfone can be accomplished rather easily. Oxidation of thiaxanthene with hydrogen peroxide in acetic anhydride gave thiaxanthene-5-oxide.[24] Poorer yields of the sulfoxide were obtained utilizing potassium permanganate as the oxidizing agent. Oxidation of thiaxanthene with hydrogen peroxide using glacial acetic acid as the solvent gave thiaxanthene-5,5-dioxide.[24] This sulfone had previously been obtained by the reaction of diphenylmethane with chlorosulfonic acid.[25] A recent paper reported the preparation of several substituted thiaxanthene-5,5-dioxides by this sulfonation procedure and indicated that these sulfones may have some potential applications as indicators.[26]

---

[22] R. R. Burtner and J. W. Cusic, *ibid.*, *65*, 1582 (1943).

[23] J. W. Cusic, U. S. Patent 2,368,006. January 23, 1945. (Original not available for examination; abstracted in *C. A.*, *39*, 3630 (1945)).

[24] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, *99*, 145 (1911).

[25] A. Lapworth, *ibid.*, *73*, 402 (1898).

[26] U. S. Etlis and G. A. Razuvaev, *J. Gen. Chem.*, *U.S.S.R.* (*Eng. transl.*), *27*, 3132 (1958).

Reaction of thiaxanthene-5-oxide with alcoholic hydrochloric acid produced 10-chlorothiaxanthene which was very unstable and by mild treatment with dilute alkali gave 10-thiaxanthenol.[24] Several other experiments were conducted which thoroughly demonstrated the sensitivity of thiaxanthene-5-oxide to heat and acidic reagents.

3. 10-Thiaxanthenol

10-Thiaxanthenol was originally synthesized by the reduction of 10-thiaxanthenone with zinc dust and alcoholic sodium hydroxide.[27] Other workers employed alcoholic potassium hydroxide with zinc dust as the reducing agent.[28,29] 10-Thiaxanthenol was found to be extremely unstable and susceptible to air oxidation, consequently erratic results were often reported.[24] A recent improvement in the synthesis was found to give high yields of good quality 10-thiaxanthenol.[30] This convenient method utilizes sodium amalgam in alcohol to reduce 10-thiaxanthenone.

Reaction of phenylmagnesium bromide with 10-thiaxanthe-

---

[27] A. Werner, Ber., 34, 3300 (1901).

[28] F. Mayer, ibid., 34, 1132 (1909).

[29] C. Finzi, Gazz. Chim. Ital., 62, 211 (1932). (Original available but not translated; abstracted in C. A., 26, 4339 (1932)).

[30] H. F. Oehlschlaeger and I. R. MacGregor, J. Am. Chem. Soc., 72, 5332 (1950).

none gives 10-phenyl-10-thiaxanthenol in high yield.[31,32] Gomberg and co-workers studied the 10-thiaxanthyl group and found that it exhibited considerable stability either as a radical or as a carbonium ion. They concluded that the 10-thiaxanthyl group resembled the triphenylmethyl and the 9-xanthyl groups in its reactions.[33,34] Some substituted 10-arylthiaxanthydrols have also been prepared.[32]

4. 10-Thiaxanthenone

The most feasible method for the synthesis of 10-thiaxanthenones was developed by Smiles and co-workers; they found that either *o*-mercaptobenzoic acid or 2,2'-dithiosalicyclic acid condensed with aromatic hydrocarbons in sulfuric acid to yield 10-thiaxanthenone derivatives.[35,36,37,38] The prepara-

---

[31] H. Bünzly and H. Decker, *Ber.*, *37*, 2931 (1904).

[32] M. Gomberg and L. H. Cone, *Ann.*, *376*, 183 (1910).

[33] M. Gomberg and W. Minnis, *J. Am. Chem. Soc.*, *43*, 1940 (1921).

[34] M. Gomberg and E. C. Britton, *ibid.*, *43*, 1945 (1921).

[35] E. Marsden and S. Smiles, *J. Chem. Soc.*, *99*, 1353 (1911).

[36] E. G. Davis and S. Smiles, *ibid.*, *97*, 1290 (1910).

[37] W. Prescott and S. Smiles, *ibid.*, *99*, 640 (1911).

[38] H. Christopher and S. Smiles, *ibid.*, *99*, 2046 (1911).

tion using 2,2'-dithiosalicyclic acid generally gives poorer yields.[37]

10-Thiaxanthenone was originally described by Ziegler[39] who ring closed 2-carboxydiphenyl sulfide in concentrated sulfuric acid. The preparation of nuclear substituted 10-thiaxanthenones by cylization of the appropriate 2-carboxydiphenyl sulfide or the corresponding sulfones has been reported.[21,40,41] The application of the ring closure method is severely limited by the availability of the requisite diphenyl sulfides or sulfones. Thus, condensation of o-mercaptobenzoic acid with substituted aromatic hydrocarbons remains about the best procedure for preparing 10-thiaxanthenone derivatives containing nuclear substituents. For example, reaction of anisole with o-mercaptobenzoic acid gave an 80% yield of methoxy-10-thiaxanthenone.[36] The position of the methoxy group was subsequently shown to be the 2-position by the cyclization of 2'-carboxy-4-methoxydiphenyl sulfide and also by the methylation of 2-hydroxy-10-thiaxanthenone.[42,43]

---

[39] J. H. Ziegler, Ber., 23, 2469 (1898).

[40] F. Ullmann and A. Lehner, ibid., 38, 740 (1905).

[41] W. Truce and O. Norman, J. Am. Chem. Soc., 75, 6023 (1953).

[42] W. B. Price and S. Smiles, J. Chem. Soc., 3154 (1928).

[43] K. C. Roberts and S. Smiles, ibid., 863 (1929).

Two possible mechanisms for the cyclization of o-mercaptobenzoic acid with benzene and its congeners have been postulated.[14,37] These will be discussed in some detail later on in this dissertation.

Direct nitration and sulfonation of 10-thiaxanthenone has been reported to yield mixtures of mono- and di- substitution products.[44] For example, nitration gave the following products; 2-nitro-, 2,8-dinitro-10-thiaxanthenone and the corresponding sulfones. All of the mono-nitrated 10-thiaxanthenones had been prepared previously by cyclization reactions.[45]

The carbonyl group in 10-thiaxanthenone does not readily participate in all the normal carbonyl addition reactions. The oxime of 10-thiaxanthenone-5,5-dioxide has been found to undergo a Beckmann rearrangement to give the lactam of 2-(2'-aminobenzenesulfonyl)benzoic acid.[46] 10-Thiaxanthenione was prepared either by the action of phosphorus pentasulfide on 10-thiaxanthenone[47] or by phosphorus pentachloride

---

[44] T. Kurihara and H. Niwa, J. Pharm. Soc. (Japan), 73, 1378 (1953). (Original available but not translated; abstracted in C. A., 49, 313 (1955)).

[45] F. Mayer, Ber., 42, 3046 (1909).

[46] W. E. Truce and J. A. Simms, J. Org. Chem., 22, 617 (1957).

[47] R. Meyer and J. Szanecki, Ber., 33, 2577 (1900).

and thioacetic acid.[48] This 10-thiaxanthenione could then react with hydrazine to give the hydrazone.[49] 10-Thiaxanthenone did not undergo the Schmidt reaction with sodium azide.[50]

The inability to react with carbonyl reagents might be attributable to the large dipole moment of 10-thiaxanthenone.[51] This possibility of significant contributions to the structure of 10-thiaxanthenone by zwitterion forms is supported by infrared data.[50,52] The ultraviolet spectrum of 10-thiaxanthenone has been reported.[53]

10-Thiaxanthenone-5-oxide has not yet been reported but 10-thiaxanthenone-5,5-dioxide has been prepared by several workers. The most convenient method for the synthesis of this sulfone is to oxidize 10-thiaxanthenone with hydrogen peroxide in acetic acid.[46,54] Treatment of benzophenone with sulfuric acid gave 10-thiaxanthenone-5,5-dioxide;[55,56] however, it was

---

[48] A. Schönberg, O. Schütz and S. Nickel, ibid., 61, 1375 (1928).

[49] A. Schönberg and T. Stolpp, ibid., 63, 3102 (1930).

[50] M. Coombs, J. Chem. Soc., 4200 (1958).

[51] A. Weizmann, Trans. Faraday Soc., 36, 978 (1940).

[52] E. R. H. Jones and F. G. Mann, J. Chem. Soc., 294 (1958).

[53] S. Kruger and F. G. Mann, ibid., 2755 (1955).

[54] F. Ullmann and O. von Glenck, Ber., 49, 2509 (1916).

[55] J. Beckmann, ibid., 6, 1112 (1873).

[56] J. Beckmann, ibid., 8, 992 (1875).

several years before the structure of the product was established.[17]

B. Reactions of Organosilylmetallic Reagents

1. With carbonyls

The interaction of organosilyllithium compounds with aliphatic ketones proceeds in a normal manner to give the corresponding α-silylcarbinols.[57] Triphenylsilyllithium added normally to acetone, cyclohexanone, 2-nonadecanone, 3-octadecanone, 8-pentadecanone and 12-tricosanone.[57] An important side-reaction was the abstraction of the acidic hydrogen from the ketone to give the silicon hydride corresponding to the silyllithium compound.[57] Other examples of this enolization have been reported.[58]

Triphenylsilylpotassium reacted with formaldehyde to yield triphenylsilylmethanol.[59] In analogous fashion, triphenylsilyllithium added normally to acetaldehyde[58,60] and propionaldehyde[61] to form 1-triphenylsilylethanol and

---

[57] H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 80, 2680 (1958).

[58] D. Wittenberg and H. Gilman, ibid., 80, 4529 (1958).

[59] H. Gilman and T. C. Wu, ibid., 76, 2502 (1954).

[60] A. G. Brook, C. M. Warner and M. E. McGriskin, ibid., 81, 981 (1959).

[61] H. Gilman and D. J. Peterson, J. Org. Chem., 23, 1895 (1958).

1-triphenylsilylpropan-1-ol, respectively.

The addition of a silylmetallic compound to benzophenone gives an "abnormal" product, one in which the silicon atom is bonded to the oxygen. Thus, benzhydryloxytriphenylsilane and not triphenylsilyldiphenylcarbinol was isolated by reaction of a triphenylsilylmetallic compound with benzophenone.[62,63] Germylmetallic compounds have been reported to undergo a normal addition to benzophenone.[64]

A rearrangement hypothesis was postulated to account for the alkoxysilane formation in the reaction of silylmetallic compounds with benzophenone. It was felt that the silylmetallic first added normally to the carbonyl, then rapidly rearranged to give the product isolated. Some credence was granted this theory when Brook[65] succeeded in synthesizing triphenylsilyldiphenylcarbinol. He reported that even under very mild basic conditions this carbinol rearranged to benzhydryloxytriphenylsilane. Recently, α-silylcarbinols derived from aliphatic ketones were shown to undergo this rearrangement under strongly alkaline conditions.[58]

---

[62] H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., 80, 607 (1958).

[63] H. Gilman and T. C. Wu, ibid., 75, 2935 (1953).

[64] H. Gilman and C. W. Gerow, ibid., 77, 5740 (1955).

[65] A. G. Brook, ibid., 80, 1886 (1958).

2. In metalation reactions

Review articles on metalation have appeared in the literature[66] and the metalation of various heterocycles has been recently correlated.[67] In summary, most metalations of heterocyclic compounds occur predominantly at the carbon atom ortho to the hetero atom. For example, metalation of dibenzofuran occurs readily with a variety of reagents to give, subsequent to carbonation, dibenzofuran-4-carboxylic acid.[68]

Silylmetallic reagents metalate only the compounds in which the hydrogens are quite active. Triphenylsilylmetallic compounds have been found to metalate triarylmethane rapidly and in high yields to give the corresponding metal salts and triarylsilanes.[69] If an excess of metalating reagent was present, it reacted with the newly formed triarylsilane to

---

[66] See for example H. Gilman and J. W. Morton. The metalation reaction with organolithium compounds. In R. Adams, ed. Organic reactions. Vol. 8, pp. 258-304. New York, N.Y., John Wiley and Sons, Inc. 1954.

[67] J. B. Honeycutt. Some correlations of carbazole derivatives with related heterocycles. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1956.

[68] For the most recent thesis concerning dibenzofuran see R. G. Johnson. Some synthetic studies with dibenzofuran. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1954.

[69] A. G. Brook and H. Gilman, J. Am. Chem. Soc., 76, 2338 (1954).

yield a tetraarylsilane.[69,70]

The superior solvating abilities of tetrahydrofuran[71] are known to have important influences on the course of several metalation reactions.[2,3,72,73,74,75] However, the use of triphenylsilyllithium in tetrahydrofuran as a metalating agent has met with limited success to date. No evidence of metalation was detected when dibenzofuran was treated with triphenylsilyllithium at room temperature,[76] or even at elevated temperature.[77] Triphenylsilyllithium reacts with diphenyl ether to give, following carbonation, only a trace of 2,2'-dicarboxydiphenyl ether.[78]

Other compounds which have fairly acidic hydrogen atoms, 9,10-dihydroanthracene,[76] diphenylmethane,[76] fluorene[76] and

---

[70] A. G. Brook and H. Gilman, _ibid_., _76_, 2333 (1954).

[71] H. C. Brown and R. M. Adams, _ibid_., _64_, 2557 (1942).

[72] H. Gilman and S. Gray, _J. Org. Chem_., _23_, 1476 (1958).

[73] H. Gilman and R. D. Gorsich, _ibid_., _22_, 687 (1957).

[74] T. G. Selin and R. West, _Tetrahedron_, _5_, 97 (1959).

[75] P. Tomboulian, _J. Org. Chem_., _24_, 229 (1959).

[76] O. L. Marrs, Iowa State University of Science and Technology, Ames, Iowa. Information on metalation studies of triphenylsilyllithium. Private communication. 1959.

[77] W. J. Trepka, Iowa State University of Science and Technology, Ames, Iowa. Data from metalation reactions. Private communication. 1959.

[78] D. Wittenberg, D. Aoki and H. Gilman, _J. Am. Chem. Soc_., _80_, 5933 (1958).

xanthene,[77] for instance, are readily metalated by triphenylsilyllithium to give the metal salts, which on carbonation give the corresponding acids.

The metalation reactions of triphenylgermyllithium have recently been reported.[79]

Diphenylamine[80] and N-(diphenylmethyl)aniline[81] were metalated by triphenylsilyllithium; however, no secondary coupling reaction occurred between the initially formed triphenylsilane and the corresponding lithium derivative.

3. With organic halides

The cleavage of phenylisopropyltriphenylsilane by sodium-potassium alloy in ether represented the first bona fide preparation of a triarylsilylmetallic compound. Benkeser and Severson,[82] in their initial investigation of the preparation and properties of triphenylsilylpotassium, found that this compound reacted readily with hydrochloric acid to give triphenylsilane, with carbon dioxide to give triphenylsilane-

---

[79] H. Gilman and C. W. Gerow, J. Org. Chem., 23, 1582 (1958).

[80] G. D. Lichtenwalter. Organosilylmetallic compounds and derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

[81] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, J. Am. Chem. Soc., 80, 4532 (1958).

[82] R. A. Benkeser and R. G. Severson, ibid., 73, 1424 (1951).

carboxylic acid and with bromobenzene to yield tetraphenylsilane. Gilman and Wu[83] reported that triphenylsilylpotassium, formed more conveniently via the sodium-potassium cleavage of hexaphenyldisilane, reacted smoothly with bromobenzene and trimethylchlorosilane to give tetraphenylsilane and 1,1,1-trimethyl-2,2,2-triphenyldisilane.

Benkeser and co-workers[84] observed that arylsilylpotassium compounds could be coupled with various organic halides, for example, bromobenzene, triethylchlorosilane, methyl iodide and p-bromobiphenyl. In the reaction of methyl iodide with triphenylsilylpotassium, hexaphenyldisilane was isolated along with methyltriphenylsilane; in fact a larger yield of the disilane was realized than the expected coupling product. This was undoubtedly the first observation of a halogen-metal interconversion reaction in silicon chemistry,[85] although it was not recognized per se at that time.

The primary coupling reaction was later extensively employed in the preparation of organopolysilanes. For instance,

---

[83] H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

[84] R. A. Benkeser, H. Landesman and D. J. Foster, ibid., 74, 648 (1952).

[85] The halogen-metal interconversion reaction is well established in organic chemical systems. See R. G. Jones and H. Gilman. The halogen-metal interconversion reaction with organolithium compounds. In R. Adams, ed. Organic reactions. Vol. 6, pp. 339-366. New York, N.Y., John Wiley and Sons, Inc. 1951.

treatment of two moles of triphenylsilylpotassium with one mole of diphenyldichlorosilane gave octaphenyltrisilane in a good yield.[86] In a study of the reaction of halobenzenes with triphenylsilylpotassium, it was demonstrated that the order of decreasing activity was: iodobenzene, bromobenzene, chlorobenzene and fluorobenzene.[87] Fluorobenzene was considerably less reactive than the other compounds. A different order of reactivity was obtained using triphenylsilyllithium with halobenzenes. The reaction of fluorobenzene with triphenylsilyllithium gave the highest yields of tetraphenylsilane (see page 21).

In an attempt to prepare triphenylmethyltriphenylsilane from the reaction of triphenylsilylpotassium and triphenylchloromethane, the only products obtained were hexaphenyldisilane and hexaphenylethane (identified as the peroxide).[88] A halogen-metal interconversion reaction was postulated to account for the products. It was suggested that the triphenylsilylpotassium underwent a halogen-metal interconversion with triphenylchloromethane to give triphenylchlorosilane and

---

[86] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and Scott H. Eidt, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>74</u>, 561 (1952).

[87] H. Gilman and T. C. Wu, <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>18</u>, 753 (1953).

[88] A. G. Brook, H. Gilman and L. S. Miller, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>75</u>, 4759 (1953).

triphenylmethyllithium. A secondary coupling reaction between triphenylchlorosilane and triphenylsilylpotassium would give the observed hexaphenyldisilane.

Halogen-metal interconversion was found to occur as the primary reaction between silylmetallics and organic halides.[89] Normal or inverse addition of triphenylsilylpotassium to cyclohexyl bromide failed to form the usual coupling product, cyclohexyltriphenylsilane. Other products, such as hexaphenyldisilane, triphenylsilane, bicyclohexyl, cyclohexene and cyclohexyl bromide were isolated instead. This was taken as corroborating evidence for the occurrence of a halogen-metal interconversion.[89] The elusive cyclohexyltriphenylsilane was subsequently prepared in a satisfactory yield by the reaction of cyclohexyllithium with triphenylchlorosilane.[90] It was concluded that the preferred method for synthesizing various primary coupling products was by the treatment of a silyl halide with an organometallic reagent.

Halogen-metal interconversion was found to be a predominant reaction between triphenylsilyllithium and alkyl or aryl bromides.[91] For example, triphenylsilyllithium and _n_-butyl bromide gave a 60% yield of hexaphenyldisilane and a

---

[89] A. G. Brook and S. Wolfe, _ibid_., _79_, 1431 (1957).

[90] H. Gilman and D. Miles, _ibid_., _80_, 611 (1958).

[91] H. Gilman and D. Aoki, _J. Org. Chem_., _24_, 426 (1959).

10% yield of n-butyltriphenylsilane. However, a similar reaction using n-butyl chloride gave a 75% yield of the primary coupling product and no hexaphenyldisilane. A recent study of the reaction of triphenylsilyllithium with epichlorohydrin and epibromohydrin has given related results.[92] The chloro compound gave no hexaphenyldisilane, only allyltriphenylsilane, 1-chloro-3-triphenylsilylpropan-2-ol and 1,3-bis(triphenylsilyl)propan-2-ol. Yet the bromo compound gave a high yield of hexaphenyldisilane along with some allyltriphenylsilane.[92] The pronounced effect of the halogens in related reactions between silylmetallics and mono or polyhalogenated compounds is known.[93]

Apparently the solvent also has some influence on the extent to which halogen-metal interconversion will occur in a given reaction. Hexaphenyldisilane is formed in trace quantities from the reaction of triphenylsilylpotassium with bromobenzene in ether.[89] The same reaction employing triphenylsilyllithium in tetrahydrofuran gave hexaphenyldisilane as the principal product.[93]

Incidental to the synthesis of tetramethylenebis(tri-

---

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

[93] G. Dappen, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of triphenylsilyllithium with alkyl and aryl halides. Private communication. 1959.

phenylsilane), by the reaction of triphenylsilyllithium with 1,4-dibromobutane, it was found that the main product was hexaphenyldisilane, apparently formed by a halogen-metal interconversion reaction.[94] There was no discernible halogen-metal interconversion when triphenylgermylpotassium reacted with triethylchlorosilane since only triphenylgermyltriethylsilane was isolated.[95]

In order to circumvent or at least diminish the halogen-metal interconversion, it has been found best to use alkyl sulfates rather than alkyl halides, in coupling reactions with silylmetallic compounds. For instance, 5-lithio-5-methyl-dibenzosilole, obtained from the lithium cleavage of 5,5'-dimethyl-5,5-bi-[dibenzosilole], reacted with dimethyl sulfate to give only 5,5-dimethyldibenzosilole.[96]

Tetrasubstituted silanes have been synthesized by reacting triphenylsilylpotassium with the appropriate halide. For example, 2-bromodibenzothiophene and 3-bromo-9-ethylcarbazole gave the corresponding silanes in good yields.[97] The same products can also be prepared from the appropriate

---

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

[95] H. Gilman and C. W. Gerow, ibid., 78, 5823 (1956).

[96] H. Gilman and R. D. Gorsich, ibid., 80, 3243 (1958).

[97] R. H. Meen and H. Gilman, J. Org. Chem., 20, 73 (1955).

organolithium compounds and triphenylchlorosilane.[97]

Dehydrohalogenation has been observed when silyllithium compounds react with certain organic halides. When triphenylsilyllithium was allowed to interact with tertiary butyl chloride, triphenylsilane was isolated in good yield. However, hexaphenyldisilane was the chief product of a reaction between triphenylsilyllithium and tertiary butyl bromide.[93]

C. Aromatic Heterocyclic Silicon Systems

1. Organosilanes containing heterocyclic groups

a. Furan The first reported silicon derivative of furan was prepared by coupling 2-furyllithium with trimethylchlorosilane.[98] The 2-furyltrimethylsilane so produced was acetylated with acetic anhydride to give 2-trimethylsilyl-5-acetylfuran. Oxidation of this latter compound with alkaline sodium hypoiodite gave 5-trimethylsilyl-2-furoic acid.[98] Rather mild oxidation of 2-trimethylsilyl-5-acetylfuran with selenium dioxide produced 5-trimethylsilyl-2-furylglyoxal.[99] The glyoxal showed surprising stability toward dilute acidic conditions. There was no silicon-carbon cleavage detected in these oxidations; however, 5-trimethylsilyl-2-furoic acid

---

[98] R. A. Benkeser and R. B. Currie, *J. Am. Chem. Soc.*, *70*, 1780 (1948).

[99] R. A. Benkeser and H. Landesman, *ibid.*, *71*, 2493 (1949).

was readily attacked by bromine in carbon tetrachloride to yield 5-bromo-2-furoic acid.[99]

In a study of the cleavage of silicon-containing carbonyl compounds, Sommer and Pioch[100] had occasion to synthesize 2-trimethylsilylethyl-2-carbetheoxy-5-methylfuran by the cyclization of the acyl levulinate in a strong acidic medium.

b. Thiophene Krause and Renwanz[101] obtained tetra-2-thienylsilane by the action of excess 2-thienylmagnesium halide on silicon tetrachloride. The Grignard reagent was prepared from 2-iodo-thiophene. Other thienyl-substituted silicon compounds were obtained by coupling organometallic thiophene derivatives with chlorosilanes. For example, reaction of 2-thienyllithium with trimethylchlorosilane and triphenylchlorosilane gave 2-thienyltrimethylsilane[98] and 2-thienyltriphenylsilane,[102] respectively. Grignard syntheses have also been employed, such as the formation of 5-bromo-2-thienyltrimethylsilane from the reaction of 5-bromo-2-thienylmagnesium bromide with trimethylchlorosilane.[103] Various 2-thienylchlorosilanes have been prepared

---

[100] L. H. Sommer and R. P. Pioch, ibid., 76, 1606 (1954).

[101] E. Krause and G. Renwanz, Ber., 62, 1710 (1929).

[102] H. Gilman, R. A. Benkeser and G. E. Dunn, J. Am. Chem. Soc., 72, 1689 (1950).

[103] R. A. Benkeser and A. Torkelson, ibid., 76, 1252 (1954).

by the reaction of chlorosilanes with 2-thienyllithium.[104,105] Hydrolysis of these chlorosilanes gave polysiloxanes which had desirable thermal stability characteristics.[106]

Mohler and Sellers[107] synthesized thienyl silicon compounds without resorting to organometallic reagents. They found that heating 2-chlorothiophene with silicochloroform and methyldichlorosilane at temperatures of 500° gave 2-thienyltrichlorosilane and 2-thienylmethyldichlorosilane.

The thienyl group can be cleaved by gaseous hydrogen chloride as well as with bromine. In a cleavage study, it was found that bromine in carbon tetrachloride cleaved 5-bromo-2-thienyltrimethylsilane about thirty times faster than it cleaved phenyltrimethylsilane.[98]

Thienyl silicon compounds can be metalated with n-butyllithium and subsequent to carbonation give acids.[98,99,103] Acetylation and mild oxidation of these thienylsilicon compounds can occur in an analogous manner to that described

---

[104] P. D. George, U. S. Patent 2,640,833. June 2, 1953. (Original not available for examination; abstracted in C. A., 48, 5227 (1954)).

[105] P. D. George, U. S. Patent 2,645,644. July 14, 1953. (Original not available for examination; abstracted in C. A., 48, 7064 (1954)).

[106] P. D. George, U. S. Patent 2,640,818. June 2, 1953. (Original not available for examination; abstracted in C. A., 47, 9055 (1953)).

[107] D. Mohler and J. E. Sellers, U. S. Patent 2,598,436. May 27, 1952. (Original not available for examination; abstracted in C. A., 47, 3875 (1953)).

above for the furyl silicon compounds.[98,99]

c. Benzothiophene In a study on the cleavage of some organosilanes, Meen and Gilman[97] had occasion to synthesize 2-benzothienyltriphenylsilane. This was accomplished by treating an ethereal solution of 2-benzothienyllithium[108] with triphenylchlorosilane to give a 71% yield of the desired product. There was extensive cleavage of the heterocyclic substituent from silicon by either acidic or alkaline reagents.

d. Dibenzothiophene Silyl-substituted dibenzothiophenes were easily obtained by coupling the organometallic derivative[97] of dibenzothiophene with a chlorosilane.[109,110] 2-Triphenylsilyl-, 4-triphenylsilyl-,[97,109] 2-trimethylsilyl-,[110] 3-trimethylsilyl-[110] and 4-trimethylsilyldibenzothiophene[109] were prepared in this manner. All of these silanes were oxidized to the corresponding 5,5-dioxides with hydrogen peroxide in glacial acetic acid. The silicon-carbon bond in the 2,3,4-trimethylsilyl isomers of dibenzothiophene are quite unstable toward acidic reagents and are readily cleaved. The corresponding sulfones apparently enhanced the silicon-carbon linkage stability to a considerable extent,

---

[108] D. A. Shirley and M. D. Cameron, J. Am. Chem. Soc., 74, 664 (1952).

[109] H. Gilman and J. F. Nobis, ibid., 72, 2629 (1950).

[110] G. Illuminati, J. F. Nobis and H. Gilman, ibid., 73, 5887 (1951).

since the dioxides were completely resistant to acidic treatment.[109,110]

4-Triphenylsilyldibenzothiophene could not be cleaved by bubbling hydrogen chloride through a glacial acetic acid solution.[109] Other cleavage studies have also indicated that triarylsilyl groups manifest greater acidic stability than trialkylsilyl groups when attached to the same nucleus.[111]

2-Triphenylsilyldibenzothiophene has also been prepared by the reaction of triphenylsilylpotassium on 2-bromodibenzothiophene.[97]

e. Dibenzofuran 2-Triphenylsilyldibenzofuran[97,109] and 4-triphenylsilydibenzofuran[97] have been synthesized by the action of triphenylchlorosilane on the corresponding organolithium compounds.

f. Benzothiazole The synthesis of 2-triphenylsilylbenzothiazole was achieved only after altering the usual preparative schemes.[97] 2-Benzothiazolyllithium[112] is only stable at temperatures below -35°, if the temperature were permitted to rise above this value, appreciable quantities of 2,2'-bibenzothiazole could be isolated from the reaction mixture. There was no reaction of 2-benzothiazolyllithium with triphenylchlorosilane at this low temperature. At a temperature

---

[111] H. Gilman and F. J. Marshall, *ibid*., *71*, 2066 (1949).

[112] H. Gilman and J. A. Beel, *ibid*., *71*, 2329 (1949).

of -10°, a 5% yield of 2-triphenylsilylbenzothiazole was obtained. Employing the more reactive triphenylbromosilane increased the yield to 19%.

g. *Carbazole* Meen and Gilman,[97] by treatment of 9-ethyl-3-carbazolyllithium with the appropriate chlorosilane, prepared diphenylbis(9-ethyl-3-carbazolyl)-, phenyltris(9-ethyl-3-carbazolyl)- and tetrakis(9-ethyl-2-carbazolyl)silane. 9-Ethyl-3-triphenylsilylcarbazole, 9-ethyl-6-chloro-2-triphenylsilylcarbazole and 9-ethyl-1-triphenylsilylcarbazole have also been reported.[97] Reaction of triphenylsilylpotassium with 3-bromo-9-ethylcarbazole gave a 57% yield of 3-triphenylsilyl-9-ethylcarbazole.[97]

h. *Quinoline* Triphenyl-[2-(5-lithio)-thienyl]silane reacted with quinoline, 6-methoxyquinoline and 4,7-dichloroquinoline to give subsequent to hydrolysis the 2-substituted quinoline.[113]

The preparation of 2-trimethylsilyl- and 2-triphenylsilylquinoline from trimethyl- and triphenylchlorosilane, respectively, and 2-quinolyllithium was unsuccessful.[114] 2-[*p*-(Trimethylsilyl)-phenyl]quinoline was synthesized by two routes; the first was the addition of *p*-(trimethylsilyl)-

---

[113] H. Gilman and M. A. Plunkett, *ibid.*, *71*, 1117 (1949).

[114] T. S. Soddy. Organometallic derivatives of quinoline and isoquinoline. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

phenyllithium to quinoline. In the second procedure trimethylchlorosilane was added to 2-(p-lithiophenyl)quinoline.[114] The reaction of triphenylsilyllithium with quinoline gave a 6.8% yield of a triphenylsilyl derivative of quinoline. The position of this substituent is not yet known.[76]

i. Pyridine Investigating pyridine as a possible solvent for the lithium cleavage of hexaphenyldisilane, triphenyl-4-(1,4-dihydropyridyl)-silane was obtained in a 63% yield. Boiling with nitrobenzene oxidized the reduced product to triphenyl-4-pyridylsilane.[115] In contrast, attack by alkyl- and aryllithium nucleophiles generally gives 1,2-addition to pyridine.[116,117] No addition product was isolated when triphenylsilylpotassium reacted with pyridine.[118] The 2-pyridyl isomer was readily synthesized by the reaction of 2-pyridyllithium[119] and triphenylchlorosilane; triphenyl-2-pyridylsilane was isolated in a 39% yield.[115]

---

[115] D. Wittenberg and H. Gilman, Chem. and Ind. (London), 390 (1958).

[116] K. Ziegler and H. Zeiser, Ber., 63, 1847 (1930).

[117] K. Ziegler and H. Zeiser, Ann., 485, 174 (1931).

[118] J. B. Honeycutt. Preparation of some nitrogen-containing organosilicon compounds. Unpublished M.S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1951.

[119] H. Gilman and S. M. Spatz, J. Org. Chem., 16, 1485 (1951).

Trimethyl-2-pyridylsilane and dichloro-bis(2-pyridyl)-silane, the only other compounds in which silicon is bound to the pyridine nucleus, are described in the literature.[120,121,122]

j. Xanthene The synthesis of 9-trimethylsilyl-, 9-triphenylsilylxanthene, dimethylbis(9-xanthyl)- and diphenylbis(9-xanthyl)silane by conventional methods has recently been accomplished.[77] An attempt to prepare 9-tribenzylsilylxanthene from 9-lithioxanthene[22] and tribenzylsilane was unsuccessful.[77,123]

k. Phenothiazine None of the desired products could be isolated in the attempted formation of the 3- and 4-triphenylsilylphenothiazines.[124] The reaction of tripheylsilylpotassium with 3-bromo-10-ethylphenothiazine gave an amorphous material which resisted purification. Reaction of 4-lithio-

---

[120] B. A. Bluestein, U. S. Patent 2,584,665. Feb. 5, 1952. (Original not available for examination; abstracted in C. A., 46, 4279 (1952)).

[121] British Thomson-Houston Co., British Patent 685,187. Dec. 31, 1952. (Original not available for examination; abstracted in C. A., 47, 4647 (1953)).

[122] British Thomson-Houston Co., British Patent 685,186. Dec. 31, 1952. (Original not available for examination; abstracted in C. A., 48, 2783 (1954)).

[123] For reactions of silicon hydrides with organolithium derivatives see H. Gilman and E. A. Zuech, J. Am. Chem. Soc., 79, 4560 (1957), and references contained therein.

[124] R. Ranck. Some reactions of phenothiazine and its derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

10-ethylphenothiazine, prepared by the reaction of n-butyllithium on 10-ethylphenothiazine-5-oxide, with triphenylchlorosilane gave a widely melting solid which could not be satisfactorily purified.[124] 4-Lithio-10-ethylphenothiazine, this time prepared from 10-ethylphenothiazine and n-butyllithium, and triphenylchlorosilane failed to give the desired 4-triphenylsilyl-10-ethylphenothiazine.[125]

Addition of triphenylsilane[126] to 10-allylphenothiazine[125,127,128] in the presence of benzoyl peroxide failed to yield any of the desired 10-(γ-triphenylsilylpropyl)-phenothiazine.

1. Acridine   Triphenylsilyllithium added to acridine in the 9,10-position to yield the intermediate 10-lithio-9-(triphenylsilyl)acridan which on hydrolysis gave 9-(triphenylsilyl)acridan.[129] The reaction of triphenylsilyllithium with other aza-aromatic heterocycles, for example, isoquinoline,

---

[125] J. F. Champaigne, Jr. N-Substituted phenothiazine derivatives. Unpublished M.S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1952.

[126] H. Merten and H. Gilman, J. Am. Chem. Soc., 76, 5798 (1954).

[127] D. A. Shirley. Derivatives of phenothiazine as chemotherapeutic agents. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1943.

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

[129] H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 23, 1586 (1958).

phenanthridine and phenazine gave only traces of substances, the structures of which were not established.[80]

m. Miscellaneous Silicon has been attached to other nitrogen-containing rings, such as pyrazolones[100] and barbiturates.[130] 1-(Triphenylsilyl)piperidine, and 1,4-bis-(triphenylsilyl)piperazine were readily prepared by the reaction of triphenylsilyllithium with the appropriate amine.[80] 1-Thianthrenyltriphenylsilane was prepared in a 10% yield by the reaction of triphenylchlorosilane on 1-thianthrenyllithium.[131]

2. Cyclic organosilicon compounds

Aromatic heterocycles containing silicon as one of the hetero atoms have shown excellent thermal and oxidative stabilities. The preparation and properties of silicon-containing ring systems has recently been summarized through April, 1957.[132] This review will therefore attempt to briefly relate some of the more important investigations since that time.

A silicon analog of 9,9-diphenylfluorene;5,5-diphenyl-

---

[130] L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., J. Am. Chem. Soc., 76, 1609 (1954).

[131] H. Gilman and D. R. Swayampati, ibid., 79, 208 (1957).

[132] R. D. Gorsich. Some cyclic organosilicon compounds and derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

dibenzosilole, was prepared by the interaction of 2,2'-dilithiobiphenyl with one equivalent of diphenyldichlorosilane. This demonstrated the relative ease which some cyclic organosilicon compounds could be synthesized.[133] Dimetalation of diphenyl ether and diphenyl sulfone and subsequent treatment of the dimetalated products with the appropriately substituted chlorosilanes gave phenoxasilin[134,135] and phenothiasilin-5,5-dioxide[136] derivatives, respectively. Recent evidence indicates that phenoxasilin derivatives can also be prepared by treatment of 2,2'-dilithiodiphenyl ether with various silicon hydrides.[77] Gilman and Gorsich,[137,138] in a study of the preparation and reactions of the dibenzosilole nucleus, found that functional dibenzosilole derivatives could be obtained in higher yields than the nonfunctional types. For example, methyl-, and phenyltrichlorosilane coupled with 2,2'-dilithiobiphenyl to give excellent yields of 5-chloro-5-methyl-, and 5-chloro-5-phenyldibenzosilole, respectively.[137]

---

[133] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 77, 6380 (1955).

[134] K. Oita and H. Gilman, ibid., 79, 339 (1957).

[135] C. H. S. Hitchcock, F. G. Mann and A. Vanterpool, J. Chem. Soc., 4537 (1957).

[136] K. Oita and H. Gilman, J. Org. Chem., 22, 336 (1957).

[137] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 1883 (1958).

[138] H. Gilman and R. D. Gorsich, ibid., 80, 3243 (1958).

This observation was in essential accord with that made by West in his preparation of alicyclic organosilicon compounds.[139]

The superior thermal stabilities of organosilicon compounds derived from aryl ethers[140,141] prompted the synthesis of several organosilicon compounds from either o- or p-phenoxyphenyllithium, or from (oxydi-o- or oxydi-p-phenylene)-dilithium.[142] 10,10-Dibenzylphenoxasilin volatilized at 470° but (oxydi-p-phenylene)bis [tribenzylisilane] volatilizes at 540-550° with only slight decomposition.[142]

Cleavage and eventual replacement of the sulfur atom by the diphenylsilylene group has been reported.[143,144] On heating diphenylsilane with sulfur-containing heterocycles, such as phenoxathiin, 10-ethylphenothiazine and thianthrene; 10,10-diphenylphenoxasilin, 5-ethyl-10,10-diphenylphenazasiline and 10,10-diphenylphenothiasilin, respectively, were isolated in very low yields. A new synthesis of phenazasiline derivatives, which circumvented the low yields and tedious work-up

---

[139] R. West, ibid., 76, 6012 (1954).

[140] K. Oita and H. Gilman, J. Org. Chem., 21, 1009 (1956).

[141] H. Gilman and J. J. Goodman, ibid., 22, 45 (1957).

[142] H. Gilman and D. Miles, ibid., 23, 1363 (1958).

[143] D. Wittenberg, H. A. McNinch and H. Gilman, J. Am. Chem. Soc., 80, 5418 (1958).

[144] H. Gilman and D. Wittenberg, ibid., 79, 6339 (1957).

involved in the replacement of sulfur method, was developed by Gilman and Zuech.[145] Reaction of N-ethyl-2,2'-dilithiodiphenylamine, prepared from N-ethyl-2,2'-dibromodiphenylamine and _n_-butyllithium, with diphenyldichlorosilane gave a 49% yield of 5-ethyl-10,10-diphenylphenazasiline. Several other derivatives of phenazasiline have been prepared utilizing this procedure.[146]

An intramolecular cleavage-cyclization reaction of silicon-containing organolithium compounds offers a new route to silacyclo derivatives.[147] Reaction of triphenylchlorosilane with tetramethylenedilithium gave 1,1-diphenylsilacyclopentane as the principal product.[147] Reaction of triphenylsilyllithium with trimethylene oxide gave 3-(triphenylsilyl)propanol in a good yield. Conversion of this carbinol to the corresponding acid followed by cyclization yielded the first reported derivative in the silanaphthalene series, namely, 2,3-dihydro-1,1-diphenyl-4H-1-silanaphthalen-4-one.[148]

---

[145] H. Gilman and E. A. Zuech, _Chem. and Ind._ (_London_), 1227 (1958).

[146] E. A. Zuech, Iowa State University of Science and Technology, Ames, Iowa. Information regarding phenazasiline chemistry. Private communication. 1959.

[147] For related cleavages of tetrahydrofuran and other ethers see (a) D. Wittenberg and H. Gilman, _J. Am. Chem. Soc._, _80_, 2677 (1958). (b) D. Wittenberg, D. Aoki and H. Gilman, _ibid._, _80_, 5933 (1958). (c) H. Normant, _Compt. Rend._, _239_, 1510 (1954).

[148] P. B. Talukdar and D. Wittenberg, Iowa State University of Science and Technology, Ames, Iowa. Information on silanaphthalene chemistry. Private communication. 1958.

In a study[81] on the addition of silylmetallic compounds to the azo and azomethine linkage, it was found that the azobenzenedilithium adduct reacts with triphenylchlorosilane to give N,N'-diphenyl-N-(triphenylsilyl)hydrazine and also the corresponding bis compound. The reaction of diphenyldichlorosilane with the azobenzenedilithium adduct gave a good yield of octaphenyl-1,2,4,5-tetraza-3,6-disilacyclohexane.[149] Similar experiments with the stilbenedilithium adduct were unsuccessful.[149]

Sommer and Bennett[150] synthesized 1-chloro-1-silabicyclo[2.2.1]heptane in order to study the stereochemical requirements for substitution at a bridgehead organosilicon compound. This bridgehead silicon derivative was found to be more reactive than its carbon analog, due chiefly to the availability of d-orbitals and the larger size of silicon relative to carbon. Other studies of bridgehead silicon atoms in different compounds have been reported.[151,152]

The first disilacyclobutane compound has been reported

---

[149] M. V. George, D. Wittenberg and H. Gilman, _J. Am. Chem. Soc._, _81_, 361 (1959).

[150] L. H. Sommer and O. F. Bennett, _ibid._, _79_, 1008 (1957).

[151] L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, _ibid._, _79_, 3296 (1957).

[152] L. H. Sommer, W. P. Barie, Jr. and D. R. Weyenberg, _ibid._, _81_, 251 (1959).

recently.[153] 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was prepared in a 60% yield by refluxing a solution of 1-chloro-4-fluoro-2,2,4-trimethyl-2,4-disilapentane in ether with magnesium turnings.

4,4-Dimethyl-4-silacyclohexanone was synthesized in a four-step sequence culminating in the pyrolysis of the thorium salt of dimethyldi-(2-carboxyethyl)silane.[154] In a comparison of the cyanohydrin dissociation constants; 4,4-dimethyl-4-silacyclohexanone was found to have a dissociation constant five times larger than its carbon analog 4,4-dimethylcyclohexanone. This was ascribed to the increased size of the silicon atom which gave a larger ring and decreased the symmetry.[154]

D. Si-H Bond and Related Types as Reducing Agents

Buchner,[155] in 1885, reported that silane (SiH_4) was capable of reducing an aqueous solution of silver nitrate to metallic silver. This was the first observation of the reducing properties of the silicon hydrides. Several years later, other investigators[156] studying the interchange of halogens

---

[153] W. H. Knoth, Jr. and R. V. Lindsay, Jr., _J. Org. Chem._, _23_, 1392 (1958).

[154] R. A. Benkeser and E. W. Bennett, _J. Am. Chem. Soc._, _80_, 5414 (1958).

[155] G. Buchner, _Ber._, _18_, 317R (1885).

[156] O. Ruff and C. Albert, _ibid._, _38_, 53 (1905).

between silicochloroform (trichlorosilane) and various inorganic fluorides noted that the Si-H system was a possible reducing agent. They reported that silicochloroform could reduce arsenic (III) to arsenic (0) and antimony (III) to antimony (0). There was no reaction with silver or lead fluoride, even on prolonged heating. Silicochloroform was also found to reduce many other reagents, such as CO_2, SO_3, SO_2, NO_2, O_2, O_3.[157,158] Stock and Somieski,[159] studying the preparation and properties of silanes, found that silane could reduce Fe(III), Cu(II) and Hg(II) to Fe(II), Cu(I) and Cu(0) and Hg(I) and Hg(0), respectively.

Trisubstituted silanes have been recognized as possible reducing agents, for example, tribenzylsilane will convert benzoylchloride to benzaldehyde.[160] Previous theoretical considerations had also indicated that the silane hydrogen was electronegative in character.[161] Price,[162] studying the mechanism of the alkaline cleavage of Si-H bonds, indicated

---

[157] O. Ruff and C. Albert, <u>ibid</u>., <u>38</u>, 2222 (1905).

[158] A. Besson and L. Fournier, <u>Compt</u>. <u>rend</u>., <u>148</u>, 1192 (1909).

[159] A. Stock and C. Somieski, <u>Ber</u>., <u>49</u>, 111 (1916).

[160] J. W. Jenkins and H. W. Post, <u>J</u>. <u>Org</u>. <u>Chem</u>., <u>15</u>, 556 (1950).

[161] L. Pauling. The nature of the chemical bond. 2nd ed. Ithaca, New York, Cornell Univ. Press. 1948. p. 70.

[162] F. P. Price, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>69</u>, 2600 (1947).

that the nucleophilic attack by hydroxyl ion on trialkylsilanes split off hydride ion.

Eaborn[163] reported the reduction of silver isothiocyanate by triethylsilane. Later,[164] he observed that trialkylsilanes and silver perchlorate reacted in a toluene solution with precipitation of metallic silver and the evolution of hydrogen.

Organosilicon hydrides add to the double bond of substituted olefins[126,165] with the formation of a Si-C bond. Recently this reaction has been of value in synthetic studies.[166] Gadsby[167] synthesized several carboxyalkylsilanes by the addition of a trialkylsilane to the double bond using benzoyl peroxide as a catalyst. Triphenylsilane was found to add to the olefinic linkage in the presence of benzoyl peroxide to give fair yields of alkyltriphenylsilanes.[126] A comparison of the behavior of triphenylsilane, triphenylgermane, and triphenyltin hydride in the presence of olefins has been

---

[163] C. Eaborn, J. Chem. Soc., 3077 (1950).

[164] C. Eaborn, ibid., 2517 (1955).

[165] R. Fuchs and H. Gilman, J. Org. Chem., 22, 1009 (1957), and the numerous, pertinent references contained therein.

[166] H. Gilman, D. H. Miles, L. O. Moore and C. W. Gerow, ibid., 24, 219 (1959).

[167] G. N. Gadsby, Research (London), 3, 338 (1950).

reported.[165] All of the hydrides added to the double bond when peroxide initiation was employed; however, triphenylsilane failed to react with olefins under ultraviolet irradiation. Apparently the triphenylsilane is not as reactive as the other hydrides. Additional information is presented below in an attempt to correlate the relative reactivities of these hydrides.

Anderson has studied the reducing power of trialkylhydrides of Group IV B elements. In a series of papers he reported the use of halides of certain transition elements and elements in regular groups in the replacement of the hydrogen attached to germanium,[168] to tin[169] and to silicon.[170] For example, triethylsilane reduces certain halides or sulfates of at least ten transition elements and five elements in regular groups either to a lower oxidation state or to the free element.[170]

Based on their reactivity with atmospheric oxygen, cadmium (II) chloride or acetic acid, Anderson concluded that triethylsilane was least reactive.[170] The same order of reactivity is obtained using the reactions of the hydrides with halides of the transition elements. A recent paper[171] reports

---

[168] H. H. Anderson, J. Am. Chem. Soc., 79, 326 (1957).

[169] H. H. Anderson, ibid., 79, 4913 (1957).

[170] H. H. Anderson, ibid., 80, 5083 (1958).

[171] H. H. Anderson and A. Hendifar, ibid., 81, 1027 (1959).

the straight-forward preparation of alkylhalosilanes by addition of an excess of the appropriate silane to certain inorganic chlorides and bromides.

Nitzsche and Wick[172] found that 1,3-dimethyldisiloxane, in the presence of 2-5% dibutyltin dilaurate, was an active reducing agent even at room temperature. It reduced carbonyl compounds to alcohols and nitro compounds to amines; however, olefinic double bonds were not attacked. The reaction generally had a brief induction period which was shortened by the addition of trace amounts of benzoyl peroxide.[172] Phenyl-, diphenyl- and triphenylsilane added to benzophenone at high temperatures, in the absence of any catalyst or activating agent to form the addition products in which the silicon atom is bonded to the oxygen.[173] Silicochloroform and triphenylsilane reacted with acetone and pentanone-3, each catalyzed by ultraviolet radiation, to give the "abnormal" addition products.[174] Under these conditions acetophenone and benzophenone gave no reaction.[174] A slight excess of

---

[172] R. Nitzsche and M. H. Wick, Angew. Chem., 69, 96 (1957).

[173] H. Gilman and D. Wittenberg, J. Org. Chem., 23, 501 (1958).

[174] R. Calas and N. Duffaut, Compt. rend., 245, 906 (1957).

diphenylsilane reduced 10-ethylphenothiazine-5-oxide to 10-ethylphenothiazine in a 76% yield at temperatures of 200-250°.[143]

Kuivila and Beumel,[175] in attempting the addition of diphenyltin dihydride to methyl vinyl ketone, isolated methyl vinylcarbinol in a good yield. These authors feel that, since no hydrolysis step is necessary, there is a transfer of two hydrogens in a noncatalyzed manner from the tin to the carbonyl. They then found that it was possible to selectively reduce several α,β-unsaturated aldehydes and ketones to the corresponding alcohols using diphenyltin dihydride. Organotin hydrides, however, are capable of undergoing a noncatalyzed addition to olefinic double bonds at moderate temperatures.[176] Two recent communications[177,178] have indicated that triphenylmetal hydrides offer promise as reducing agents. Refluxing bromobenzene with triphenyltin hydride yielded 60-75% of the hydrogenolysis product, benzene.[177] Triphenyltin hydride also reduced carbonyl groups to the corresponding

---

[175] H. G. Kuivila and O. F. Beumel, J. Am. Chem. Soc., 80, 3798 (1958).

[176] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, J. Appl. Chem. (London), 7, 356 (1957).

[177] L. A. Rothman and E. I. Becker, J. Org. Chem., 24, 294 (1959).

[178] J. G. Noltes and G. J. M. van der Kerk, Chem. and Ind. (London), 294 (1959).

alcohols.[178] The use of dialkylaluminum hydrides[179,180] as reducing agents has been reported although all the reactions have an analogous stoichiometry to lithium aluminum hydride.[181]

---

[179] A. E. G. Miller, J. W. Biss and L. H. Schwartzman, J. Org. Chem., 24, 627 (1959).

[180] K. Ziegler, K. Schneider and J. Schneider, Ann., 623, 9 (1959).

[181] N. G. Gaylord. Reduction with complex metal hydrides. New York, N.Y., Interscience Publishers. 1956.

III. EXPERIMENTAL

All melting points are uncorrected. Reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen[182,183] in sodium-dried solvents. The tetrahydrofuran (THF) was dried by refluxing over sodium metal for at least 24 hrs. and distilling, immediately before use, from lithium aluminum hydride. Petroleum ether refers to the fraction, b.p. 60-70°, unless otherwise indicated.

A. Chemistry of Thiaxanthene and Related Compounds

1. Thiaxanthene

10-Thiaxanthenone was reduced to thiaxanthene by the procedure of Mustafa and Hilmy.[18] These workers employed a one gram sample and realized a 74% yield of crude thiaxanthene.

A solution of 25.0 g. (0.1179 mole) of 10-thiaxanthenone dissolved in 800 ml. of dry benzene was added dropwise with

---

[182] L. Meites and T. S. Meites, Anal. Chem., 20, 948 (1948).

[183] (a) K. Oita. Direct preparation of some organolithium compounds from lithium and RX compounds. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955. (b) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949). (c) H. Gilman and A. H. Haubein, ibid., 66, 1515 (1944).

rapid stirring to a suspension of 13.42 g. (0.354 mole) of lithium aluminum hydride in 1000 ml. of ether, maintaining slight reflux throughout the addition. The grey suspension was refluxed for 4 hrs. and then set aside overnight at room temperature.

After addition of the reaction mass to water and treatment with aqueous ammonium chloride until acid to litmus, the ethereal layer was washed well with water, dried and concentrated to give 17.0 g. (73%) of crude thiaxanthene, m.p. 122-126°. Two recrystallizations from ethanol (Norit) gave 12.7 g. (54.5%) of white thiaxanthene, m.p. 129-130°, lit.[17] 128°.

Several unsuccessful attempts were made to prepare thiaxanthene by the reaction of diphenylmethane with sulfur in the presence of aluminum chloride. A possible explanation for the lack of success in these experiments will be presented in the discussion.

2. Reaction of thiaxanthene-5-oxide with hydrobromic acid

A mixture of 4.0 g. (0.0187 mole) of thiaxanthene-5-oxide,[24] 10 ml. of water and 20 ml. of 48% hydrobromic acid was stirred at room temperature for 2 hrs. and then at reflux for 1 hr. At the end of this time the pink solid was filtered, washed and dried to give 3.5 g. of material, melting over the range 105-175°.

Recrystallization from ethanol gave 1.0 g. (26%) of 10-thiaxanthenone, m.p. 215-217°, identified by a mixed melting point and a comparison of the infrared spectrum. The ethanolic filtrate was poured over ice to give 1.1 g. (29%) of thiaxanthene, m.p. 126-129°; identified by the method of mixture melting points.

A repeat of this experiment gave essentially the same results. 9-Xanthhydryl chloride is known to dismutate to 9-xanthenone and xanthene, possibly through the acid catalysis of xanthhydrol.[184] Other references[20,29] will be discussed later.

Reaction of thiaxanthene-5,5-dioxide[25] and 10-thiaxanthenone-5,5-dioxide with hydrobromic acid under analogous conditions gave a 90% and 93.4% recovery of starting materials.

3. 10-Thiaxanthenecarboxylic acid from thiaxanthene and triphenylsilyllithium

Seven and nine-tenths grams (0.04 mole) of thiaxanthene was dissolved in 50 ml. of THF and, after cooling to 0°, 0.04 mole of triphenylsilyllithium[1] was added dropwise over a 1-hr. period. After addition was complete the reaction mixture was stirred at ice-bath temperature for 0.5 hr. and then per-

---

[184] G. W. H. Cheeseman, *J. Chem. Soc.*, 458 (1959).

mitted to warm to room temperature. Color Test I[185] was strongly positive after 16 hrs. of stirring. The dark-red solution was carbonated by pouring onto a Dry Ice-ether slurry.

Extraction of the organic suspension with 300 ml. of a 2.5% sodium hydroxide solution and slow acidification of the chilled basic extract gave 6.5 g. (64.3%) of a white powder, m.p. 222-225°. Two recrystallizations from isopropanol gave 4.5 g. (44.6%) of 10-thiaxanthenecarboxylic acid, m.p. 226-227°. Burtner and Cusic[22] reported a melting point of 227° for 10-thiaxanthenecarboxylic acid.

The only solids isolated from the organic layer were 0.5 g. (6.3%) of thiaxanthene and 2.2 g. (20%) of triphenylsilanol; each identified by the method of mixture melting points.

4. 10-Triphenylsilylthiaxanthene

10-Lithiothiaxanthene was prepared by treating 10 g. (0.050 mole) of thiaxanthene suspended in 75 ml. of ether with 0.05 mole of *n*-butyllithium[183] in 75 ml. of ether at gentle reflux for 2 hrs. After cooling the orange 10-lithiothiaxanthene solution to room temperature, 14.8 g. (0.050

---

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

mole) of triphenylchlorosilane in 75 ml. of ether was slowly added. Upon completion of the addition, stirring was continued for 18 hrs. at room temperature. After hydrolysis, separation of layers, washing of the aqueous layer with additional ether, the ether layers were combined and dried. Concentration of the organic layer gave a yellow solid which was taken up in benzene and chromatographed. Elution with benzene gave 11.2 g. (49%) of 10-triphenylsilylthiaxanthene, m.p. 174-176°. Recrystallization from benzene raised the melting point to 175-176°. The infrared spectrum showed the characteristic absorption bands for a tertiary hydrogen and a silicon-phenyl grouping.

Anal.[186] Calcd. for $C_{31}H_{24}SSi$: Si, 6.14. Found: Si, 6.27, 6.29.

10-Triphenylsilylthiaxanthene was converted to the corresponding sulfone in a 93% yield by oxidation with hydrogen peroxide in glacial acetic acid. 10-Triphenylsilylthiaxanthene-5,5-dioxide melted at 210-211° and the infrared spectrum indicated the presence of the sulfone grouping in the molecule.

Anal. Calcd. for $C_{31}H_{24}O_2SSi$: Si, 5.76. Found: Si, 5.59, 5.64.

---

[186] Silicon analyzes were performed by the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, _ibid._, _72_, 5767 (1950).

5. 10-Thiaxanthenone

Ten grams (0.065 mole) of *o*-mercaptobenzoic acid was slowly added to 100 ml. of concentrated sulfuric acid and 30 ml. of benzene. The resulting tan suspension was stirred for 10 hrs., then permitted to stand for an additional 10 hrs. The reaction mixture was heated on a steam bath for 1 hr., cooled, poured slowly over ice, filtered, and washed acid-free. The yellow solid was suspended in 10% sodium hydroxide, filtered and washed alkali-free to yield crude 10-thiaxanthenone, m.p. 212-214°. Recrystallization from chloroform and then glacial acetic acid, using the directions given by Gomberg and Britton,[34] gave 25.0 g. (60.1%) of yellow 10-thiaxanthenone, m.p. 213-214°, lit.[46] 213-214°.

Preparation of 10-thiaxanthenone from 2,2'-dithiodibenzoic acid, benzene, and concentrated sulfuric acid gave yields about 10% lower than by the above procedure.

6. 2-Amino-10-thiaxanthenone

a. By reduction of 2-nitro-10-thiaxanthenone

2-Nitro-10-thiaxanthenone[21] was reduced to 2-amino-10-thiaxanthenone in a 60.6% yield by the reported procedure of Mann and Turnbull,[187] m.p. 227°, lit.[45] 227°.

---

[187] F. Mann and J. Turnbull, *J. Chem. Soc.*, 747 (1951).

b. Hydroxylamine with 10-thiaxanthenone (attempted) The direct amination of 9-xanthenone has been reported.[188] 9-Xanthenone when treated with hydroxylamine and ferrous sulfate in sulfuric acid at 140-150° gave 2-amino-9-xanthenone. An adaptation of this brief procedure to 10-thiaxanthenone gave only starting material and tars.

Five grams (0.0236 mole) of 10-thiaxanthenone and 3.0 g. (0.043 mole) of hydroxylamine hydrochloride were added to 100 g. of concentrated sulfuric acid. To this suspension was slowly added 5 g. of ferrous sulfate in 6 ml. of water. There was the immediate evolution of a red gas, probably an oxide of nitrogen. The reaction mass was heated to 140-150° over a 2-hr. period and held at this temperature for 4 hrs.

After cooling to room temperature, the brown reaction mass was poured over ice, filtered and washed acid-free. The yellow-brown cake, m.p. 170-180°, was extracted with benzene to give 3.1 g. (62%) of 10-thiaxanthenone, m.p. 208-212°, identified by a mixed melting point. The residue from the benzene extract was an oily solid which resisted crystallization.

7. 2-Bromo-10-thiaxanthenone

a. Cyclization Ten grams (0.065 mole) of *o*-mercapto-

---

[188] J. F. Dé Turski. German Patent 287,756. July 14, 1914. *Friedländer*, **12**, 120 (1914). (Original available but not translated; abstracted in *C. A.*, **10**, 2128 (1916)).

benzoic acid was slowly added to 100 ml. of concentrated sulfuric acid and excess bromobenzene (14 ml., 0.134 mole). The resulting tan suspension was stirred for 10 hrs., then permitted to stand for an additional 10 hrs. The odor of sulfur dioxide was evident during the reaction. The reaction mixture was heated on a steam bath for 1 hr., cooled, poured slowly over ice, filtered, and washed acid-free. The yellow solid was thoroughly triturated with 10% sodium hydroxide, filtered and washed alkali-free to yield 11.5 g. (61%) of 2-bromo-10-thiaxanthenone, m.p. 161-163°. Acidification of the alkali extract gave 2.0 g. (18.8%) of 2,2'-dithiodibenzoic acid, m.p. 286-288°.

Recrystallization of the 2-bromo-10-thiaxanthenone from a mixture of ethanol and chloroform gave a yellow solid, m.p. 166-167°. Marsden and Smiles[35] reported a melting point of 141°. An infrared spectrum indicated the presence of a carbonyl group and of 1,2,4-trisubstitution in the molecule.

Preparation of 2-bromo-10-thiaxanthenone from 2,2'-dithiosalicyclic acid, bromobenzene, and concentrated sulfuric acid gave lower yields than by the above procedure.

b. Diazotization of 2-amino-10-thiaxanthenone To a stirred suspension of 3.0 g. (0.0135 mole) of 2-amino-10-thiaxanthenone, 10 ml. of 48% hydrobromic acid and 10 ml. of water, cooled to 0°, was added a solution of 3.0 g. of sodium nitrite in 10 ml. of water. The temperature of the mixture was maintained at 0-5° during the addition of the sodium nitrite solution. After a period of 10 min., 45 ml. of freshly prepared copper (I) bromide[189] solution in hydrobromic acid was added to the mixture. A vigorous reaction followed the addition of the catalyst, and the red diazotized mixture became brown. The mixture was subsequently heated on the steam-bath for 30 min. and allowed to cool. The supernatant liquid was decanted off, and the brown residue was treated with hydrobromic acid and washed with water.

The crude black material was dissolved in benzene and the solution was chromatographed using benzene as the eluent. From the eluate was obtained 2.0 g. (52.4%) of crude 2-bromo-10-thiaxanthenone, m.p. 163-167°. Recrystallization from ethanol gave 1.0 g. (26.2%) of product, m.p. 166-167°. A mixed melting point with the material obtained from the cyclization reaction described above showed no depression. Equations are presented in the discussion which depict all of these reactions.

8. <u>2-Chloro-10-thiaxanthenone</u>

Ten grams (0.065 mole) of o-mercaptobenzoic acid was slowly added to 100 ml. of concentrated sulfuric acid and 30

---

[189] W. C. Fernelius. Inorganic syntheses. Vol. 2. New York, N.Y., McGraw-Hill Book Co., Inc. 1946.

ml. of chlorobenzene. The resulting yellow suspension was stirred for 10 hrs., then permitted to stand for an additional 10 hrs. The reaction mixture was heated on a steam bath for 1 hr., cooled, poured slowly over ice, filtered, and washed acid-free. The yellow solid was suspended in 10% sodium hydroxide, filtered and washed alkali-free to yield 8.6 g. (53.4%) of 2-chloro-10-thiaxanthenone, m.p. 150-152°. Recrystallization from a mixture of ethanol and chloroform raised the melting point to 152-153°. An infrared spectrum indicated the presence of a carbonyl group and of 1,2,4-trisubstitution in the molecule.

Anal. Calcd. for $C_{13}H_7ClOS$: C, 63.30; H, 2.86. Found: C, 63.35, 63.41; H, 3.08; 3.15.

A Sandmeyer reaction on 2-amino-10-thiaxanthenone as in a manner analogous to that used for the preparation of 2-bromo-10-thiaxanthenone, gave a 46% yield of 2-chloro-10-thiaxanthenone, m.p. 150-151.5°, which was identical with the material obtained by the cyclization reaction.

9. 2-Methyl-10-thiaxanthenone

Ten grams (0.065 mole) of *o*-mercaptobenzoic acid was slowly added to 100 ml. of concentrated sulfuric acid and 30 ml. of toluene. The resulting yellow suspension was stirred for 10 hrs., then permitted to stand for an additional 10 hrs. The reaction mixture was heated on a steam bath for

1 hr., cooled, poured slowly over ice, filtered, and washed acid-free. The yellow solid was suspended in 10% sodium hydroxide, filtered and washed alkali-free to yield 7.9 g. (53%) of methyl-10-thiaxanthenone, melting over the range 98-110°. Several recrystallizations from ethanol did not improve this melting range. An infrared spectrum of this solid showed only carbonyl and 1,2,4-trisubstitution absorption bands.

Smiles and Davis[36] reported a melting point of 96-97° for the product they isolated from the reaction of o-mercaptobenzoic acid and toluene. 2-Methyl-10-thiaxanthenone[190] has a melting point of 123°.

10. Reaction of triphenylsilyllithium with 10-thiaxanthenone

To a stirred solution of 8.48 g. (0.04 mole) of 10-thiaxanthenone in 75 ml. of THF was added triphenylsilyllithium (0.04 mole) over a period of 1 hr. The reaction mixture was stirred at room temperature for 22 hrs. at the end of which time Color Test I[185] was slightly positive. Subsequent to hydrolysis with 10% ammonium chloride, 3.6 g. (34.6%) of hexaphenyldisilane, m.p. 360-363°, was separated by filtration.

---

[190] F. Mayer, Ber., 43, 584 (1910).

The yellow organic layer was separated, dried, and the solvent concentrated to give a yellow solid. Chromatographic purification on alumina using benzene as the eluent gave 5.9 g. (35%) of crude white solid, m.p. 175-179.5°. Two recrystallizations from a mixture of benzene and petroleum ether gave 2.0 g. (12%) of thiaxanthdryloxytriphenylsilane, m.p. 181-182.5°. An infrared spectrum of this compound showed absorption characteristic of silicon-oxygen and silicon-phenyl but no absorption characteristic of the hydroxyl group.

Anal. Calcd. for $C_{31}H_{24}OSSi$: Si, 5.95. Found: Si, 5.91, 6.14.

Further elution with benzene gave 1.0 g. (11.8%) of 10-thiaxanthenone, m.p. 210-213°, identified by a mixed melting point with starting material.

A previous reaction between triphenylsilyllithium and 10-thiaxanthenone gave a 27% yield of hexaphenyldisilane; however, no other pure products could be isolated.

11. 10-Thiaxanthenone-5-oxide (attempted)

Seven grams (0.033 mole) of 10-thiaxanthenone was dissolved in 250 ml. of refluxing absolute ethanol. Ten milliliters of 30% hydrogen peroxide was added and stirring was continued at reflux for 5 hrs. One hundred and seventy milliliters of the solvent were then removed by distillation and the remaining undistilled portion was poured into about 500 to

600 ml. of water which had been previously heated to 80°. Upon cooling, 6.5 g. (93%) of 10-thiaxanthenone, m.p. 215.5-217°, were separated. A mixed melting point with the starting material was undepressed. A second attempt at the preparation of 10-thiaxanthenone-5-oxide gave a 94% recovery of starting material.

10-Thiaxanthenone-5,5-dioxide, m.p. 187-189°; lit.[46,54] 187°, was prepared in an 87% yield by the hydrogen peroxide oxidation of 10-thiaxanthenone in glacial acetic acid.

12. 2-Bromo-10-thiaxanthenone-5,5-dioxide

a. Oxidation of 2-bromo-10-thiaxanthenone Three grams (0.0103 mole) of 2-bromo-10-thiaxanthenone was dissolved in 40 ml. of glacial acetic acid. To the solution was added 5 ml. of 30% hydrogen peroxide; the reaction mixture was heated to reflux for 4 hrs. Greenish white needles separated upon cooling, which after filtration and drying weighed 2.9 g. (87.4%) and melted at 231-233°. After one recrystallization from glacial acetic acid the white crystals melted at 233-234°. The infrared spectrum indicated the presence of the sulfone grouping in the molecule.

Anal. Calcd. for $C_{13}H_7BrO_3S$: Br, 24.73; S, 9.92. Found: Br, 24.68, 24.82; S, 10.03, 10.11.

b. Cyclization of 4-bromo-2-carboxydiphenyl sulfone Using the procedure of Ullmann and Lehner,[40] 1.0 g. (0.00293 mole) of 4-bromo-2-carboxydiphenyl sulfone[191] was heated at 185-195° with 20 ml. of concentrated sulfuric acid for 20 min. Pouring the mixture on ice gave 0.70 g. (74%) of a white solid, m.p. 232-234°. Admixture of this solid with the 2-bromo-10-thiaxanthenone-5,5-dioxide obtained above showed no depression in melting point. The infrared spectra of the compounds were identical.

13. 2-Chloro-10-thiaxanthenone-5,5-dioxide

Two grams (0.00805 mole) of 2-chloro-10-thiaxanthenone was dissolved in 30 ml. of glacial acetic acid. To the solution was added 4 ml. of 30% hydrogen peroxide and the reaction mixture heated to reflux for 4 hrs. Pouring over ice gave 1.8 g. (85%) of 2-chloro-10-thiaxanthenone-5,5-dioxide, which after one recrystallization from glacial acetic acid melted at 226°. The infrared spectrum indicated the presence of the sulfone grouping in the molecule. Ullmann and Lehner[40] prepared 2-chloro-10-thiaxanthenone-5,5-dioxide by cyclization of 4'-chloro-2-carboxydiphenyl sulfone and reported a melting point of 222°.

14. 2-Methyl-10-thiaxanthenone-5,5-dioxide

Three and seven-tenths grams (0.0164 mole) of methyl-10-

---

[191] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, *73*, 3013 (1951).

thiaxanthenone was dissolved in 25 ml. of glacial acetic acid. To the solution was added 5 ml. of 30% hydrogen peroxide and the reaction mixture heated at reflux for 4 hrs. Pouring over ice gave 4.0 g. (94.7%) of yellow crystals, m.p. 158-190°. Fractional recrystallization from ethanol gave 3.2 g. (76%) of 2-methyl-10-thiaxanthenone-5,5-dioxide, m.p. 199°, lit.[41] 199°; and 0.5 g. (12%) of a yellow powder, m.p. 158.5-160°. The latter substance gave absorption bands characteristic of the carbonyl and 1,2,4-trisubstitution. This compound is assigned the structure of 3-methyl-10-thiaxanthenone-5,5-dioxide.

Anal. Calcd. for $C_{14}H_{10}O_3S$: S, 12.38. Found: S, 12.33, 12.46.

B. Reactions of Triphenylsilyllithium with Heterocycles

1. 9-Ethylcarbazole and dibenzofuran derivatives

a. 9-Ethyl-3-carbazolyltriphenylsilane Triphenylsilyllithium, prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane, was added cautiously to a stirred solution of 5.48 g. (0.02 mole) of 3-bromo-9-ethylcarbazole[192,193] in 30 ml. of

---

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

[193] H. Gilman and R. H. Kirby, J. Org. Chem., 1, 146 (1936).

THF. The reaction was slightly exothermic and Color Test I[185] was negative shortly after complete addition. The mixture was hydrolyzed, then filtered and the residue washed carefully with ether leaving 3.0 g. (57.7%) of hexaphenyldisilane, m.p. 358-361°, identified by a mixed melting point with an authentic sample.

The light green 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 9-ethyl-3-carbazolyltriphenylsilane, m.p. 213-216°. A mixture melting point with an authentic sample[97] was undepressed.

b. <u>Reaction of triphenylsilyllithium with halogenated heterocycles</u> 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 1.

2. 10-Ethylphenothiazine derivatives

a. <u>10-Ethylphenothiazine</u> To a stirred solution of 7.5 g. (0.033 mole) of 10-ethylphenothiazine in 100 ml. of ether was added triphenylsilyllithium (0.033 mole) over a period of 1 hr. The reaction mixture was stirred at gentle reflux for 24 hrs.; at the end of which time the green solution was carbonated by pouring onto a Dry Ice-ether slurry.

Table 1. Reaction of triphenylsilyllithium with halogenated heterocycles

Reactant	Moles	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

The organic suspension was extracted with three 100-ml. portions of 10% sodium hydroxide. The chilled basic extract was slowly acidified with 5% hydrochloric acid to give 0.5 g. (5.6%) of a light green solid, m.p. 160-170°. Two recrystallizations from glacial acetic acid gave 0.15 g. (1.7%) of a green solid, m.p. 173-178°. A mixed melting point with authentic 10-ethylphenothiazine-4-carboxylic acid,[194] m.p. 178-179°, melted at 172-178°. An infrared spectrum indicated the presence of a carboxyl group in the molecule.

The organic layer after washing, drying and concentrating gave a yellow oil. Chromatographic purification on alumina gave 30% yield of 10-ethylphenothiazine, m.p. 101-104°, and 4.0 g. of a white solid, melting over the range 100-135°. An infrared spectrum of this latter substance indicated it to be a mixture of triphenylsilanol and 4-(triphenylsilyl)butanol.[147] Further elution gave only oils which were not further investigated.

b. 10-Ethylphenothiazine-5-oxide   Triphenylsilyllithium (0.018 mole) was cautiously added during 0.5 hr. to 4.37 g. (0.018 mole) of 10-ethylphenothiazine-5-oxide[195] suspended in 30 ml. of THF at 0°. After stirring for 4 hrs.,

---

[194] H. Gilman, P. R. Van Ess and D. A. Shirley, J. Am. Chem. Soc., 66, 1216 (1944).

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

two additional equivalents of triphenylsilyllithium were added and the resulting mixture agitated for 5 hrs. at 0°. The light green solution was carbonated by pouring onto a Dry Ice-ether slurry.

The organic suspension was extracted with three 100-ml. portions of 10% sodium hydroxide. The chilled basic extract was slowly acidified with 5% hydrochloric acid; only a faint turbidity appeared. None of the desired 10-ethylphenothiazine-4-carboxylic acid was isolated.

The organic layer after washing, drying and concentrating gave a greenish oil. Chromatographic purification on alumina gave 27% triphenylsilane, 35% 10-ethylphenothiazine and 11% triphenylsilanol. All of these compounds were identified by mixed melting points and comparison of their infrared spectrum with authentic samples.

c. <u>10-Ethylphenothiazine-5,5-dioxide</u> Triphenylsilyllithium (0.02 mole) was added cautiously during 30 min. to 5.18 g. (0.02 mole) of 10-ethylphenothiazine-5,5-dioxide[195,196,197] suspended in 30 ml. of THF. The color of the suspension gradually changed from brown to red. Color

---

[196] H. Gilman and R. D. Nelson, *J. Am. Chem. Soc.*, *75*, 5422 (1953).

[197] H. I. Bernstein and L. R. Rothstein, *ibid.*, *66*, 1866 (1944).

Test I[185] was slightly positive after 4 hrs. of stirring at room temperature. The solution was hydrolyzed, the water layer was washed with ether and discarded. The combined organic layers were dried over sodium sulfate and the solvent removed by distillation to give a tan solid. Several recrystallizations from ethanol gave 2.5 g. (48.3%) of recovered 10-ethylphenothiazine-5,5-dioxide, m.p. 161-163°; identified by a mixed melting point and a comparison of the infrared spectrum.

3. Preparation of 10-ethylphenothiazine derivatives

a. 3-Bromo-10-ethylphenothiazine-5-oxide   Thirty grams (0.098 mole) of 3-bromo-10-ethylphenothiazine[198] was dissolved in 660 ml. of refluxing absolute ethanol in an atmosphere of nitrogen.[124] To this solution was added 34 ml. of 30% hydrogen peroxide and stirring was continued at reflux for 5 hrs. Four hundred and 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

---

[198] H. Gilman and J. Eisch, ibid., 77, 3862 (1955).

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[198] 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 heated for 2 hrs. 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 accordance with the above procedure. The results of these preparations are given in Table 2.

Table 2. Some 10-ethylphenothiazine-5,5-dioxides

Compound oxidized	M.p. of dioxide	Moles	30% H_2O_2 ml.	Solvent (HOAc), ml.	Yield (%)	Sulfur analyses	
						Calcd.	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.

d. 2-Chloro-10-ethylphenothiazine Methyllithium[72] was added over a 1-hr. period to an ethereal solution of 58.5 g. (0.25 mole) of 2-chlorophenothiazine[199,200] at ice-bath temperature until Color Test I[185] was positive. To the orange reaction mixture was added 43 g. (0.28 mole) of freshly distilled diethyl sulfate in 200 ml. of THF. 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.

An attempt to prepare 2-chloro-10-ethylphenothiazine by the "no-solvent" method[124,128] was unsuccessful as only starting material could be isolated. Recently,[201] tetrahydro-

---

[199] Generously donated by Parke, Davis and Company, Detroit, Michigan.

[200] R. J. Galbreath and R. K. Ingham, J. Org. Chem., 23, 1804 (1958).

[201] H. Gilman and R. O. Ranck, ibid., 23, 1014 (1958).

furan was found to be a suitable solvent for the preparation of some N-substituted phenothiazine derivatives.

An attempt to prepare a Grignard reagent of 2-chloro-10-ethylphenothiazine in refluxing THF was unsuccessful. Subsequent carbonation failed to yield any of the known 2-carboxy-10-ethylphenothiazine.[202]

e. <u>2-Chloro-10-ethylphenothiazine-5-oxide</u> Ten grams (0.0383 mole) of 2-chloro-10-ethylphenothiazine was dissolved in 250 ml. of refluxing absolute ethanol in an atmosphere of nitrogen. To this solution was added 13 ml. of 30% hydrogen peroxide and stirring was continued at reflux for 5 hrs. One hundred and seventy milliliters of the solvent was then removed by distillation and the remaining undistilled portion was poured into about 500 ml. of water which had been previously heated to 80°. Upon cooling, 10.0 g. (94.3%) of a light pink solid melting at 169.5-171° crystallized. 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.

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

---

[202] R. Baltzby, M. Harfenist and F. J. Webb, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>68</u>, 2673 (1946).

f. 3-Bromo-7-nitro-10-ethylphenothiazine Several reductive halogenations have been reported in the literature.[195,198,203,204,205] The procedure employed in this preparation was essentially that used by Eisch.[198] 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 in 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 3-Bromo-10-ethylphenothiazine was nitrated using a procedure developed by Kehrmann and Zybs.[206] Ten grams (0.0326 mole) of 3-bromo-10-ethylphenothiazine was dissolved in 250 ml. of glacial acetic acid; 10 ml. of concentrated nitric acid in

---

[203] A. C. Schmalz and A. Burger, ibid., 76, 5455 (1954).

[204] H. Gilman and D. R. Swayampati, ibid., 77, 5944 (1955).

[205] T. L. Fletcher, M. J. Namkung and H. L. Pan, Chem. and Ind. (London), 660 (1957).

[206] F. Kehrmann and P. Zybs, Ber., 52, 130 (1919).

40 ml. of glacial acetic acid was added over a period of thirty minutes. The solution was allowed to stand for two days, then poured into water. The precipitated yellow solid was recrystallized from glacial 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 concentrated 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 hrs., at which time the yellow color had disappeared. The cooled mixture, now containing a pale yellow precipitate, was made strongly basic with aqueous sodium hydroxide and then 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 missing from 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 hrs. 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.

i. 3,7-Dibromo-10-ethylphenothiazine-5,5-dioxide

i. 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. At the end of this time 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 1. The pure 3,7-dibromo-10-ethylphenothiazine-5,5-dioxide melts at 217-219°.

ii. 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 according to the procedure of Saunders.[207] 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.[189] The mixture was heated to 80°, diluted with water and filtered. 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°. A mixture melting point with the material obtained by the reductive bromination of 3-bromo-10-ethylphenothiazine-5-oxide followed by oxidation (see above) was not depressed.

Other reported diazotization reactions of N-alkylated phenothiazine amines have varied in their success. A Sandmeyer reaction was carried out with 3-amino-10-ethylphenothiazine-5,5-dioxide to give 3-bromo-10-ethylphenothiazine-5,5-dioxide,[195] although the yield was low. Diazotization of 3-amino-10-methylphenothiazine was unsuccessful,[208] yet the corresponding sulfone gave a 42% yield of 3-chloro-

---

[207] K. H. Saunders. The aromatic diazo compounds. London, Edward Arnold and Co. 1949. p. 13.

[208] C. Finzi, _Gazz_. _Chim_. _Ital_., _62_, 175 (1932). (Original available but not translated; abstracted in _C_. _A_., _26_, 4338 (1932)).

10-methylphenothiazine-5,5-dioxide from the diazotized amine and cuprous chloride.[209] Apparently, the sulfone grouping enhances the diazotization possibilities.

j. 3,7-Dichloro-10-ethylphenothiazine-5-oxide A mixture of 27.8 g. (0.1 mole) of 3-chloro-10-ethylphenothiazine-5-oxide,[195,210] 100 ml. of water and 100 ml. of concentrated 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 hrs., 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.

---

[209] D. S. Antonov and E. Karakasheva, Bull. Inst. Chim. Acad. Bulgare Sci., 2, 113 (1953). (Original not available for examination; abstracted in C. A., 49, 5422 (1955)).

[210] J. W. Diehl. Some derivatives of 10-ethylphenothiazine. Unpublished M.S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1953.

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

4. Incorporation of the triphenylsilyl group into the 10-ethylphenothiazine molecule

a. 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. The reaction mass was stirred for 1 hr. at the end of which time Color Test I[185] was slightly positive. Twenty-five grams (0.0858 mole) of triphenylchlorosilane in 200 ml. of ether was added and the reaction stirred overnight at room temperature. Careful hydrolysis, separation of layers, drying and vacuum concentration of the organic layer gave a brown-white solid of indefinite melting point. Chromatographic purification on alumina gave a 60% recovery of phenothiazine and a 50% yield of triphenylsilanol; each identified by mixture melting points with authentic samples. None of the desired 10-triphenylsilylphenothiazine was isolated.

b. N-Triphenylsilyldicyclohexylamine (attempted) Triphenylsilyllithium (0.04 mole) was cautiously added to 7.25 g. (0.04 mole) of dicyclohexylamine, b.p. 60° (0.1 mm.), in 50 ml. of THF. After the addition was complete, the reaction mixture was stirred at room temperature for 24 hrs. At the end of this time Color Test I[185] was still strongly positive. 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 well, dried with sodium sulfate and concentrated to yield a green oil. Chromatography on alumina afforded only 15% triphenylsilane and 31% triphenylsilanol. None of the desired N-triphenylsilyldicyclohexylamine could be isolated.

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

c. <u>1-Triphenylsilylphenothiazine (attempted)</u> 1,10-Dilithiophenothiazine[211] 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 so as to maintain gentle reflux. After refluxing overnight, Color Test I[185] was slightly positive and the light orange mixture was cautiously hydrolyzed. The layers were separated and the ether layer dried with sodium sulfate, then concentrated to give a green-brown sticky solid. Chromatography on alumina gave a 67% recovery of phenothiazine, a 70% yield of triphenyl-

---

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

silanol and a 5% yield of hexaphenyldisiloxane, all identified by their melting points and mixed melting points with authentic samples. None of the desired 1-triphenylsilylphenothiazine was obtained.

d. 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 cautiously added 100 ml. of a THF solution of triphenylsilyllithium (0.018 mole). The reaction was slightly exothermic and Color Test I[185] was negative shortly after complete addition. The mixture was hydrolyzed then filtered and the residue was washed carefully with ether leaving 2.7 g. (57.6%) of hexaphenyldisilane, m.p. 358-360°, identified by a mixed melting point with an authentic sample.

The tan organic layer was separated, dried with sodium sulfate, filtered and the solvent removed to leave 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 bond absorption band.

Anal. Calcd. for $C_{33}H_{27}NSSi$: Si, 5.78. Found: Si, 5.55, 5.67.

e. 10-(2-Triphenylsilylethyl)phenothiazine Triphenylsilyllithium (0.04 mole) was added cautiously to a stirred solution of 10.47 g. (0.04 mole) of 10-(2-chloroethyl) phenothiazine[128] in 70 ml. of ether. After stirring at room temperature for 30 hrs., Color Test I[185] was slightly positive. The mixture was hydrolyzed, then filtered and the residue washed carefully with ether leaving 6.1 g. (58.6%) of hexaphenyldisilane, m.p. 356-358°, identified by a mixed melting point with an authentic sample.

The light-yellow organic layer was separated, dried, and the solvent removed to leave a viscous yellow oil. Boiling with ethanol and decanting gave 6.4 g. (32.9%) of 10-(2-triphenylsilylethyl)phenothiazine, m.p. 169-174°. Two recrystallizations from ethyl acetate gave a white solid, m.p. 176-177°. The ethanolic filtrate gave only oils on concentration. The infrared spectrum of 10-(2-triphenylsilylethyl)phenothiazine 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.

f. 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 cautiously added 0.04 mole of triphenylsilyllithium in 100 ml. of THF. After stirring overnight, the color of the mixture was dark-red. Some suspended white solid was noted in the reaction mass.

Color Test I[185] was negative and subsequent to hydrolysis, 5.6 g. (53.8%) of hexaphenyldisilane, m.p. 360-363°, was separated by filtration.

The red organic layer was separated, dried, and the solvents removed to leave a sticky brown oil. Boiling with a benzene-ethanol mixture, followed by chromatography of this mixture on alumina and elution with benzene 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.

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

A previous attempt[124] to prepare 3-triphenylsilyl-10-ethylphenothiazine by the reaction of triphenylsilylpotassium with 3-bromo-10-ethylphenothiazine gave only an amorphorous solid, m.p. 178-180°.

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. Possibly cleavage took place prior to oxidation since it is known[109] that the sulfone group has a stabilizing effect toward acidic cleavage.

g. <u>3,7-Bis(triphenylsilyl)-10-ethylphenothiazine-5,5-dioxide</u> 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 hrs. Color Test I[185] 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 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.

<u>Anal</u>. 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 a 17.5% yield of coupled product, slightly impure, m.p. 270-275°.

h. <u>4-Triphenylsilyl-10-ethylphenothiazine</u> Triphenylsilyllithium (0.0150 mole) was added cautiously to 5 g. (0.0135 mole) of 4-iodo-10-ethylphenothiazine[195] in 50 ml. of ether over a period of one hr. Color Test I[185] was strongly positive after the addition was completed. After stirring for 24 hrs., Color Test I[185] 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 removed to leave a viscous light yellow oil. Chromatographing on alumina with petroleum ether gave 2.3 g. (46%) of starting material, identified by the method of mixture melting points. Elution with carbon tetrachloride gave 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°. Further elution with different solvents gave only resinous oils. 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.

A previous attempt[124] to prepare this material by the reaction of triphenylchlorosilane with 4-lithio-10-ethylphenothiazine was unsuccessful. The 4-lithio-10-ethyl phenothiazine was prepared by the action of *n*-butyllithium on 10-ethylphenothiazine-5-oxide. Treatment of 10-ethylphenothiazine with *n*-butyllithium followed by reaction with triphenylchlorosilane also failed to give the desired 4-triphenylsilyl-10-ethylphenothiazine.[125]

i. Reactions of triphenylsilyllithium with halogenated 10-ethylphenothiazines These reactions are shown in Table 3.

C. Preparation of Cyclic-silicon Compounds

1. *o*-(Methyldiphenylsilyl)benzoic acid

Methyldiphenyl-(*o*-tolyl)silane,[146] 1.8 g. (0.0062 mole), was suspended in a mixture of 100 ml. of glacial acetic acid, 30 ml. of acetic anhydride and 3 ml. of concentrated sulfuric acid were added, followed by 10 g. (0.1 mole) of anhydrous chromium trioxide in three portions during 10 minutes. The temperature was held at 20° for 20 minutes and then the dark green mixture was poured rapidly onto crushed ice and stirred

Table 3. Reactions of triphenylsilyllithium with halogenated 10-ethylphenothiazines

Reactant: 10-ethylphenothiazine derivative	Moles	Solvent	Yield (%) $Ph_3SiSiPh_3$	Yield (%) coupled product	M.p.	Silicon analyses Calcd.	Silicon analyses 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	273-276.5°	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.

for several minutes. After filtering, the residue was taken up in ether and extracted with 2% sodium hydroxide. Slow acidification of the alkali extract with 5% hydrochloric acid gave 0.8 g. (40.6%) of crude o-(methyldiphenylsilyl)benzoic acid, m.p. 187-190°. Two recrystallizations from a benzene-petroleum ether mixture gave 0.4 g. (20.3%) of white solid, m.p. 193-194°. The infrared spectrum indicated a carbonyl and a silicon-phenyl absorption band.

Anal. Calcd. for $C_{20}H_{18}O_2Si$: Si, 8.82. Found: Si, 8.76, 8.78.

2. o-(Triphenylsilyl)benzoic acid (attempted)

a. Oxidation of triphenyl-(o-tolyl)silane Triphenyl-(o-tolyl)silane,[212] 1.80 g. (0.0052 mole), was suspended in a mixture of 100 ml. of glacial acetic acid; 30 ml. of acetic anhydride and 3 ml. of concentrated sulfuric acid were added, followed by 10 g. (0.1 mole) of anhydrous chromium trioxide in three portions during 10 minutes. The temperature was held at 20° for 15 minutes, and then the dark green suspension was poured rapidly onto crushed ice and stirred for several minutes. After filtering, the residue was taken up in ether and extracted with 2% sodium hydroxide. Slow acidification of the

---

[212] H. Gilman and G. N. R. Smart, J. Org. Chem., 15, 720 (1950).

alkali extract with 5% hydrochloric acid gave only a trace of a gummy solid. Washing of the organic layer with water, drying and removal of the solvent left only a tarry residue which resisted crystallization.

Several other attempts were made to oxidize triphenyl-(o-tolyl)-silane making minor variations in the temperature and stirring time. These were uniformly unsuccessful.

The oxidation of a para-methyl group to the corresponding carboxylic acid using chromium trioxide has been accomplished.[213,214] However, oxidation of an ortho-methyl group gave only negligible yields of the desired acid.[215]

b. Reaction of the lithium salt of o-lithiobenzoic acid with triphenylchlorosilane The following experiment is an adaptation of a published procedure.[216]

A suspension of 10.05 g. (0.05 mole) of o-bromobenzoic acid and 100 ml. of ether was cooled to -70° with the aid of a Dry Ice-acetone bath. There was added under a nitrogen atmosphere, with vigorous stirring, 0.1 mole of n-butyllithium in 130 ml. of ether over a 5-min. period. The reaction mix-

---

[213] H. Gilman and C. G. Brannen and R. K. Ingham, J. Am. Chem. Soc., 78, 1689 (1956).

[214] D. Lewis and G. Gainer, ibid., 74, 2931 (1952).

[215] R. A. Benkeser and H. R. Krysiak, ibid., 76, 599 (1954).

[216] H. Gilman and C. E. Arntzen, ibid., 69, 1537 (1947).

ture was stirred for an additional 10 min. after which time 29.5 g. (0.1 mole) of triphenylchlorosilane in 200 ml. of ether was added over a 20-min. period, while maintaining a bath temperature of -70°. Color Test I[185] was positive after the addition was complete. After stirring for 2 hrs. at -60°, the reaction mixture was permitted to stir and slowly warm to room temperature over a period of 16 hrs. Color Test I[185] was still slightly positive.

The reaction mixture was hydrolyzed with dilute ammonium chloride; the layers were separated, and the ethereal layer extracted with 3% sodium hydroxide. The chilled basic extract was acidified carefully with 5% hydrochloric acid. The resulting precipitate, after several recrystallizations from cyclohexane, was identified as o-bromobenzoic acid, m.p. 145-148°; the recovery was 1.7 g. (17%).

The organic layer was washed well with water, dried and the solvents concentrated to give a yellowish oily solid. Chromatographic separation on alumina gave only 56% triphenylsilanol and 3.1% hexaphenyldisiloxane, identified by mixed melting points and a comparison of their infrared spectra.

c. Reaction of triphenylsilyllithium with o-bromobenzoic acid Triphenylsilyllithium (0.04 mole) was added to 4.05 g. (0.02 mole) of o-bromobenzoic acid suspended in 50 ml. of ether at room temperature. The reaction was slightly exothermic and Color Test I[185] was negative after complete addition. The mixture was hydrolyzed, then filtered and the residue was washed with ether leaving 7.4 g. (71%) of hexaphenldisilane, m.p. 356-360°, identified by a mixed melting point with an authentic sample.

Extraction of the organic layer with 3% sodium hydroxide and careful acidification of the chilled basic extract gave 24.7% recovery of o-bromobenzoic acid, m.p. 144-147°; a mixed melting point with the starting material was undepressed.

The organic layer after washing and drying was concentrated to give a green oil. No crystalline products could be isolated by chromatographing this oil on alumina.

A repeat of this experiment using three equivalents of triphenylsilyllithium gave similar results except that the yield of hexaphenyldisilane was only 40.6%.

3. Reaction of diphenylsilane with thiaxanthene

The diphenylsilane was prepared by the reduction of diphenyldichlorosilane (Dow Corning) with lithium aluminum hydride according to the procedure of Benkeser and co-workers[84] except that the solvent employed was tetrahydrofuran instead of ether. With the application of this slightly modified procedure the yield of product was raised from 76% reported earlier[84] to 89% based on the chlorosilane, b.p. 65-66° (0.05 mm.), n_D^{20} 1.5783. A mixture of 17.0 g. (0.0858 mole) of thiaxanthene and 15.8 g. (0.0858 mole) of diphenylsilane[84] was refluxed (temperature was approximately 270-280°) without added solvent for seven days. During this time a slow evolution of hydrogen sulfide took place. At the end of seven days the evolution of hydrogen sulfide had essentially ceased.

The pale yellow oil was transferred to a distillation flask and distilled at reduced pressure. The first fraction [1.3 g., b.p. 72-85° (0.15 mm.)] was identified as diphenylsilane (8.5% recovery) by its infrared spectrum. The second fraction [8.0 g., b.p. 120-130° (0.15 mm.)] crystallized to a solid melting at 130-132°. This was identified as thiaxanthene by a mixed melting point (47% recovery). The third and fourth fractions were combined [4.3 g., b.p. 130-155° (0.2 mm.)], and the infrared spectrum of the oily solid indicated the presence of triphenylsilane (19.3% yield).[217] Refluxing of a small portion of this oily solid with ethanolic sodium hydroxide gave hexaphenyldisiloxane, m.p. 222-226°, mixed melting point undepressed. The last fraction [3.0 g., b.p. 215-230° (0.2 mm.)] was a waxy solid with a slight yellow color. The solid was dissolved in hot petroleum ether and chromatographed on alumina. Elution with the same solvent gave 2.0 g. of material melting over the range 148-175°.

---

[217] The triphenylsilane may have been formed by the disproportionation of diphenylsilane. See H. Gilman and D. H. Miles, J. Org. Chem., 23, 326 (1958), and related disproportionation references reported therein.

Treatment of this product with boiling ethanol left 0.4 g. (1.3%) of crude tetraphenylsilane, m.p. 220-226°; a mixed melting point with an authentic sample was undepressed.

Concentration of the ethanol gave 1.0 g. (3.4%) of a white solid, m.p. 148-152°. Three recrystallizations from ethanol gave a compound, thought to be 5,5-diphenyl-10H-dibenzosilin, m.p. 152-153°. The infrared spectrum showed the presence of the silicon-phenyl and methylene absorption bands in the molecule.

Anal. Calcd. for $C_{25}H_{20}Si$: C, 86.20; H, 5.78. Found: C, 86.75, 87.00; H, 5.73, 5.79.

In a thermal stability test,[140] the compound turned pale yellow at 380°, light brown at 400°, micro bubbles at 410° and volatilized at 440° without decomposition.

D. Reactions of Si-H Compounds with Carbonyl Containing Compounds

1. Reaction of a diphenylsilane with 10-thiaxanthenone

a. At 230° Nine and two-tenths grams (0.05 mole) of diphenylsilane and 10.6 g. (0.05 mole) of 10-thiaxanthenone were heated to 220-230° over a 1-hr. period and held at this temperature for 2 hrs. Upon cooling to room temperature, a yellow solid crystallized which was filtered to give 9.8 g. (92.4%) of 10-thiaxanthenone, m.p. 212-214°, identified by a mixed melting point with an authentic sample.

b. <u>At reflux</u> Twenty-one and three-tenths grams (0.1 mole) of 10-thiaxanthenone and 18.4 g. (0.1 mole) of diphenylsilane were heated to reflux over a 1-hr. period. Boiling started at 260°, then the temperature rose rapidly to about 310°. The yellow color changed to red and some white solid sublimed. The temperature slowly dropped to 260° where it was held for 20 hrs. Upon cooling to room temperature, a red solid formed which was dissolved in hot petroleum ether. Chromatography of this petroleum ether solution on alumina gave a pink-red solid, m.p. 124-128°. Recrystallization from ethanol (Norit) gave 7.6 g. (38.4%) of thiaxanthene, m.p. 128-130°, identified by a mixed melting point and comparison of the infrared spectrum with an authentic specimen.

No other solid could be isolated from the column by further elution with various solvents.

c. <u>At reflux for various lengths of time</u>

<u>time</u>	<u>yield (%)</u>
3 days	35.4
20 hrs.	38.4[a]
12 hrs.	63.6[a,b]
4 hrs.	37.4

(a) In these experiments approximately 2.0 g. of a pink solid, melting at 315-320°, containing no silicon and not soluble in the common solvents, was isolated. This might possibly be dithioxanthyl, m.p. 325°.[218] The infrared spectrum was inconclusive.

(b) An experiment was conducted utilizing a nitrogen atmosphere; a 61% yield of reduced product was realized.

2. Reaction of diphenylsilane with benzophenone

a. At 220-230°[173] Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.1 g. (0.05 mole) of benzophenone were heated for 2 hrs. at 220-230°. Distillation gave an 86% recovery of starting material.

b. At 230-235° This experiment was a repeat of the experiment described above except that the temperature was held at 230-235° for 4 hrs. Distillation gave a 5.5% recovery of starting materials, identified by their infrared spectra. The distillation residue was taken up in petroleum ether, filtered, and concentrated to give 13.8 g. (75.4%) of benzhydryloxydiphenylsilane, m.p. 78-80°. Recrystallization from ethanol raised the melting point to 80-81.5°. A mixed melting point with an authentic sample[173] showed no depression.

c. At reflux This experiment was a repeat of part (a) except that the temperature was permitted to go to reflux. At approximately 265°, the temperature rose quickly to 340°

---

[218] A. Schönberg and A. Mustafa, J. Chem. Soc., 657 (1945).

then reverted to 265° where it was held for 12 hrs. Distillation of the viscous oil gave 3.1 g. (36.9%) of diphenylmethane, b.p. 68-70° (0.025 mm.), n_D^{18} 1.5650, m.p. 23.5-25°. Commercially available diphenylmethane has a m.p. of 24-26° and a n_D^{16} 1.5696. An infrared spectrum of this material was identical with that of an authentic specimen. Chromatography of the waxy distillation residue gave only oils, an infrared spectra of which showed the silicon-oxygen absorption band.

3. Reaction of diphenylsilane

a. With 9-fluorenone Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.0 g. (0.05 mole) of 9-fluorenone were heated to reflux over a 1-hr. period. At 270°, a violent exothermic reaction took place and the temperature rose rapidly to 330°. The color changed from yellow to red and a white solid sublimed. The temperature reverted to 270° where it was held for 12 hrs.

The brown cake was dissolved in petroleum ether and chromatographed on alumina giving 5.0 g. (60.3%) of a white solid, m.p. 101-108°. Two recrystallizations from ethanol gave 3.1 g. (37.3%) of fluorene, m.p. 112-115°; a mixed melting point was undepressed. Further elution of the column gave only oils which could not be crystallized.

b. With 9-xanthenone Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.8 g. (0.05 mole) of

9-xanthenone were heated to reflux over a 1-hr. period. Boiling started at 260°, then the temperature rose rapidly to 320°. It slowly dropped back to 260° where it was held for 12 hrs.

Dissolution of the brown cake in petroleum ether and chromatography on alumina gave 2.5 g. (27.5%) of xanthene, m.p. 101-103°, a mixed melting point was not depressed. Further elution of the column failed to give any crystalline materials.

c. With anthraquinone Ten and four-tenths grams (0.05 mole) of anthraquinone and 18.4 g. (0.1 mole) of diphenylsilane were heated to reflux (about 275°). The temperature rose rapidly to a maximum of 360° then slowly reverted to 275° and maintained at this value for 12 hrs. The greenish brown reaction mass was dissolved in benzene, filtered and concentrated to give a bright yellow solid, m.p. 205-216°. Two recrystallizations from ethanol gave 4.0 g. (44.8%) of anthracene, m.p. 216-217.5°. A mixed melting point with an authentic sample was not depressed.

d. With phenanthraquinone Ten and four-tenths grams (0.05 mole) of phenanthraquinone and 18.4 g. (0.1 mole) of diphenylsilane were heated to reflux (about 270°) and maintained for 12 hrs. There was no exothermic reaction and the reaction mass gradually assumed a deep red appearance. Distillation gave only a 5% recovery of diphenylsilane. Chromatography of the distillation residue on alumina with benzene gave a 31.8% recovery of phenanthraquinone, m.p. 204-207°. Further elution gave only tars and gums which resisted crystallization.

e. With benzhydrol Nine and two-tenths grams (0.05 mole) of benzhydrol and 9.2 g. (0.05 mole) of diphenylsilane were heated to reflux, the temperature was about 170°, and held for 12 hrs. The viscous, clear oil was distilled to give 9.0 g. (97.8%) of diphenylsilane, b.p. 104-105° (3.5 mm.) n_D^{20} 1.5783. The infrared spectrum showed the presence of a silicon-hydrogen absorption band. The distillation residue gave a 60% yield of benzhydryl ether which after recrystallization from ethanol melted at 109-111°, a mixed melting point with an authentic specimen was undepressed.

f. With acetophenone Six grams (0.05 mole) of acetophenone and 9.2 g. (0.05 mole) of diphenylsilane were heated to reflux (about 220°) and held at this temperature for 12 hrs. Distillation of the viscous oil gave a 40% recovery of acetophenone, b.p. 60-62° (0.5 mm.), n_D^{20} 1.5349; and a 70% yield of recovered diphenylsilane, b.p. 78-80° (0.5 mm.) n_D^{20} 1.5841. The infrared spectrum of each material was identical with that of an authentic sample.

g. With 4-chlorobenzophenone Nine and two-tenths grams (0.05 mole) of diphenylsilane and 10.8 g. (0.05 mole) of 4-chlorobenzophenone were heated to reflux (about 270°).

An exothermic reaction took place with the temperature reaching a maximum of 330° before it slowly dropped to 270°.

Distillation gave 6.9 g. (68%) of colorless 4-chlorodiphenylmethane, b.p. 122-123.5° (2.2 mm.), n_D^{20} 1.5854. The infrared spectrum indicated the absence of a carbonyl absorption band and the spectrum was, in general, quite similar to that of diphenylmethane.

Chromatography of the distillation residue on alumina and elution with benzene gave 0.7 g. (7.1%) of crude white solid, m.p. 170-175°. Two recrystallizations from a mixture of benzene and petroleum ether gave 0.5 g. (5.2%) of hexaphenylcyclotrisiloxane, m.p. 187-189°. A mixture melting point with an authentic sample[143] was not depressed.

h. With 4-methylbenzophenone Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.8 g. (0.05 mole) of 4-methylbenzophenone were heated to reflux (about 275°) over a 1-hr. period. The temperature rose rapidly to 330° and the colorless oil became yellow. The temperature slowly dropped to 275° where it was maintained for 12 hrs.

Distillation afforded 3.5 g. (38.5%) of 4-methyldiphenylmethane, b.p. 87-89° (0.35 mm.), n_D^{20} 1.5683. The infrared spectrum of the liquid was superimposable with that of an authentic sample (n_D^{20} 1.5682).

Chromatography of the distillation residue failed to yield any crystalline products.

i. With quinoline Nine and two-tenths grams (0.05 mole) of diphenylsilane was mixed with 6.5 g. (0.05 mole) of freshly distilled quinoline in a nitrogen atmosphere. The clear reaction mass was heated to reflux, about 260°, and held at this temperature for 12 hrs. There was no sudden exothermic reaction. Distillation of the light yellow oil gave 4.9 g. (75.4%) of quinoline, b.p. 60° (0.01 mm.), n_D^{20} 1.6144 and 8.3 g. (90%) of diphenylsilane, b.p. 68° (0.01 mm.), n_D^{20} 1.5827. The infrared spectrum of each material was identical with that of an authentic sample.

j. With phenanthridine Nine and two-tenths grams (0.05 mole) of diphenylsilane and 8.95 g. (0.05 mole) of phenanthridine were heated to reflux (about 250°) and held at this temperature for 12 hrs. There was no exothermic reaction noted. Distillation of the viscous, yellow oil gave a 20% recovery of diphenylsilane and a 31.3% recovery of phenanthridine, b.p. 130-135° (0.01 mm.), m.p. 106-108°. Chromatography of the waxy, brown distillation residue on alumina gave oils which could not be crystallized or further purified.

4. Heating of benzhydryloxydiphenylsilane

Twelve and eight-tenths grams (0.035 mole) of benzhydryloxydiphenylsilane was heated, without added solvent or catalyst, up to 270° and maintained for 12 hrs. Distillation gave 2.6 g. (44.2%) of diphenylmethane, b.p. 93-95° (2 mm.), m.p. 25-26°, $n_D^{17.5}$ 1.5793. The infrared spectrum was superimposable with that of an authentic sample.

Chromatography of the distillation residue on alumina gave 0.3 g. (4.9%) of benzhydryl ether, m.p. 108-109.5°. Further elution failed to give any crystalline materials. The oils showed silicon-phenyl and silicon-oxygen absorption bands in the infrared.

5. Reaction of phenylsilane with 10-thiaxanthenone

Phenylsilane,[84] 5.4 g. (0.05 mole) and 10.6 g. (0.05 mole) of 10-thiaxanthenone were heated slowly to reflux temperature for 8 hrs. then it was permitted to cool to room temperature. Petroleum ether was added and the resulting slurry filtered to give 10.1 g. (95.4%) of recovered 10-thiaxanthenone, m.p. 213-215°; a mixed melting point with the starting material was undepressed.

6. Reaction of triphenylsilane

a. With benzophenone Thirteen grams (0.05 mole) of triphenylsilane[219] and 9.1 g. of benzophenone (0.05 mole) were heated to reflux (about 280°) for 12 hrs. Dissolution of the reaction mass in petroleum ether, filtering and concentrating

---

[219] H. Gilman and H. W. Melvin, Jr., *J. Am. Chem. Soc.*, *71*, 4050 (1949).

gave 10.5 g. (47.6%) of benzhydryloxytriphenylsilane, m.p. 81-83°. A mixed melting point with an authentic sample[62] was undepressed.

b. With bromobenzene Fifty grams (0.318 mole) of bromobenzene was added to 91 g. (0.3498 mole) of triphenylsilane and the reaction mass heated to reflux for 15 hrs. There was no color change during the reaction. Distillation gave a 79% recovery of bromobenzene, n_D^{17} 1.5613. Chromatography of the distillation residue afforded an 85% yield of triphenylsilane, m.p. 46-48°, and a trace of hexaphenyldisiloxane, m.p. 225-228°. There was no triphenylbromosilane isolated; nor any benzene, the expected hydrogenolysis product of bromobenzene.

c. With anthraquinone Thirteen grams (0.05 mole) of triphenylsilane and 5.2 g. (0.025 mole) of anthraquinone were heated to reflux (about 235-240°) and held there for 12 hrs. Upon cooling to room temperature, a yellow gum remained. Several recrystallizations from ethanol gave 3.0 g. (25.6%) of pale yellow solid, m.p. 120-122°. An infrared spectrum of this compound showed silicon-phenyl, silicon-oxygen and carbonyl bands in the molecule.

Anal. Calcd. for $C_{32}H_{24}O_2Si$: Si, 5.98. Found: Si, 5.82, 6.02.

The analysis and infrared imply that triphenylsilane added to only one carbonyl grouping.

IV. DISCUSSION

A. Chemistry of the Thiaxanthene System

The principal handicap in the investigation of the chemistry of the thiaxanthene system rests with the relative difficulty in preparing the parent heterocycle on a large scale. The standard procedure in the preparation of thiaxanthene is to reduce 10-thiaxanthenone with hydrogen iodide and red phosphorus, or by lithium aluminum hydride. The 10-thiaxanthenone is in turn synthesized by the reaction of o-mercaptobenzoic acid with benzene in sulfuric acid. It was felt that perhaps thiaxanthene could be synthesized by a thionation reaction, sometimes referred to as the Ferrario reaction. Several attempts were made to prepare thiaxanthene by the reaction between diphenylmethane and sulfur in the presence of anhydrous aluminum chloride; however, the reaction mixture generally turned dark and afforded only intractable tars. Ziegler[220] indicated that diphenylmethane and sulfur heated to 250° gave mostly tetraphenylethylene. Radziewanowski[221] found that diphenylmethane and aluminum chloride yielded anthracene, with some benzene being observed. The possibility of complex reactions occurring is rather substantial if

---

[220] J. H. Ziegler, Ber., 21, 779 (1888).

[221] C. Radziewanowski, ibid., 27, 208 (1894).

the two above reactions were run together in the same flask. Due to the unfavorable experimental results and the discouraging literature reports this particular line of endeavor was abandoned.

Cyclization of o-mercaptobenzoic acid with mono-substituted benzene derivatives yields 10-thiaxanthenone compounds in which the position of the substituent is unknown.[35,36] This condensation also occurs using 2,2'-dithiosalicyclic acid instead of o-mercaptobenzoic acid.[37] Christopher and Smiles[38] in a review of the preparative methods for 10-thiaxanthenone suggested a sulfenic acid mechanism for this cyclization reaction. o-Mercaptobenzoic acid is first oxidized by sulfuric acid to the corresponding sulfenic acid which condenses with benzene to yield the intermediate 2-carboxydiphenyl sulfide. Acid-catalyzed ring closure would then yield the 10-thiaxanthenone compound. Very little work was done to elucidate the positions of the substituents in the 10-thiaxanthenone derivatives.

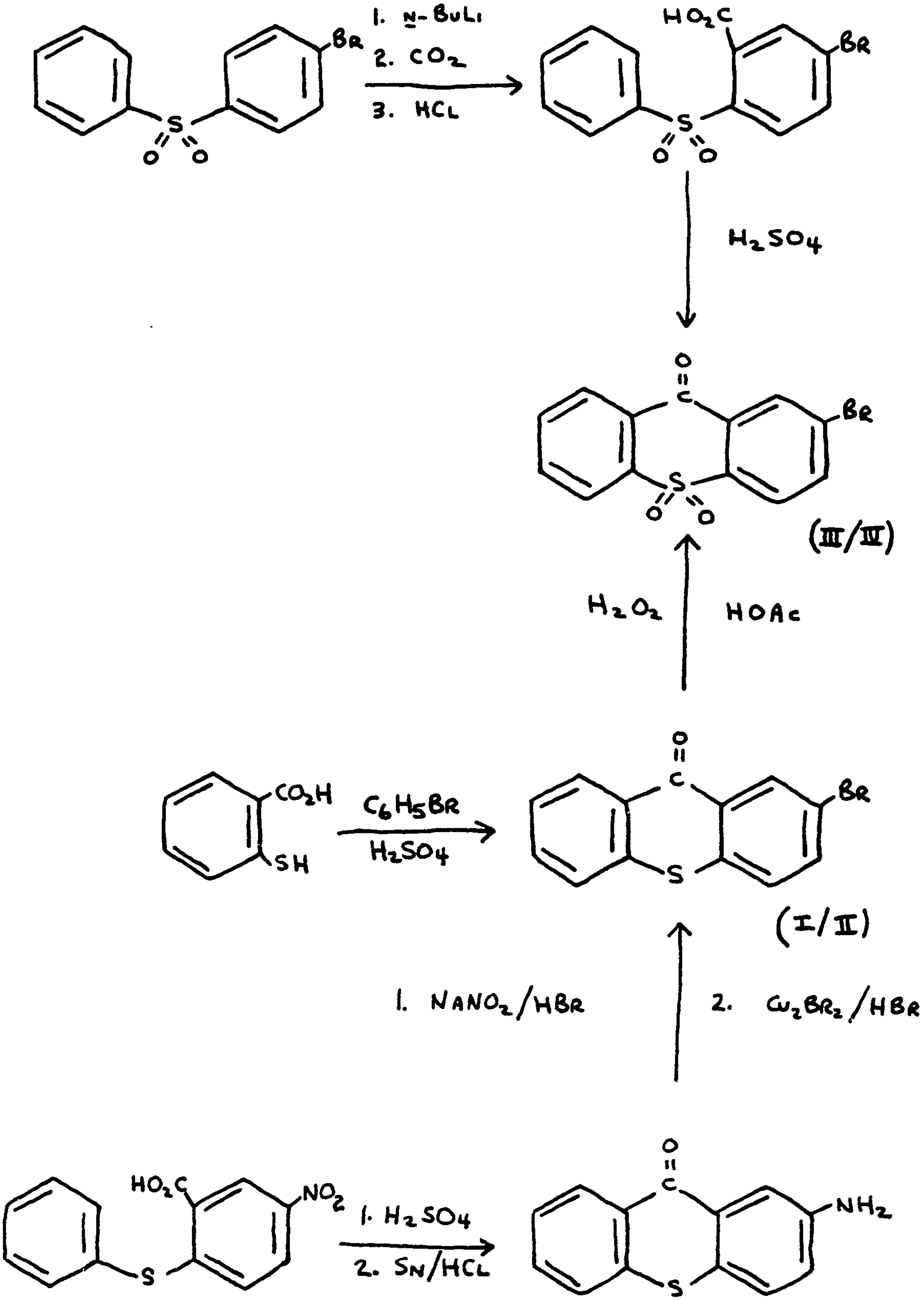
Several years later, Roberts and Smiles[43] demonstrated that the methoxy group was in the 2-position when anisole condensed with o-mercaptobenzoic acid. Archer and Suter,[14] in their investigation of 1-alkylamino and 1-dialkylaminoalkylamino-10-thiaxanthenone derivatives suggested a modified mechanism for the condensations. They contended that the initial step in the reaction is the oxidation of the mercapto group to the disulfide. Protonation of the disulfide occurs and condensation of the sulfur function with the aromatic compound takes place.

Reaction of bromobenzene with o-mercaptobenzoic acid gave a bromo-10-thiaxanthenone(I), m.p. 166-167°, which does not agree with that of 141°, reported for the bromo-10-thiaxanthenone prepared by Smiles[35] in an analogous manner. The bromine atom was shown to be in the 2-position by the following sequence of reactions. A Sandmeyer reaction on 2-amino-10-thiaxanthenone gave 2-bromo-10-thiaxanthenone(II) which showed no depression in melting point when admixed with the above bromo-10-thiaxanthenone(I). Additional evidence was furnished by the infrared absorption measurements which showed 1,2,4-trisubstitution in bromo-10-thiaxanthenone. This indicated that the bromine atom was probably not in the 1- or 4-positions.

The position of the bromine substituent was also established by another route. Metalation of 4-bromodiphenyl sulfone with n-butyllithium followed by carbonation gave 4-bromo-2-carboxydiphenyl sulfone.[191] No halogen-metal interconversion was observed in this reaction although Truce and Amos did observe a trace of o-benzenesulfonylbenzoic acid from this reaction. Cyclization of the 4-bromo-2-carboxydiphenyl sulfone in concentrated sulfuric acid gave 2-bromo-10-thiaxanthenone-5,5-dioxide(III). This sulfone was found to be identical with the substance(IV) obtained by the oxidation of bromo-10-thiaxanthenone(I) with 30% hydrogen peroxide in glacial acetic acid. A summary of the reactions is shown in the equations on page 101.

Chloro-10-thiaxanthenone was prepared by the reaction of chlorobenzene with o-mercaptobenzoic acid in concentrated sulfuric acid. Diazotization of 2-amino-10-thiaxanthenone followed by treatment with copper(I) chloride in hydrochloric acid yielded 2-chloro-10-thiaxanthenone and this compound was identical with that obtained from the cyclization reaction. Oxidation of 2-chloro-10-thiaxanthenone with 30% hydrogen peroxide in glacial acetic acid gave 2-chloro-10-thiaxanthenone-5,5-dioxide, m.p. 226°. Ullmann and Lehner[40] prepared this sulfone by the ring closure of 4'-chloro-2-carboxydiphenyl sulfone and reported a melting point of 222°.

When toluene was condensed with o-mercaptobenzoic acid, a mixture was obtained which melted over a range of 98-110° even after repeated recrystallizations. Oxidation of this mixture gave a 76% yield of 2-methyl-10-thiaxanthenone-5,5-dioxide, m.p. 199°. Truce and Norman[41] prepared 2-methyl-10-thiaxanthenone-5,5-dioxide by cyclization of a mixture of *ortho* carboxy sulfones and found a melting point of 197-198°. A second substance was obtained from the oxidation of the crude methyl-10-thiaxanthenone, it melted at 158.5-160°. The analysis was in agreement with a methyl-10-thiaxanthenone-


Br
1. n-BuLi
2. CO2
3. HCl
S
O
O
HO2C
Br
H2SO4
O
C
Br
S
(III/IV)
H2O2
HOAc
CO2H
SH
C6H5Br
H2SO4
Br
(I/II)
1. NaNO2/HBr
2. Cu2Br2/HBr
HO2C
NO2
1. H2SO4
2. Sn/HCl
NH2

5,5-dioxide and since the infrared indicated 1,2,4-trisubstitution in the compound, the methyl group was thought to be in the 3-position.

The structure of the substituted 10-thiaxanthenone indicates that sulfide formation is probably the initial step in a mechanism. Reaction of _o_-mercaptobenzoic acid with 4-methylanisole gave only one 10-thiaxanthenone, namely, 1-methyl-4-methoxy-10-thiaxanthenone.[43] To account for only one product in this condensation reaction, sulfide formation must be the first step. It is well known that mercaptans are readily oxidized to disulfides in sulfuric acid;[14,222] so the possibility of a sulfenic acid intermediate appears doubtful. A possible mechanism for these _o_-mercaptobenzoic acid cyclizations in concentrated sulfuric acid is shown in the equations on page 103.

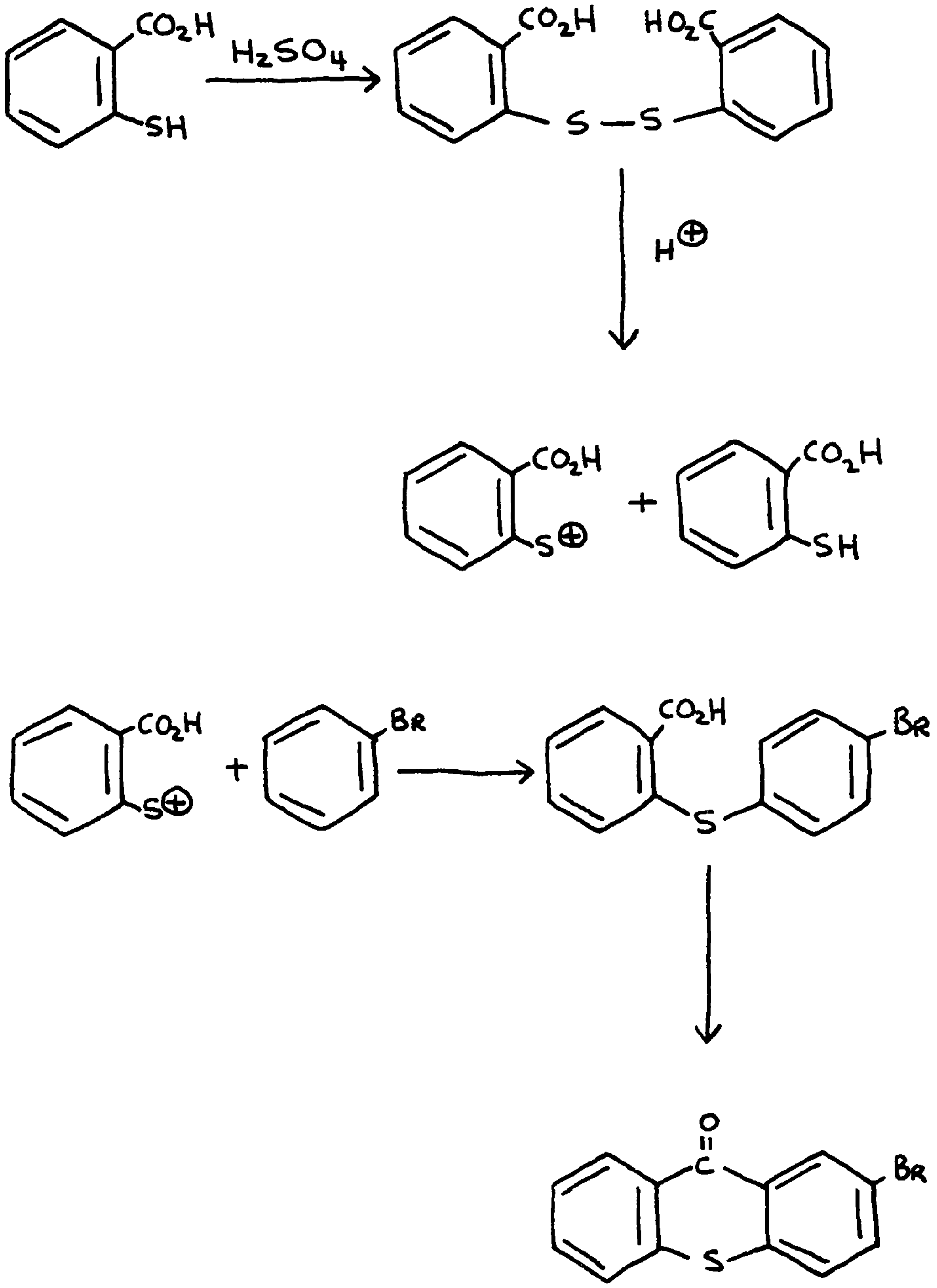
The mercapto group is oxidized to the disulfide, a one electron transfer reaction;[223] this disulfide immediately decomposes forming a sulfenium ion.[224] An electrophilic attack by the sulfenium ion on bromobenzene would occur in the

---

[222] J. Stenhouse, _Ann_., _149_, 250 (1869).

[223] R. B. Woodward and R. H. Eastman, _J_. _Am_. _Chem_. _Soc_., _68_, 2229 (1946).

[224] N. Kharasch, _J_. _Chem_. _Educ_., _33_, 585 (1956). This article contains an extensive and splendid bibliography on sulfenium ions.


CO₂H
SH
H₂SO₄
CO₂H
HO₂C
S — S
H⊕
CO₂H
S⊕
+
CO₂H
SH
CO₂H
S⊕
+
Br
CO₂H
S
Br
O
C
S
Br

electron dense para-position. The para condensation is preferred over the ortho because of the more favorable steric conditions. Acid-catalyzed ring closure would give the observed 2-substituted 10-thiaxanthenone. The principal by-product, 2,2'-dithiosalicyclic acid, is also accounted for by this scheme.

An attempt to aminate 10-thiaxanthenone directly by treatment with hydroxylamine and ferrous sulfate in sulfuric acid in an analogous manner to that used for 9-xanthenone was unsuccessful. The patent[188] reports that the direct amination of 9-xanthenone gave 2-amino-9-xanthenone, m.p. 174°. The melting point of authentic 2-amino-9-xanthenone is 205°; none of the mono-aminated-9-xanthenones have melting points in the neighborhood of 174°.[225]

The inability to synthesize 10-thiaxanthenone-5-oxide by the peroxide oxidation of 10-thiaxanthenone might possibly be attributed to the large dipole moment of 10-thiaxanthenone.[51] This may also explain the failure of 10-thiaxanthenone to react with ordinary carbonyl reagents. This charge separation in 10-thiaxanthenone prevented a reaction with sodium azide in sulfuric acid.[50] Conversion to 10-thiaxanthenone-5,5-dioxide destroys this charge separation, restoring the activ-

---

[225] S. Wawzonek. Xanthones, xanthenes, xanthydrols, and xanthylium salts. In R. Elderfield, ed. Heterocyclic compounds. Vol. 2, pp. 419-500. New York, N.Y., John Wiley and Sons, Inc. 1951.

ity of the carbonyl group. This dioxide then reacted smoothly in the Schmidt reaction to give the same lactam obtained by the Beckmann rearrangement of the oxime of the sulfone.[46]

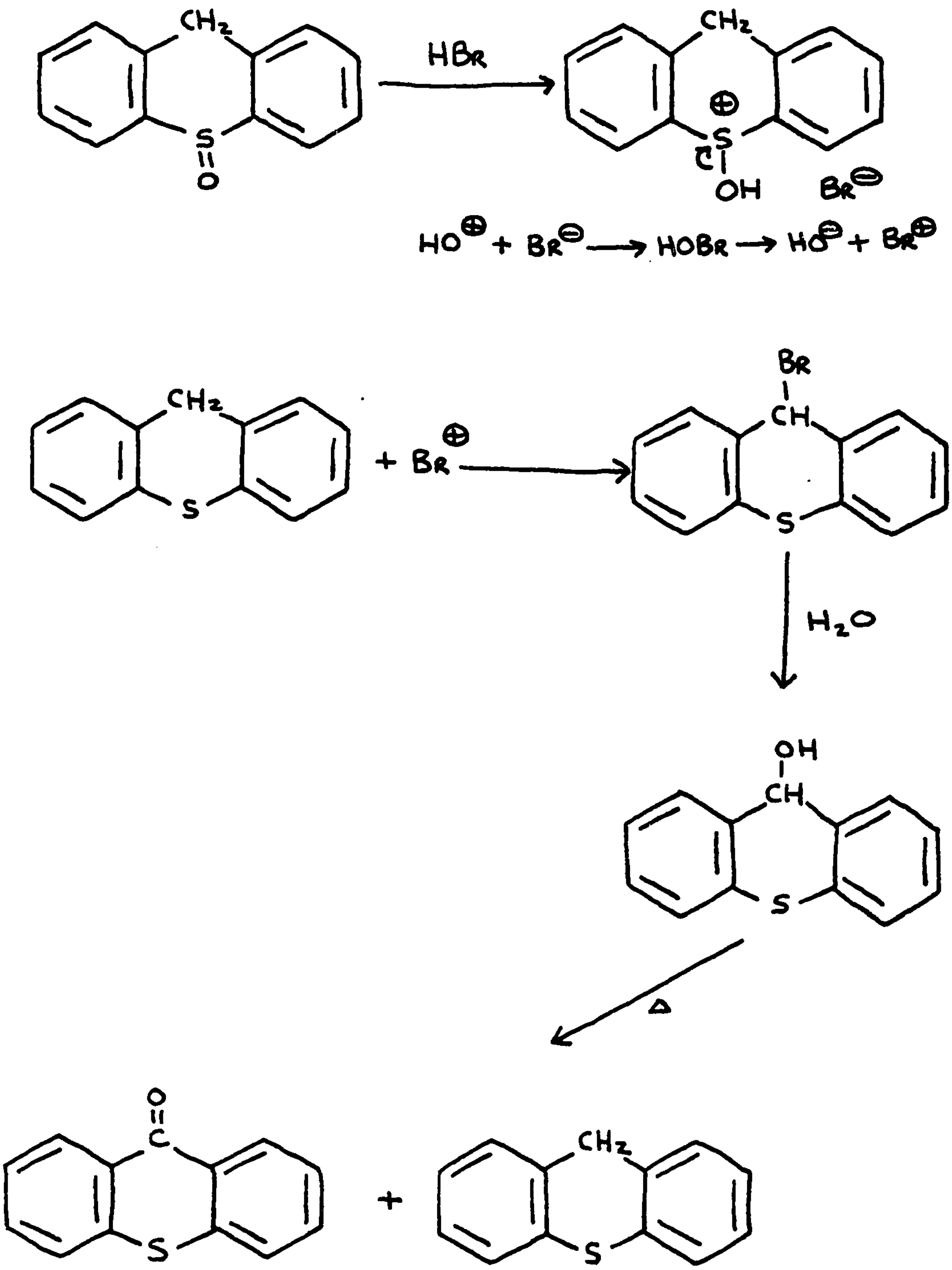
Carbonyl compounds are generally reduced to carbinols by lithium aluminum hydride; however, action of this reducing agent on 10-thiaxanthenone yielded thiaxanthene.[18] There have been other instances of this hydrogenolysis reported in the literature, for example, o-aminobenzyl alcohol gives a 53% yield of o-toluidine.[226] A high electron density at the substituted methylene group seems to favor the hydrogenolysis.

Reaction of thiaxanthene-5-oxide with dilute hydrobromic acid gave an equimolar ratio of 10-thiaxanthenone and thiaxanthene. A mechanistic interpretation of this reaction is depicted in the equations on page 106.

Initial protonation of the sulfoxide with subsequent reduction would form one molar equivalent of bromine which would then attack thiaxanthene to yield the unstable 10-bromothiaxanthene. In an analogous reaction with hydrochloric acid, Hilditch and Smiles[24] were actually able to isolate 10-chlorothiaxanthene for short periods of time. Hydrolysis of 10-bromothiaxanthene, under the conditions of the experiment, would yield 10-thiaxanthenol which could readily dispropor-

---

[226] L. H. Conover and D. S. Tarbell, J. Am. Chem. Soc., 72, 3586 (1950).


CH₂
S
O
HBr
CH₂
⊕
S
OH
Br⊖
HO⊕ + Br⊖ → HOBr → HO⊖ + Br⊕
CH₂
S
+ Br⊕
Br
CH
S
H₂O
OH
CH
S
Δ
O
C
S
+
CH₂
S

tionate giving the observed products. Similar disproportionations of 10-thiaxanthenol have been reported.[20,29,227] Disproportionation also occurs with 9-xanthenol.[184]

The reaction of triphenylsilyllithium with 10-thiaxanthenone gave a 34.6% yield of hexaphenyldisilane and a 12% yield of thiaxanthydryloxytriphenylsilane. The structure of the latter alkoxy compound was assigned on the basis of the infrared data which indicates the absence of the hydroxyl group and the presence of the silicon-oxygen bond. A previous experiment in which triphenylsilyllithium reacted with 10-thiaxanthenone gave a 27% yield of hexaphenyldisilane, but no other products could be isolated. This is the first instance of hexaphenyldisilane being found in such a high yield in reactions of this type and no explanation can be offered at this time.

B. Triphenylsilyllithium as a Metalating Agent

The use of triphenylsilyllithium as a metalating agent will undoubtedly have to be restricted to systems in which the hydrogens are quite acidic. The reaction of triphenylsilyllithium with thiaxanthene followed by carbonation gave a 44.6% yield of 10-thiaxanthenecarboxylic acid. Where-as the employ-

---

[227] A. Schönberg and A. Mustafa, J. Chem. Soc., 305 (1944).

ment of n-butyllithium afforded a 68% yield of the same acid.[22] It is interesting to note that no 10-triphenylsilylthiaxanthene was isolated from the reaction of triphenylsilyllithium on thiaxanthene. The carbon-lithium bond is known to react with triphenylsilane[123] yet there was apparently little interaction between triphenylsilane and 10-lithiothiaxanthene. The 10-triphenylsilylthiaxanthene was readily obtained in a 49% yield by the reaction of triphenylchlorosilane and 10-lithiothiaxanthene.

Gentle refluxing of triphenylsilyllithium with 10-ethylphenothiazine gave only a trace of crude 10-ethylphenothiazine-4-carboxylic acid subsequent to carbonation. 4-(Triphenylsilyl)butanol,[147] the cleavage product from tetrahydrofuran and triphenylsilyllithium, was also isolated.

There was no apparent reaction between 10-ethylphenothiazine-5,5-dioxide and triphenylsilyllithium since only starting material could be isolated. It has been reported that the reaction of triphenylsilyllithium with dibenzothiophene-5,5-dioxide does not proceed at room temperature nor at reflux.[228]

Only the sulfoxide grouping was reduced when triphenylsilyllithium interacted with 10-ethylphenothiazine-5-oxide since a 35% yield of 10-ethylphenothiazine was obtained.

---

[228] D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 1898 (1959).

The other products isolated were triphenylsilanol (11%) and triphenylsilane (27%); the latter product indicates that perhaps some metalation had taken place.

C. Reactions of Triphenylsilyllithium with Heterocycles

The reaction of triphenylsilyllithium with halogenated heterocycles depends upon the solvent employed and the halogen. The general conclusions from several reactions are as follows:

(a) The chlorine atom generally gives more coupling product and less hexaphenyldisilane than the bromine atom. (See Table 1 on page 60 and Table 3 on page 81.) These results are in agreement with those of triphenylsilyllithium with alkyl and aryl halides.[93]

(b) Use of mixed solvents, that is, ether and tetrahydrofuran gives a higher yield of coupling product than the use of only tetrahydrofuran.

All of these coupled heterocyclic compounds had previously been synthesized by different procedures.[97]

It became of interest to investigate one particular heterocycle, namely, 10-ethylphenothiazine, and attempt to incorporate the triphenylsilyl grouping in as many positions as possible. Several oxide and dioxide derivatives had to be prepared, generally employing the conditions established by

Ranck.[124,201]

An attempt to prepare 10-triphenylsilylphenothiazine by interaction of triphenylchlorosilane with 10-lithiophenothiazine was unsuccessful. This result is not surprising since other workers have been unable to prepare silylamines in which the nitrogen was attached to an aromatic system.[229] For example, refluxing triphenylchlorosilane and N-lithiocarbazole in ether for twenty hours, or heating at 270-280° for four hours, gave only starting materials.[229] It is possible that the phenyl group attached to the nitrogen withdraws electrons from the nitrogen-lithium salt, consequently decreasing the nucleophilic ability to a point where no reaction takes place with the silicon-chlorine bond. The probability of steric factors must not be discounted; however, since no silylamine was isolated from the reaction of triphenylsilyllithium with dicyclohexylamine.

2-Triphenylsilyl-10-ethylphenothiazine and 10-(2-triphenylsilylethyl)phenothiazine were readily prepared by the reaction of triphenylsilyllithium with 2-chloro-10-ethylphenothiazine and 10-(2-chloroethyl)phenothiazine, respectively.

3-Triphenylsilyl-10-ethylphenothiazine was obtained from

---

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

triphenylsilyllithium and either 3-chloro- or 3-bromo-10-ethylphenothiazine; the chloro compound gave a slightly better yield. This material was also isolated by the reaction of triphenylchlorosilane on 3-lithio-10-ethylphenothiazine. Ranck[124] reacted triphenylsilylpotassium with 3-bromo-10-ethylphenothiazine and found only an amorphorous solid which he felt might be impure 3-triphenylsilyl-10-ethylphenothiazine. The melting point of his amorphous solid was 178-180° which is close to the authentic sample which melted at 184.5-186°.

4-Triphenylsilyl-10-ethylphenothiazine was prepared in a 14.8% yield by the reaction of 4-iodo-10-ethylphenothiazine with triphenylsilyllithium. This coupling reaction appeared to be the only route not previously attempted. Champaigne[125] reacted triphenylchlorosilane with 4-lithio-10-ethylphenothiazine and Ranck[124] did several modifications of this reaction, yet neither isolated any pure product. The reaction of the 4-iodo derivative was run in mixed solvents to increase the possible formation of coupled 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, and the 2- and 3- have relatively high melting points.[230] 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 prepare a 3,7-dihalogenated-10-ethylphenothiazine derivative. 3-Bromo-10-ethylphenothiazine was converted to the sulfoxide and this compound reductively halogenated with aqueous hydrobromic acid to give crude 3,7-dibromo-10-ethylphenothiazine. The dibromo derivative was an oil and resisted purification so it was converted to the corresponding sulfone with hydrogen peroxide in glacial acetic acid. 3,7-Dichloro-10-ethylphenothiazine-5,5-dioxide was prepared in an analogous manner. The position that the second halogen takes in the reductive halogenation step is not definitely established but it is assumed to be the 7-position. This position of the second halogen atom is inferred by analogy with the mechanism proposed for the formation of the mono-halogenated derivative.[198,203]

This orientation into the 3- and 7-positions parallels that observed in formylation.[231] Reaction of either 3,7-dibromo- or 3,7-dichloro-10-ethylphenothiazine-5,5-dioxide

---

[230] S. P. Massie and P. K. Kadaba, _J. Org. Chem._, _21_, 347 (1956).

[231] N. P. Buu-Hoï and N. Hoán, _J. Chem. Soc._, 1834 (1951).

with triphenylsilyllithium gave a wide melting material which could not be adequately purified.

D. Preparation of Cyclic-silicon Compounds

Impetus was given to the synthesis of cyclic organosilicon compounds by the recognition of their most desirable high-temperature properties. There has been good success realized in the preparation of phenazasilin compounds via the halogen-metal interconversion of N-ethyl-2,2'-dibromodiphenylamine followed by interaction with the appropriate dichlorosilicon derivative.[145,146] It was hoped that perhaps 2,2'-dibromodiphenylmethane would react in an analogous manner. However, after a many-step synthesis, the precious 2,2'-dibromodiphenylmethane was stubbornly inert to reactions with metals.[232] The only observed effect of treatment with sodium in boiling xylene or magnesium at elevated temperatures was a slight reduction to diphenylmethane.[232]

The interaction of diphenylsilane with sulfur-containing heterocycles at elevated temperature is another procedure for the introduction of the diphenylsilylene grouping into a molecule.[143,144] The reaction time is lengthy, the work-up difficult and the yields are generally quite low by this method. In the particular case of 10-thiaxanthenone, it is

---

[232] L. Thorp and E. A. Wildman, J. Am. Chem. Soc., 37, 372 (1915).

rather arduous to prepare a sufficient amount of the starting material, namely, thiaxanthene. Despite the ominous overtones the reaction between diphenylsilane and thiaxanthene was moderately successful since a trace (3% crude yield) of material was isolated. The infrared spectrum showed the presence of the silicon-phenyl and methylene absorption bands in the molecule. The carbon and hydrogen analysis of this solid proved to be marginal. The substance was provisionally assigned the structure of 5,5-diphenyl-10H-dibenzosilin. The usual products attributable to the high-temperature disproportation of diphenylsilane were also obtained.[217]

The third possible route was patterned after the success achieved in preparing 2,3-dihydro-1,1-diphenyl-4H-1-silanaphthalen-4-one by the cyclization of the acid chloride of 3-triphenylsilylpropionic acid.[148] Methyldiphenyl-(o-tolyl)-silane[146] was converted to o-(methyldiphenylsilyl)benzoic acid by chromic acid oxidation in a 20.3% yield. However, application of a similar oxidative procedure to triphenyl-(o-tolyl)silane gave only tars and oils. Modification of the temperature and duration of the reaction failed to alter the results. It has been reported that the oxidation of an ortho-methyl group to the corresponding acid gave only very negligible yields,[215] yet para-methyl groups can be converted smoothly to the corresponding acids.[213,214] This relative resistance to oxidation of ortho-methyl groups may be the result of steric hindrance due to the phenyl groups.

A second approach at obtaining o-(triphenylsilyl)benzoic acid was through a halogen-metal interconversion with o-bromobenzoic acid followed by addition of triphenylchlorosilane. The reaction was unsuccessful as none of the product could be isolated. This particular method represents a feasible route providing the very low temperature can be maintained; addition time reduced to the minimum and an elaborate purification procedure developed.

Several attempts to prepare o-(triphenylsilyl)benzoic acid by the interaction of o-bromobenzoic acid with various equivalents of triphenylsilyllithium failed to yield any of the desired acid. It is interesting to note that high yields of hexaphenyldisilane were realized, probably via a halogen-metal interconversion.

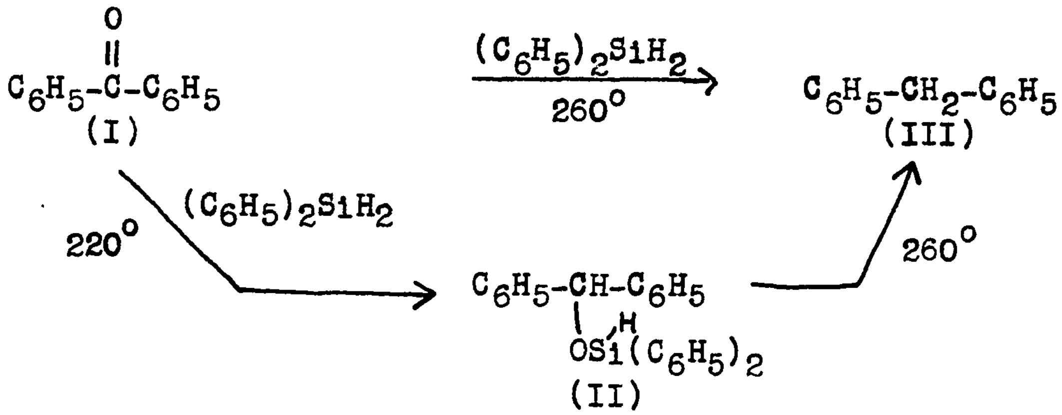
E. Si-H Bond and Related Types as Reducing Agents

In order to more thoroughly investigate the reaction between thiaxanthene and diphenylsilane it was felt that perhaps direct interaction of diphenylsilane and 10-thiaxanthenone might prove of interest. First, however, the possible alkoxy formation of the carbonyl with the silicon-hydride was determined. There was no reaction between diphenylsilane and 10-thiaxanthenone at 220-230°, conditions analogous to the formation of benzhydryloxydiphenylsilane from benzophenone and diphenylsilane.[173] At reflux, in a process akin to serendipity it was found that diphenylsilane reduced the carbonyl in 10-thiaxanthenone to a methylene grouping. The possible use of the Si-H bond and related types as reducing agents was then undertaken. It appears that the conversion of the carbonyl to the methylene group by the Si-H unit has not been previously reported.

In a typical experiment, equimolar quantities of 10-thiaxanthenone and diphenylsilane were heated, in the absence of any added catalyst or activating agent, to reflux (about 260^{o}). Within a few minutes, an exothermic reaction took place with the temperature rising as high as 310^{o}, then it reverted spontaneously to 260^{o} where it was held for 12 hours. There was no gas given off during the reaction. Chromatography of the cooled mass gave a 63% yield of thiaxanthene. Employing an inert atmosphere of nitrogen had a negligible effect on the yield.

9-Fluorenone, benzophenone and 9-xanthenone were reduced to fluorene, diphenylmethane and xanthene in yields of 60%, 37% and 27%, respectively, employing similar procedures. The presence of a substituent in the 4-position of benzophenone seemed to have little effect on this reduction since 4-methyl- and 4-chlorobenzophenone were reduced to the corresponding methylenes in good yields.

A possible intermediate in the reduction route of benzophenone(I) was established as benzhydryloxydiphenylsilane(II). This latter compound when heated up to reflux temperature (about 260°) gave a 44% yield of diphenylmethane(III). A small quantity (5%) of benzhydryl ether and resinous-oils were also obtained from this reaction.



Reaction of diphenylsilane and benzhydrol at 170° gave a high recovery of diphenylsilane and a 60% yield of benzhydryl ether. Since anthraquinone gave a 45% yield of anthracene under the general conditions of the reduction, a prior formation of the Si-O bonded intermediate may be common to many of these high temperature reactions. Phenanthraquinone underwent a vigorous reaction, however, phenanthrene was not isolated. There does exist the possibility of 10-thiaxanthenone being reduced to 10-thiaxanthenol which immediately disproportionates to thiaxanthene and 10-thiaxanthenone. The yield from this disproportionation reduction would be limited to a maximum value of 50%. Since the yields are generally around 60% in the diphenylsilane reduction of 10-thiaxanthenone, this mode of reduction appears unlikely.

The fate of the silicon moiety is not definite, however, it is thought that the resin-like material obtained in each reaction is a mixture of cyclosiloxanes; the resin shows the characteristic Si-O-Si absorption. Some (7%) hexaphenylcyclotrisiloxane was isolated along with a 68% yield of 4-chlorodiphenylmethane from the reaction of diphenylsilane with 4-chlorobenzophenone. Traces of hexaphenylcyclotrisiloxane were also found in the reaction of diphenylsilane with 10-ethylphenothiazine-5-oxide.[143]

There was no reduction product isolated from the reaction of diphenylsilane with quinoline, phenanthridine or acetophenone, as only starting materials were recovered.

The use of diphenylsilane as a selective reducing agent is apparently limited to diaryl type ketones. The yields are comparable to other methods of reduction; yet the product from the Si-H reduction is severely contaminated with the resinous cyclosiloxanes. If the reduced product could be removed by distillation, then the contamination by cyclosiloxanes would present little difficulty.

Reaction of phenylsilane on 10-thiaxanthenone gave a 95.4% recovery of starting materials. Since the temperature was low, in the neighborhood of 120°, no reaction took place. At elevated temperatures there is a distinct hazard due to the possible formation of silane.

Triphenylsilane is known to form addition products with benzophenone.[173] The reaction of triphenylsilane with benzophenone at reflux gave the same product as that obtained at lower temperatures, namely, benzhydryloxytriphenylsilane.[173] No diphenylmethane was isolated from this reaction. When bromobenzene was refluxed with triphenylsilane only starting materials and a trace of hexaphenyldisiloxane were obtained. There was no triphenylbromosilane isolated; nor any benzene, the expected hydrogenolysis product of bromobenzene.

Reaction of two equivalents of triphenylsilane with anthraquinone at reflux gave a 25% yield of a compound; the analysis and infrared of which imply that triphenylsilane added across only one carbonyl grouping.

F. Suggestions for Further Research

The current research interest rests with the synthesis and study of the chemical and physical properties of organic compounds containing silicon as a hetero atom. Cyclic-silicon compounds have been recognized as possessing several of the target physical properties. It might be of interest to continue the study of the preparation and cyclization of o-(triphenylsilyl)benzoic acid. Bromination of triphenyl-(o-tolyl)silane with N-bromosuccinimide followed by hydrolysis would give o-(triphenylsilyl)benzyl alcohol. Oxidation of this alcohol to the corresponding acid could be a possible route for obtaining o-(triphenylsilyl)benzoic acid. More vigorous direct oxidation procedures for triphenyl-(o-tolyl)-silane might also be investigated. Reaction of equimolar quantities of triphenylsilyllithium with various 1,2-dihalobenzenes using ether as a solvent might afford some o-halophenyltriphenylsilane. Preparation of the Grignard reagent of this halo derivative in tetrahydrofuran followed by carbonation should yield the corresponding acid. Cyclization of the acid chloride of this o-(triphenylsilyl)benzoic acid might give 5,5-diphenyl-10H-dibenzosilin-10-one. Reduction of the ketone grouping to the methylene would afford 5,5-diphenyl-10H-dibenzosilin, the identity of which could be verified by comparison with the compound previously isolated in the high-temperature reaction of diphenylsilane with thiaxanthene.

Reactions of cinnoline or benzocinnoline with silylmetallics, for example, triphenylsilyllithium, might be of value in the quest for cyclic-silicon derivatives. Reaction of benzocinnoline with lithium could possible yield a dilithium adduct analogous to that obtained from azobenzene or stilbene. This dilithium intermediate could then be treated with various dihalosilanes to form cyclic-silicon derivatives.

The possible explanation for the high yield of hexaphenyldisilane obtained in the reaction of triphenylsilyllithium with 10-thiaxanthenone might be investigated. Reactions of triphenylsilyllithium with related type ketones, such as 9-fluorenone, could be undertaken to determine the generality of this hexaphenyldisilane formation.

Continuation of the reactions of halogenated heterocycles with triphenylsilyllithium might be of some value in elucidating the reactivity of halides toward silylmetallics. For instance, a comparison of the reactivity of the bromine atom versus the chlorine atom could be determined by reacting triphenylsilyllithium with 2-bromo-7-chloro-9-ethylcarbazole.

The use of the Si-H bond as a possible reducing agent might be further investigated to determine if variation of the groups attached to the silicon atom has some influence on the selectivity of the reagent. The effect of catalysts on this Si-H type reduction might be studied.

Preparation of the first nuclear substituted silicon derivative of thiaxanthene might be accomplished by the following procedure. Treatment of 4-bromodiphenyl sulfone with n-butyllithium followed by triphenylchlorosilane would give 4-triphenylsilyldiphenyl sulfone. Metalation and carbonation of this latter compound would give 2-carboxy-4-triphenylsilyl-10-thiaxanthenone-5,5-dioxide. This latter compound might also be synthesized by application of a recently reported rearrangement of aryl sulfones.[233] Truce and Ray[233] found that _n_-butyllithium induced a rearrangement of phenyl _o_-tolyl sulfone and some of its methylated homologs to the corresponding _o_-benzylbenzenesulfinic acids. 4-Triphenylsilylphenyl _o_-tolyl sulfone, prepared from 4-bromophenyl _o_-tolyl sulfone, could be converted to 2-triphenylsilyl-10-thiaxanthenone-5,5-dioxide _via_ rearrangement and subsequent oxidation and cyclization.

---

[233] W. E. Truce and W. J. Ray, Jr., _ibid_., _81_, 481 (1959).

V. SUMMARY

The chemistry of thiaxanthene and related compounds has been reviewed with emphasis placed on the nuclear substituted derivatives.

A brief historical review of the reactions of organosilylmetallic reagents with carbonyl compounds and with organic halides has been presented.

A survey of heterocyclic silicon compounds and the use of Si-H compounds as reducing agents has also been presented.

The position of the nuclear substituent in several 10-thiaxanthenone derivatives has been established by two routes. A mechanism incorporating a sulfenium ion accounts for the products obtained in the acidic condensation of o-mercaptobenzoic acid with benzene and its congeners.

Unique but mechanistically explainable products were found in the reductive halogenation of thiaxanthene-5-oxide.

The reaction of triphenylsilyllithium with halogenated heterocycles was studied employing different heterocycles and varying the halogen, solvents, and time of reaction. Results of this work indicate that reaction of triphenylsilyllithium with Ar-X compounds varies appreciably with the nature of the halogen and solvents. The bromine atom gives a higher yield of hexaphenyldisilane via a halogen-metal interconversion reaction than does the chlorine atom. The use of mixed solvents gives a higher yield of coupling product.

A particular heterocycle, 10-ethylphenothiazine, was chosen and the triphenylsilyl group was placed in several positions. 2-Triphenylsilyl-, 3-triphenylsilyl- and 4-triphenylsilyl-10-ethylphenothiazine were prepared by the reaction of triphenylsilyllithium with the appropriate halogenated 10-ethylphenothiazine derivative. 10-(2-Triphenylsilyl)phenothiazine was prepared in an analogous manner. It is hoped that these various coupled products will prove useful as high temperature lubricant additives. Several new derivatives of 10-ethylphenothiazine were also prepared.

The possibility of synthesizing cyclic-silicon compounds was investigated, and in the course of one experiment a carbonyl was reduced to a methylene by diphenylsilane. The novel high temperature reduction of carbonyl groups employing diphenylsilane as the reducing agent was studied and a possible intermediate in a mechanism for this reaction established.

VI. ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Henry Gilman for the suggestions, constructive criticism and encouragement given throughout the course of this investigation.

Thanks are due to E. I. DuPont de Nemours and Company for financial assistance provided in the form of a fellowship which made part of this work possible.

This study was also supported in part by the United States Air Force under contract AF 33(616)-6127 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.