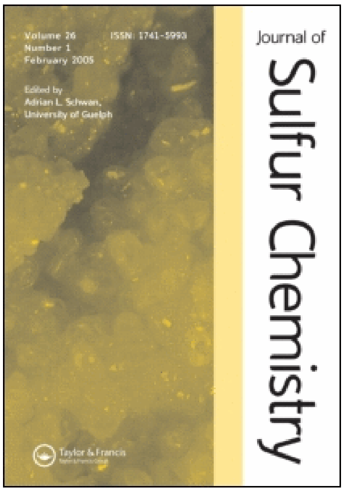

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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To cite this Article Lukevics, E. , Skorova, A. E. and Pudova, O. A.(1982) 'Thiophene Derivatives of Group iv b Elements', Journal of Sulfur Chemistry, 2: 5, 177 — 205
To link to this Article: DOI: 10.1080/01961778208082436
URL: http://dx.doi.org/10.1080/01961778208082436

Sulfur Reports
Volume 2 (5), October 1982, pp. 177–212
0196-1772/82/0205–0177/$06.50/0

Printed in the United States of America

THIOPHENE DERIVATIVES OF GROUP IV B ELEMENTS

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INTRODUCTION

Aromatic and heteroaromatic derivatives of group IV B elements $ArMR_3$ (M = Si, Ge, Sn, Pb) belong to one of the most interesting classes of compounds from a theoretical point of view. The electronic effects observed in these compounds cannot be accounted for by the positive inductive influence of the MR_3 group. The electron acceptor properties of elementorganic substituents with respect to the aromatic ring are still poorly understood and are commonly explained by the interaction between the π-electron system of the aromatic ring and the vacant d-orbitals of the element atom (p_π–d_π interaction).

To date, the results of experiments with phenyl[1-3] and furyl[4] derivatives of group IV B elements have been surveyed in review articles. The reviews available on thiophene derivatives are rather outdated,[5-7] not easily accessible[5,8] or deal with only specific aspects of synthesis and chemical properties, mainly of thienylsilanes.[3,5-8] At the same time, intramolecular electronic effects can be conveniently studied in thienylsilanes, -germanes, -stannanes, and -plumbanes. Moreover, some organosilicon and -germanium compounds have been found to exhibit specific biological activity.

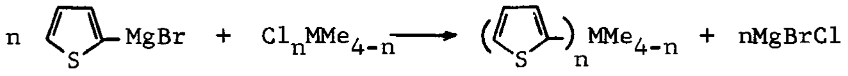
Bearing in mind the aforesaid we present here a survey of literature data and our own experimental results concerning synthesis, chemical, physico-chemical and biological properties of thiophene derivatives of group IV B elements which had appeared in the literature before 1982.

I. METHODS OF SYNTHESIS

1.1. Synthesis of derivatives with an elementorganic substituent at the thiophene ring

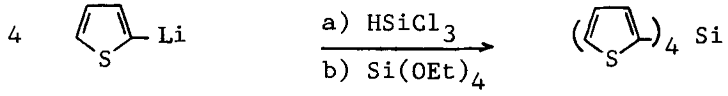
Thiophene derivatives of group IV B elements are commonly obtained in the laboratory using the reaction of thienyllithium[9-13] or thienylmagnesium halides[13-34] with halo-[9-24] or alkoxysilanes,[13-15,18,24,25] halo-[14,15,27] and ethoxygermanes,[13] halostannanes[11,14-16,28-33] and haloplumbanes.[14-16,28,34] The reaction proceeds in an inert solvent (ether, tetrahydrofuran, hexane) and in the case of thienyllithium yields 60–80% of the thienyl derivative R_SMAlk_3 (R_S = thienyl).

In the reaction between thienylmagnesium bromide and $Me_{4-n}MCl_n$, the transition from thienylgermanes to -silanes and -stannanes is accompanied by lower yields of products. The same effect is observed with increasing number of thiophene rings attached to



M = Si, Ge, Sn (n = 1-4); M = Pb (n = 1)

This is contrasted by tetra-(2-thienyl)-germane and tetra-(2-thienyl)-stannane, their yields being twice as high as those of methyltri-(2-thienyl)-germane and methyltri-(2-thienyl)-stannane and amount to 60%. On the other hand, we failed to obtain tetra- and trithienyl derivatives of silicon in yields above 10% due to only partial substitution of chlorine atoms. Higher yields of tetra-(2-thienyl)-silane could be achieved with excess 2-thienylmagnesium iodide[16] and by treating 2-thienyllithium with trichlorosilane[14,15] (a) and tetraethoxysilane[14,15] (b):

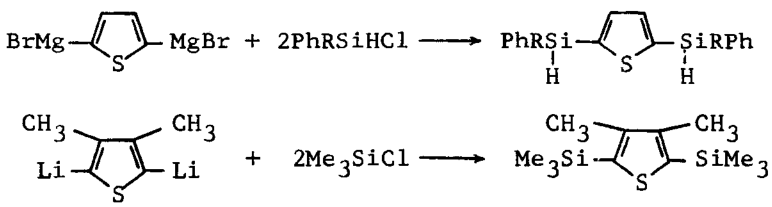


Organometallic synthesis provides thiophene derivatives with various functional substituents at the group IV B element. Thus, thienylsilanes with hydrogen,[15,17–22] chlorine[18,23,24] or ethynyl,[26] vinyl,[15,21] chloromethyl,[15] and ethoxy[13,18,24,25] groups at the silicon atom, thienylgermane with ethoxy groups,[13] thienylstannanes with chlorine[30–33] and vinyl groups,[31–33] thienylplumbanes with chlorine attached to the lead atom[34] have been synthesized:

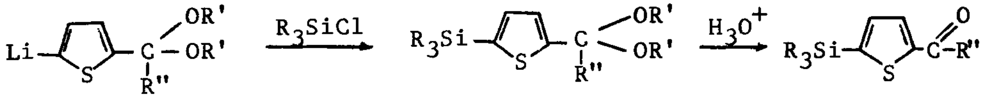
Z = Li, MgCl; M = Si, Ge, Sn, Pb;

X = H, Cl, OEt, $CH_2{=}CH$, $HC{\equiv}C$, CH_2Cl

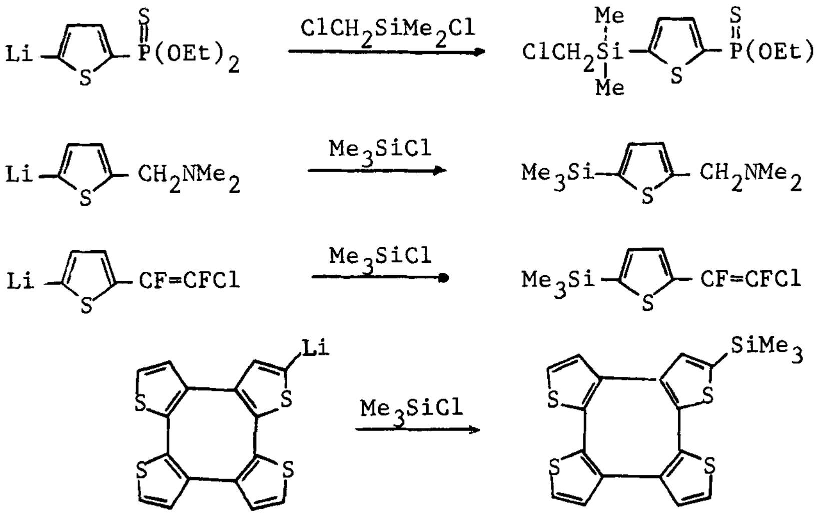
Disilyl derivatives have been obtained by treating 2,5-dimagnesium[20] and 2,5-dilithium[35] derivatives with chlorosilanes:



If the thiophene ring contains functional substituents resistant to the action of organolithium compounds, silyl groups are introduced into the molecule by way of organolithium synthesis:[36–38]

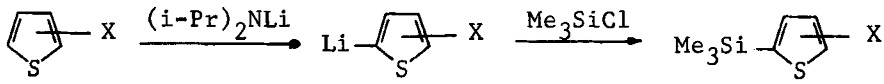


A similar reaction can be performed using organophosphorus derivatives of thiophene,[39,40] *N,N*-dimethylaminomethyl-thiophene,[41] (1,2-difluoro-2-chlorovinyl)-thiophene[42] and cyclotetrathiophene:[43]



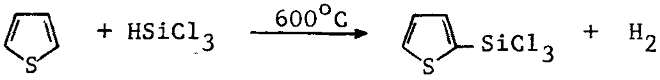
A single[44-46] or two[47] chlorine atoms in perchloro derivatives of thiophene can be selectively substituted for lithium. It is also possible to obtain trichloro-2-thienylmagnesium chloride from tetrachlorothiophene.[48] The resulting organometallic derivatives have been used as starting compounds to obtain thienylsilanes with chlorine atoms in the thiophene ring.

Lithium diisopropylamide, a highly selective metalating agent,[49-51] leads to proton-lithium exchange, even in compounds with active groups, resulting in thienylsilanes with diverse substituents in the ring:

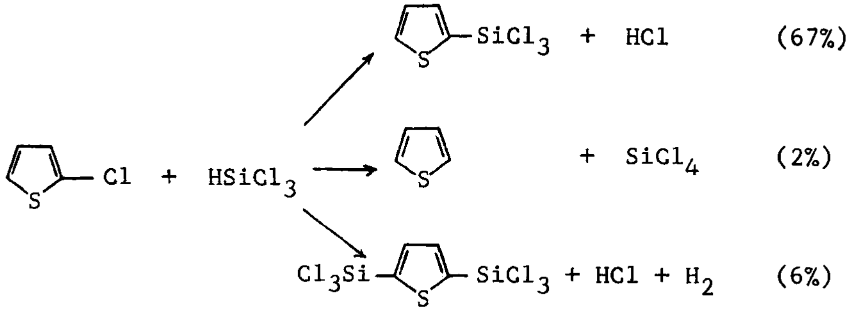


$X = Br,\ NO_2,\ COOH$

A convenient procedure has been developed for the synthesis of thienylchloro- and thienylorganochlorosilanes that involves interaction between chloro-, organylchlorosilanes, vinyltrichlorosilane, or hexachlorodisilane with thiophene[52] and its chloro derivatives[52-62] in the gas phase. Passage of thiophene and trichlorosilane vapors through a tube heated to 600°C gives 2-thienyltrichlorosilane (20% yield) together with negligible amounts of the 3-isomer:[52]



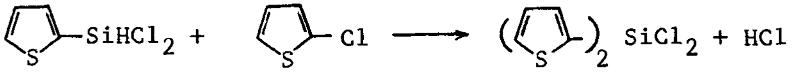
Trichlorosilane reacts with 2-chlorothiophene along three pathways:[52]



Similarly, 2,5-disilyl substituted products are obtained from 2,5-dichlorothiophene.[52,56-58]

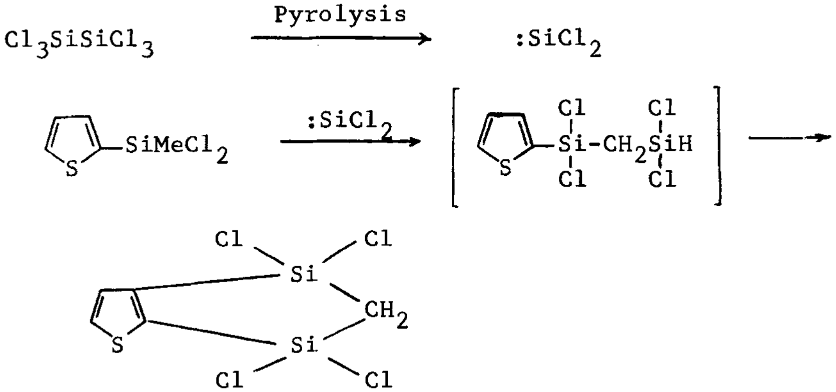
The kinetics of the reactions of 2-chlorothiophene with methyldichlorosilane and trichlorosilane have been studied by adding initiators and inhibitors of radical reactions to the mixture.[60] Two mechanisms have been proposed based on the character of the active species formed: silyl radicals or silylenes. As at 520–580°C no side products are formed, the reaction apparently involves $SiCl_2$, whereas at higher temperatures the $\cdot SiCl_3$ radical takes part in the process leading to side products.

The gas phase method of synthesis conducted at high temperatures can be used to prepare a variety of thienyl-containing organosilicon compounds. For example, the reaction of halothiophenes with thienyldichlorosilane yields dithienyldichlorosilane:[63,64]



Thienylchlorosilane condensation with chlorobenzene and vinyl chloride proceeds in a similar fashion.[63]

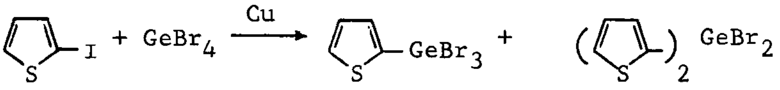
Co-pyrolysis of hexachlorodisilane with methyl-(2-thienyl)-dichlorosilane affords heterocyclic products containing a disilylmethylene group:[65,66]



Dichlorosilylene formed during hexachlorodisilane pyrolysis is believed[66] to attack the C—H bond of the methyl group at the silicon atom; the following step involves closure of the ring. The yield of 4,4,6,6-tetrachloro-4,6-disila-5*H*-cyclopenta[2,3-*b*]thiophene amounts to 20%.

Thienyltrichlorosilane and some of its derivatives can be obtained from halothiophenes not only in the gas phase, but also by treating the latter with hexachlorodisilane or trichlorosilane in the presence of a tertiary amine.[67] The reaction occurs at the boiling temperature of the reaction mixture.

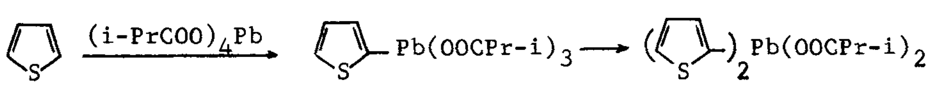
A convenient method has been devised for thienyltribromogermane synthesis by boiling a mixture of 2-iodothiophene, germanium tetrabromide, and copper powder:[68]



Besides the monothienyl derivative the reaction also gives dithienyldibromogermane[68] (13% yield).

Dithienyldiiodostannane was synthesized from 2-iodothiophene and tin by heating them to 150°C in a nitrogen atmosphere in the presence of pyridine and triethylamine:[69]

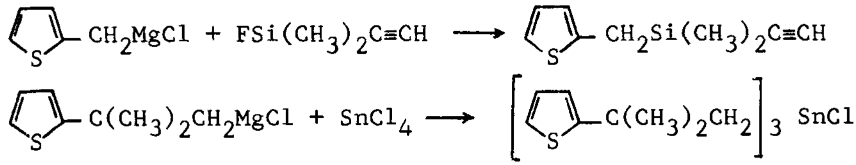
A dithienyl derivative of lead is formed at room temperature in the solution of an organic tetravalent lead salt in excess thiophene:[70]



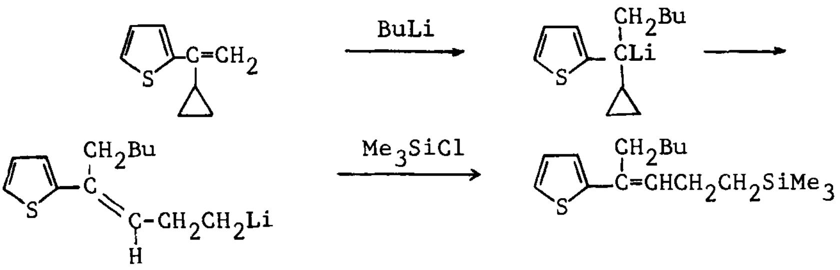
An unstable monothienyl product is first formed which is later converted into a dithienyl derivative.

1.2. Synthesis of thiophene derivatives with a group IV B element in the side chain

Organomagnesium synthesis is equally applicable to the synthesis of compounds in which the thiophene ring is separated from a silicon[26] or tin[71] atom by a carbon chain:

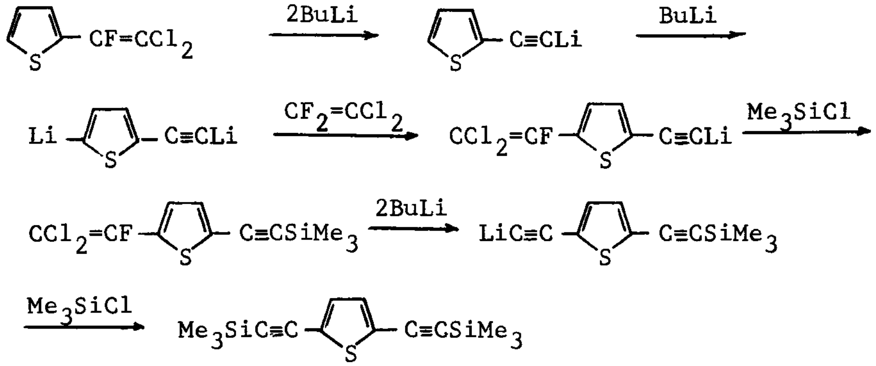


1-Cyclopropyl-1-(2-thienyl)-ethylene treated with butyllithium yields after subsequent trimethylchlorosilane treatment a vinyl derivative[72] with the *cis*- and *trans*-isomers in the ratio 1.2:5:



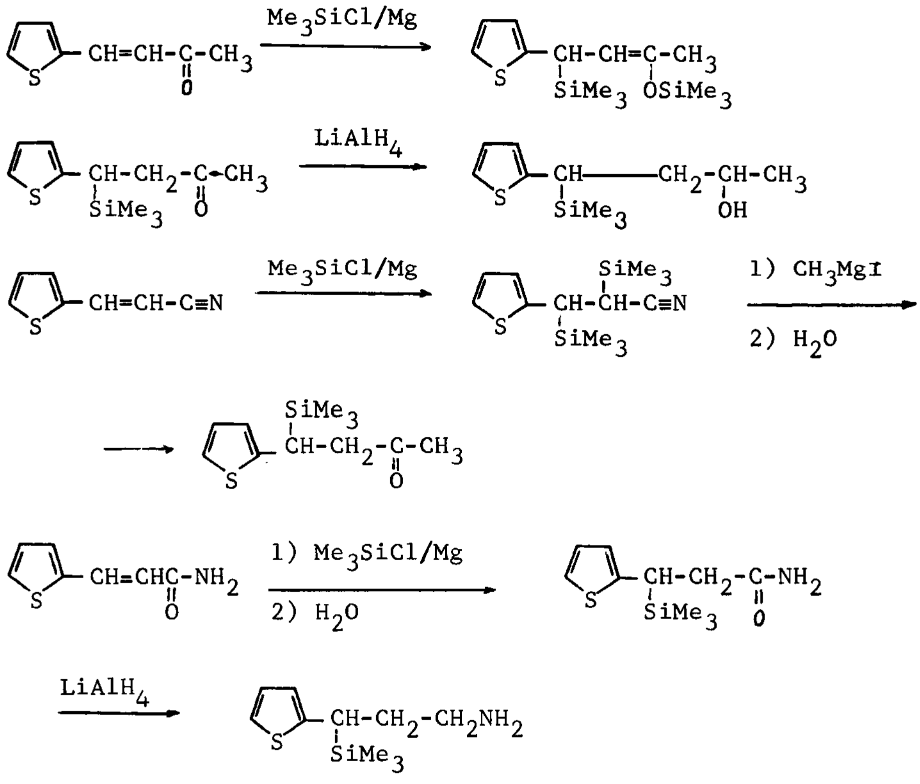
Treatment of 2-(2,2-dichloro-1-fluoroethenyl)-thiophene with two equivalents of butyllithium affords lithium acetylides. Further addition of butyllithium lithiates the 5-

position of the heterocycle to give a dilithium compound which serves as key intermediate for synthesis of silylated ethynylthiophenes:[73]

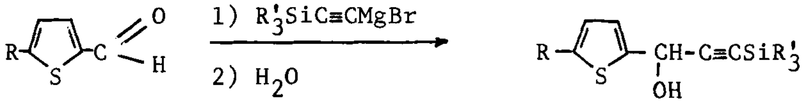


The reaction of bromoethynyltrimethylsilane with 2-thienylcopper gives a compound where the thiophene ring is separated from silicon atom by an ethynyl group:[74]

Silylation of unsaturated ketones,[75] nitriles,[75] and amides[76] in the thiophene series using the Me₃SiCl-Mg-hexamethapol system occurs in position 1,4 with ketones and 1,2 with nitriles and amides:

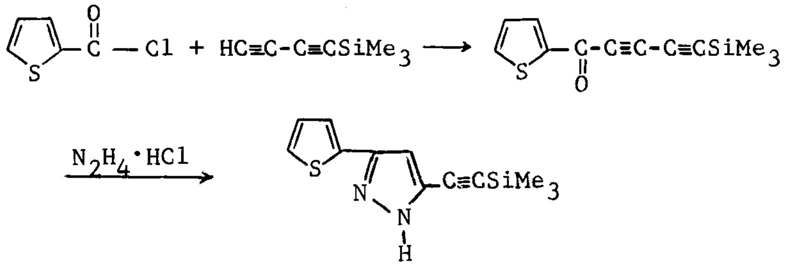


Treatment of carbonyl derivatives of thiophene with trialkylsilylethynylmagnesium bromide leads to thienylsilylacetylenic alcohols:[77,78]

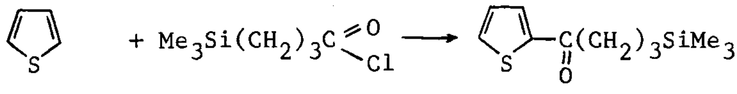


The latter undergo oxidation with manganese dioxide to give ketones or can be hydrogenated to vinyl derivatives.[78]

Acylation of organosilyl acetylenes with 2-thiophenecarboxylic acid chloride results in ketones[79] *e.g.*:

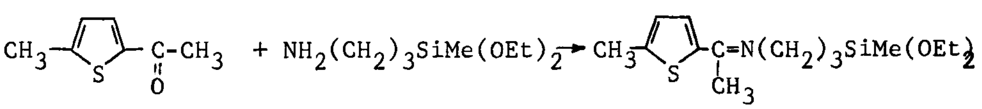


A silicon-containing ketone has been obtained by acylating thiophene with γ-trimethylsilylbutyric chloride in the presence of tin tetrachloride:[80]



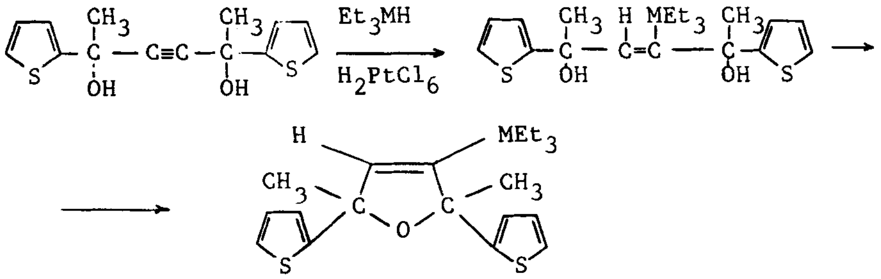
Subsequent reduction of the ketone with lithium aluminium hydride gives 2-[4-(trimethylsilyl)-butyl]-thiophene.[80]

Acetylthiophene derivatives react with organosilicon amines containing a γ-amino group with respect to the silicon atom to afford ketimines:[81]

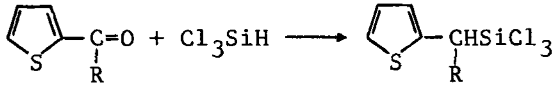


The resulting ketimines undergo hydrogenation to amines on a platinum catalyst.[82]

Triethylsilane and triethylgermane add to the triple bond of 2,5-di-(α-thienyl)-hex-3-yne-2,5-diol in the presence of Speier's catalyst. However, the reaction is not terminated at the addition step, but proceeds further with dehydration and ring closure:[83]

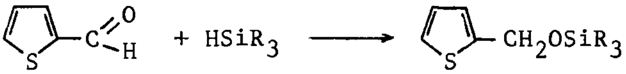


Trichlorosilane in the presence of tripropylamine reacts with thienyl ketones in acetonitrile to give thienylsilanes with the silicon atom separated from the thiophene ring by a single carbon atom:[84]

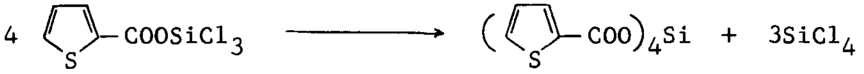


R = Ph, 2-thienyl

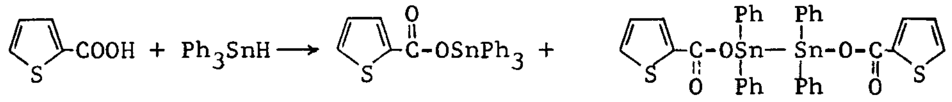
In the presence of hexachloroplatinic acid trialkylsilanes add to the carbonyl group of 2-thiophenealdehyde:[85]



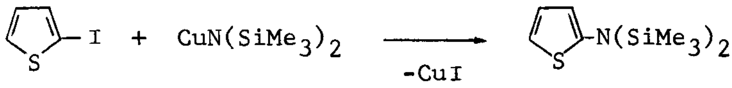
Under the action of excess silicon tetrachloride 2-thiophenecarboxylic acid is converted to the corresponding acyloxytrichlorosilane[86] which upon storage disproportionates to tetrathenoyloxysilane and silicon tetrachloride:



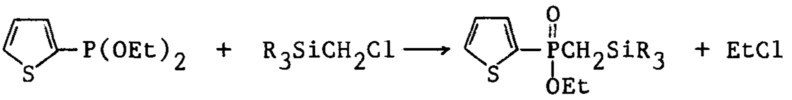
In the reaction between triphenylstannane and 2-thiophenecarboxylic acid in equimolar ratio two products are formed:[87]



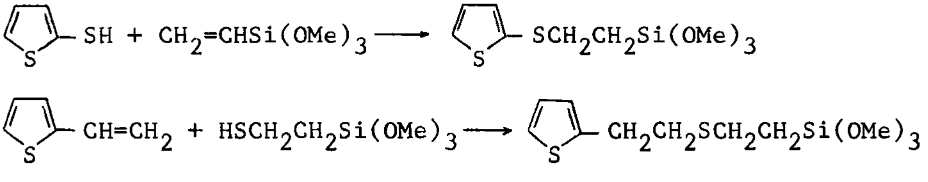
Synthesis of a thienylaminosilane is effected by treating 2-iodothiophene with hexamethyldisilazanyl copper:[88]



To obtain silicophosphorus derivatives of thiophene the Arbuzov reaction between diethyl 2-thienylphosphinate and chloromethyltriorganosilanes has been utilized:[89]



Photochemical addition of 2-thiophenethiol and (2-mercaptoethyl)-trimethoxysilane to the double bond of vinyltrimethoxysilane or 2-vinylthiophene results in thienylthioalkylmethoxysilanes:[90]

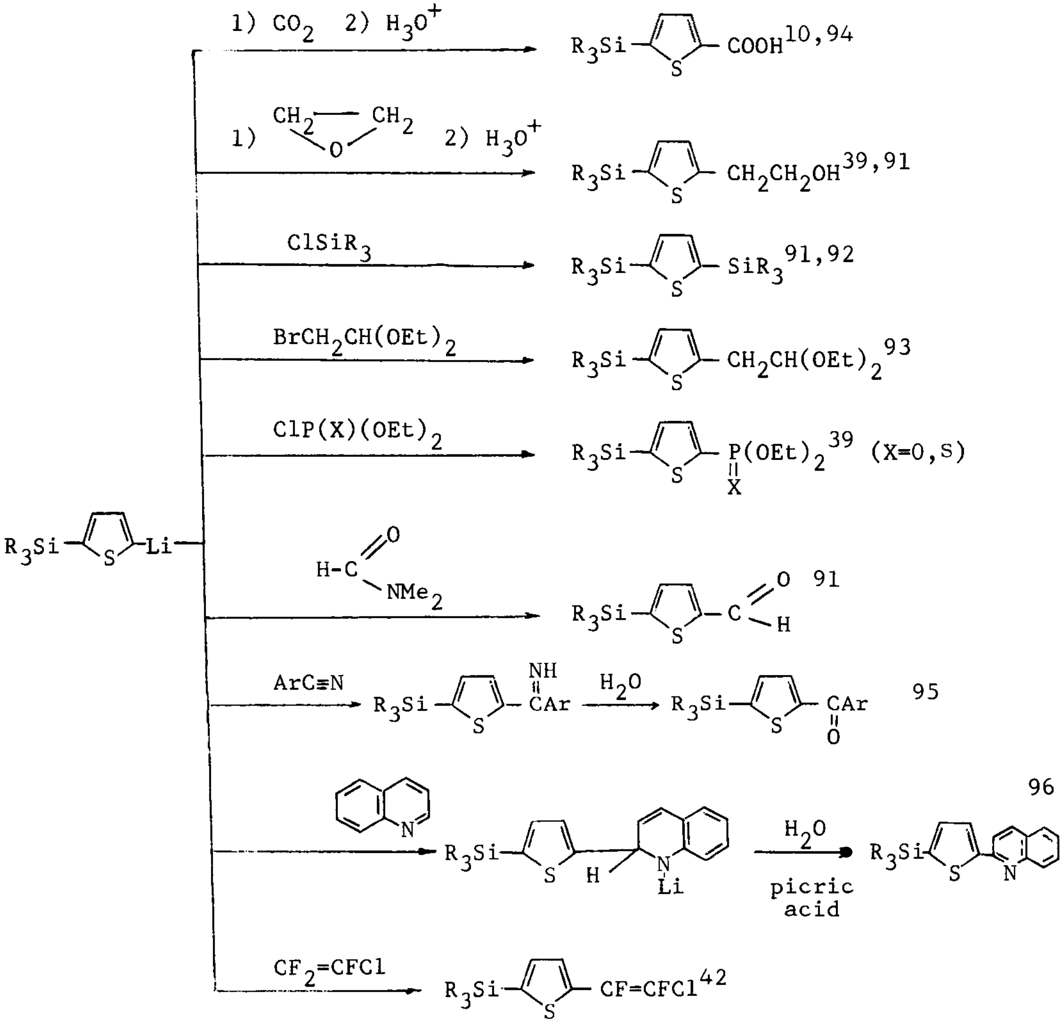


II. CHEMICAL PROPERTIES

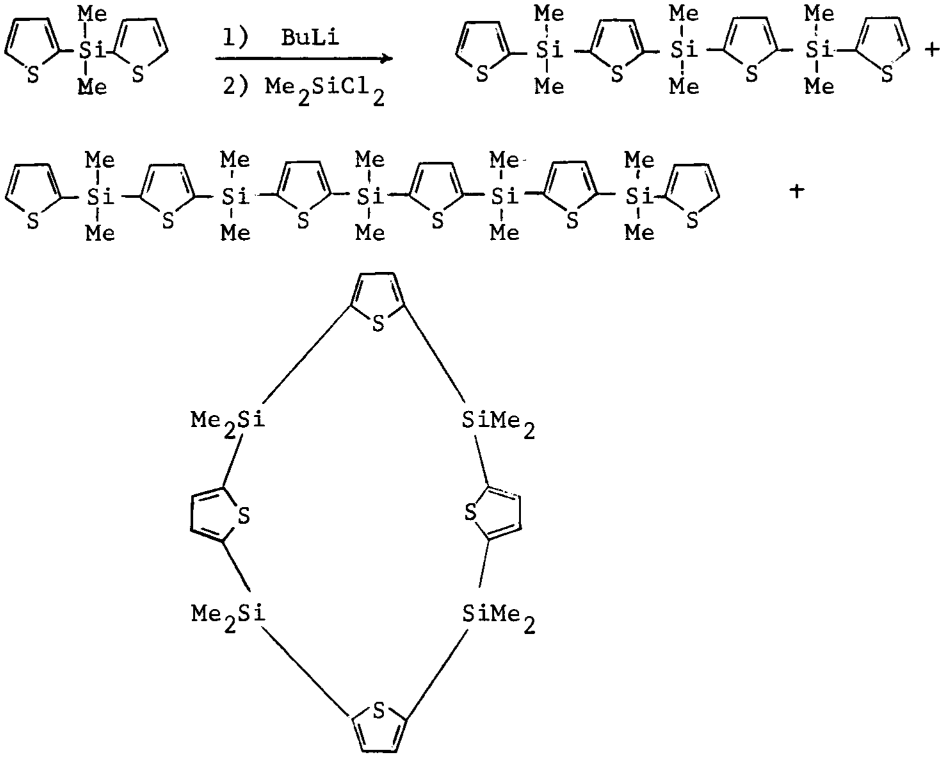
The reactions of thiophene derivatives of group IV B elements can be classified into three groups.[6,7] The first group of reactions involves the thiophene ring, the second one involves functional substituents at the element, the third type proceeds with element-heterocycle bond cleavage.

2.1. *Reactions involving the thiophene ring*

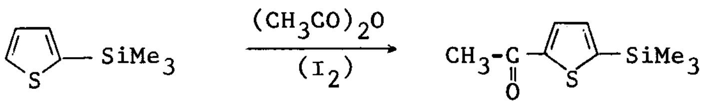
Compounds with a thiophene ring containing various functional substituents besides silyl groups have been synthesized using lithium derivatives[10,39,91–97] obtained by treatment of 2-thienylsilane with butyllithium:



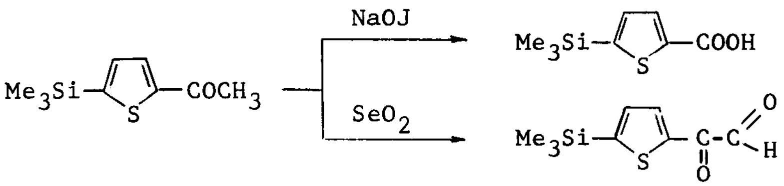
The reaction of butyllithium with dimethyldi-(2-thienyl)-silane gives compounds containing a lithium atom in one or both thiophene rings. The resulting organolithium compounds react with dimethyldichlorosilane[98] to yield a mixture of acyclic and cyclic products:



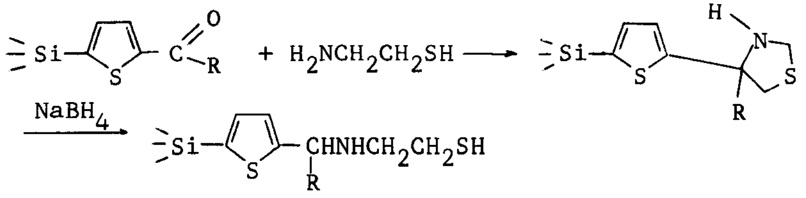
Acylation of trimethyl-(2-thienyl)-silane with acetic anhydride was carried out using a mild catalyst (iodine):[10]



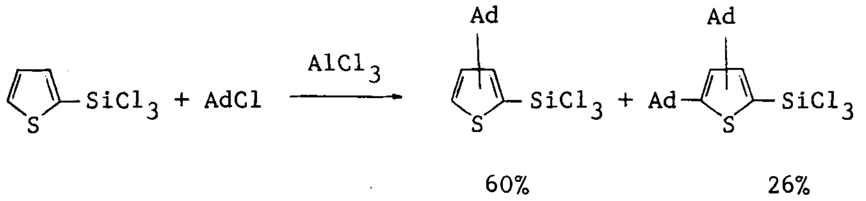
The 2-acetyl-5-trimethylsilylthiophene obtained in the reaction is readily oxidizable with hypoiodite[10] to afford an acid or with selenium dioxide to give a glyoxal:[99]



Carbonyl compounds have also been employed to synthesize derivatives of 2-mercaptoethylamine:[38]

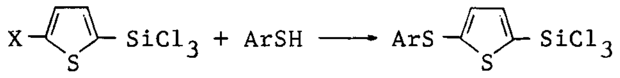


A condensation leading to the thiazolidine is easy to conduct in the case of a silylthiophenealdehyde (R = H) whereas an acetyl derivative (R = CH_3) reacts only in the presence of catalytic amounts of iodine. Alkylation involving adamantyl halides and thienylchlorosilanes[100,101] takes place at 140–180°C in the presence of aluminium chloride:

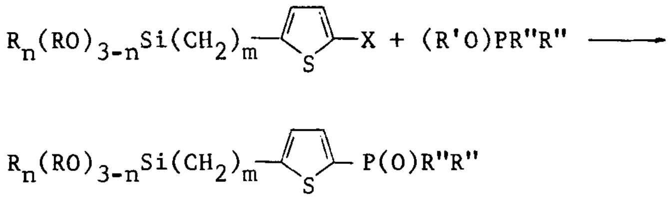


Cleavage of the Si—$C_{\text{thiophene}}$ bond is not observed under these conditions.

Thienylalkylchlorosilanes undergo substitutive halogenation[102] with gaseous chlorine, sulfuryl chloride, or bromine at 60–90°C to give halothienylalkylchlorosilanes. The reaction of thienylchlorosilane halides with hydrogen sulfide[103] and aromatic or heterocyclic thiols[104] proceeds in the gas phase at 400–650°C to yield sulfides:



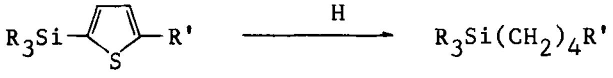
It is a well-established fact that halogens on the thiophene ring of thienylsilanes are substituted for a phosphine oxide group under the action of phosphinite in the presence of a nickel dihalide:[105]



$n = 0\text{–}3;\ m = 0\text{–}2.$

Tetra-(2-thienyl)-germane nitration was carried out under mild conditions with acetyl nitrate at −30°–0°C to afford tetra-(5-nitro-2-thienyl)- and tetra-(4-nitro-2-thienyl)-germanes in the ratio 3 : 1.[106]

Raney nickel induces reductive desulfuration of thienylsilanes.[91] However, the yields of end products are low:

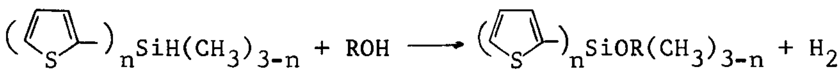


$R' = CH_3,\ Si(CH_3)_3;\ \ CH_2CH_2OH$

2.2. *Reactions involving the functional groups of elementorganic substituents*

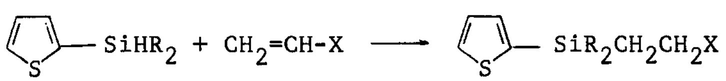
Silicofunctional derivatives of thiophene undergo various reactions at the silicon atom without affecting the M—$C_{\text{thiophene}}$ bond and thiophene ring.

Thienylhydrosilanes are highly reactive in dehydrocondensation[107-111] reactions and hydrosilylation of the double bond. Dehydrocondensation with aliphatic alcohols takes place in the presence of organic bases[107-110] or group VIII metals (*e.g.* palladium[111] on charcoal support) acting as catalysts. No catalyst is required in the reaction with amino alcohols:[107]



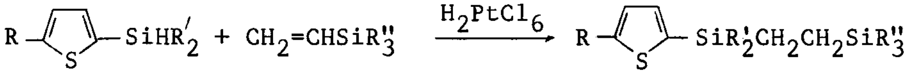
The reaction rate tends to increase with increasing number of thienyl groups in the hydrosilane molecule and with increasing electron-attracting properties of the R substituent.[107,110]

Hydrosilylation of the double bond in unsaturated compounds catalyzed by chloroplatinic acid results in various carbofunctional thienyl-containing silanes:

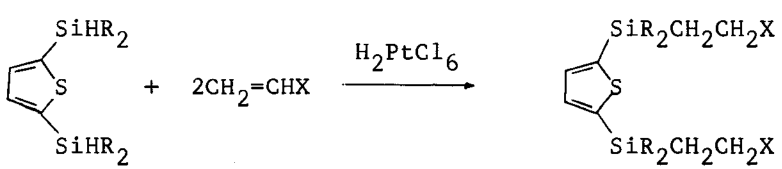


X = CH_2Cl[63], CH_2CN[63,112], CH_2NR_2[15,112,113], $CH_2OC_6H_5$[63], CN[63]

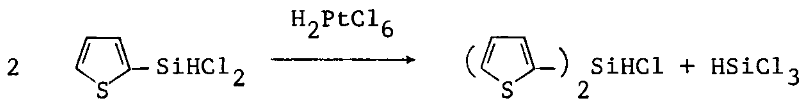
Thienylhydrosilane addition to various vinylsilanes,[19-22,114,115] takes place at atmospheric pressure:



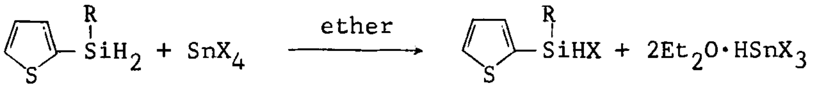
Similarly, disubstituted thiophenes such as 2,5-bis-(methylphenylsilyl)-thiophene and 2,5-bis-(dimethylsilyl)-thiophene react with allylamine,[112,113] *N,N*-bis-(trimethylsilyl)-allylamine,[116] 1-vinylsilatrane,[19] vinyl- and allyltrialkylsilanes[20,115] to give the corresponding symmetric derivatives:



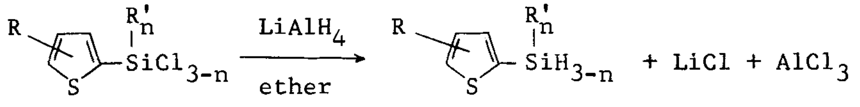
The analysis of the reaction products obtained by the addition of thienylhydrosilanes to unsaturated compounds catalyzed by chloroplatinic acid revealed the presence of compounds resulting from the addition of disproportionation products of the initial hydrosilane. The behavior of thienylhydrosilanes was therefore studied in the presence of platinum catalysts.[117] It was found that under the present conditions thienyldichlorosilane undergoes disproportionation to dithienylchlorosilane and trichlorosilane:



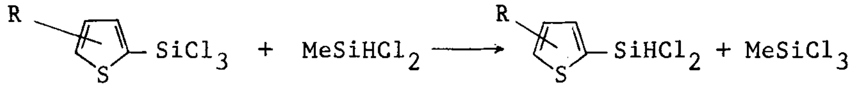
Treatment of thienylhydrosilanes with sulfuryl chloride leads to substitution of hydrogen by a chlorine atom.[118] To obtain thienylhalohydrosilanes, thienylhydrosilanes are treated with tetrachlorostannane at −10°C:[119]



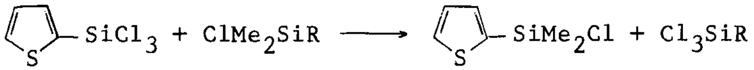
Thienylorganochlorosilanes and thienyltrichlorosilanes undergo reduction by lithium aluminum hydride to give the corresponding di- and trihydrides:[119]



The reaction can be carried out with methyldichlorosilane[120] in the presence of catalytic amounts of hexamethapol:

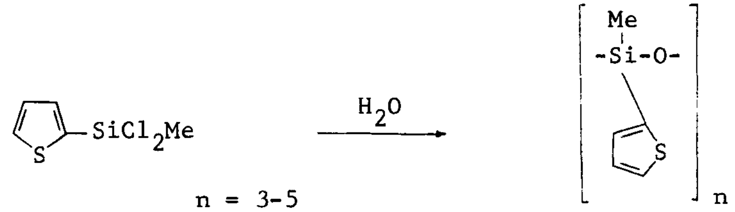


A homolytic radical-exchange reaction between hydro- and alkenylsilanes and thienylchlorosilanes is observed at 500–700°C in the gas phase:[121]



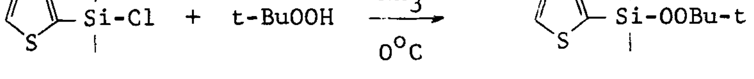
$R = H, CH = CH_2$

Hydrolysis of the Si—Cl bond in thienylchlorosilanes[23,122–126] and of the Sn—Cl bond in tri-(2-thienyl)-chlorostannane[127] has been performed. Methyl-(2-thienyl)-dichlorosilane is hydrolyzed in aqueous potassium carbonate or bicarbonate,[23] a mixture of tri-, tetra-, and pentameric methyl-(2-thienyl)-cyclosiloxanes being formed as a result of the reaction:



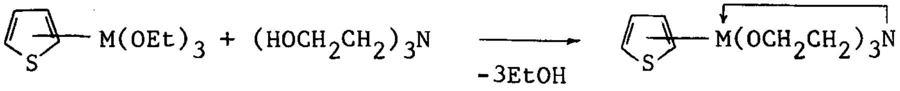
To increase the thermal stability and resistance of polysiloxanes to organic solvents, methylchlorosilanes are cohydrolyzed with bis-(dimethylchlorosilyl)-thiophene,[123,124] the latter amounting to 10–40% of the initial mixture.

Thienylchlorosilanes readily undergo alcoholysis with lower (methanol,[128] ethanol[129]) and higher (1-octanol[130]) alcohols as well as thiolysis with 1-decanethiol.[131] Methylthienyldichloro- and thienyltrichlorosilanes treated with *t*-butyl hydroperoxide in ether at 0°C in the presence of gaseous ammonia form organosilicon peroxides:[132]



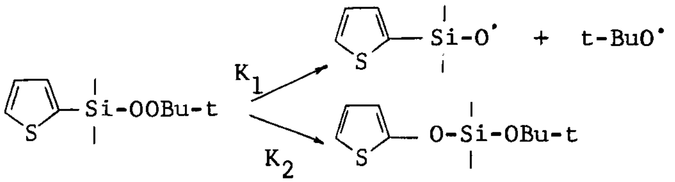
Treatment of (2-thenoyloxy)-trichlorosilane with organic fatty acids leads to mixed acyloxysilanes:[133]

2- and 3-Thienyltriethoxysilanes[19,134–136] and 2-thienyltriethoxygermane[19] undergo transesterification with triethanolamine to form thienylsilatranes and a thienylgermatrane:



The reaction is particularly facile in the case of 2-thienylgermatrane; no heating is required, the germatrane precipitates immediately upon the mixing of the starting compounds.

Organosilicon peroxides containing a thienyl group at the silicon atom are thermally unstable:[132,137]



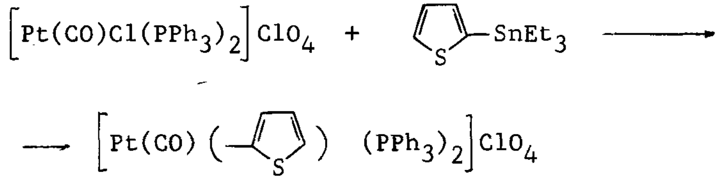
The influence of various groups on the silicon atom (Me, Et, $ClCH_2$, Br, Ph, $PhCH_2$, 2-thienyl) on the rate and mechanism of the thermal decomposition of peroxides[137] indicates that no correlation exists in lg K_r-σ^* coordinates; hence the peroxide reactivity is not entirely due to the inductive constants of the substituents. For thienyl derivatives the heterolytic process (K_2) predominates, its contribution amounting to 85%.

2.3. Reactions leading to M-thiophene bond cleavage

Treatment of thiophene derivatives of group IV B elements with a water–methanol solution of perchloric acid,[9,138,139] sulfuric acid in acetic acid-water,[139–141] hydrogen chloride,[142] potassium permanganate in water,[92] bromine,[143] acyl chlorides,[144–146] sodium methoxide,[11] aziridine,[147] pyrrolidine,[15,148] piperidine[15,148] and morpholine[148] in the presence of catalytic amounts of alkali metals[15,147] or butyllithium,[148] organolithium compounds,[97,149–151] iron,[152] and platinum[153–158] complexes is known to lead to element-$C_{thiophene}$ bond cleavage.

Trialkyl-(2-thienyl)-silanes are slower to decompose in methanol solution of sodium methoxide than the corresponding organotin compounds.[11] The reaction rate is controlled mainly by the alkyl substituents at the element. For example, the replacement of a trimethylsilyl group by triethylsilyl brings about an almost 180-fold decrease in the reaction rate constant.[11] The reaction of a platinum complex[155] with triethyl-(2-thienyl)-

stannane gives a thienyl-containing complex in 31% yield, whereas triisopropyl-(2-thienyl)-stannane fails to react:

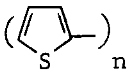


The reactivity of the Sn—$C_{thiophene}$ bond is higher than that of the Si—$C_{thiophene}$ bond towards benzoyl chloride[144] and the cycloocta-1,5-diene platinum dichloride complex.[153] Trimethyl-(2-thienyl)-silane undergoes acylation (17%), whereas trimethyl-(2-thienyl)-stannane yields phenyl (2-thienyl) ketone (45%):[144]

In the $Pt(cod)Cl_2$ complex (cod stands for 1,5-cycloocta-diene), a chlorine atom is substituted by a thienyl group (98% yield) upon treatment with trimethyl-(2-thienyl)-stannane, the yield being only 15% in the case of the corresponding silane.[153]

III. PHYSICAL PROPERTIES

3.1. NMR spectra

The general pattern of ^1H NMR spectra of thiophene derivatives is determined by the electronic effects of the substituents. A sharp increase in the chemical shifts δ of the ring protons upon transition from alkyl- to silylthiophenes[159–161] is associated with the strong acceptor p_π–d_π-interaction of group IV B elements which significantly exceeds their positive inductive effect. All signals assigned to the ring protons of thienylsilanes,[14,15] -germanes,[14,15] -stannanes[14,15,162] and -plumbanes[14,15,163] are shifted toward low-field values as compared to thiophene. With increasing number of thiophene rings at the M element in the compounds  MMe_{4-n} the shielding of the ring and methyl group protons (see Table I) is diminished.[14]

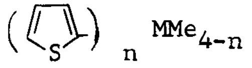
Substitution of methyl groups at the silicon atom for alkoxy group or fluorine[15] leads to a decrease of the p_π–d_π-interaction with the ring. The acceptor properties with respect to the π-electron system of thiophene are also diminished when going from 2- and 3-thienyltriethoxysilanes to the corresponding silatranes.[136]

The spin–spin coupling constants of the ring protons in 2-substituted thiophenes $(R_S)_4M$ (R_S = 2-thienyl, M = Si, Sn, Pb) have been found to correlate with the electronegativities of the substituents.[164]

In the ^{13}C NMR-spectra the signals of the carbon nuclei in the thiophene ring of $(R_S)_nMMe_{4-n}$ compounds are shifted to lower fields compared to thiophene.[14,15] With increasing number of thienyl groups at the element M the shielding of the C(2) nuclei

TABLE I

The ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn, ^{207}Pb Chemical Shifts of Compounds



			δ ^{1}H, ppm				δ ^{13}C, ppm				
n	M	δ M, ppm	H(3)	H(4)	H(5)	CH_3	C(2)	C(3)	C(4)	C(5)	CH_3
1	Si	−6.00	7.27	7.17	7.61	0.34	139.9	134.1	128.2	130.5	0.5
2	Si	−15.03	7.33	7.20	7.62	0.68	137.4	135.5	128.4	131.5	0.5
3	Si	−24.14	7.42	7.23	7.70	0.96	135.3	137.2	128.5	132.4	0.8
4	Si	−34.07	7.53	7.26	7.76	—	134.0	138.4	129.3	134.0	—
1	Ge		7.20	7.19	7.55	0.48	140.0	132.7	128.0	129.6	0.1
2	Ge		7.26	7.20	7.59	0.80	138.1	134.0	128.2	130.5	0.3
3	Ge		7.35	7.22	7.65	1.03	135.7	135.3	128.3	131.3	0.6
4	Ge		7.43	7.27	7.69	—	133.7	136.5	128.4	132.1	—
1	Sn	−27.46	7.15	7.19	7.57	0.35	136.7	135.0	128.0	130.8	−7.8
2	Sn	−63.91	7.30	7.26	7.66	0.66	134.8	136.1	128.3	131.5	−7.0
3	Sn	−104.53	7.40	7.28	7.72	0.92	132.8	137.1	128.4	132.2	−6.3
4	Sn	−148.61	7.48	7.32	7.78	—	131.3	137.8	128.5	132.8	—
1	Pb	−42.1	7.19	7.20	7.40	1.08	140.9	134.8	127.8	130.4	0.6

and deshielding of the C(3), C(4), C(5) carbon nuclei in the ring and of the methyl group[14,15,165] are observed. Moreover, the chemical shifts of the ring carbons and the number of heterocyclic substituents show almost a linear correlation.

The replacement of one methyl group in tetramethylsilane,[14,15] -stannane,[14,15,166] -plumbane[14,15] by a 2-thienyl group shifts the silicon, tin, and lead signals to higher fields (Table I) supporting the assumption of p_π–d_π-interaction in these compounds. The increase in the number of thiophene rings at silicon and tin atoms is accompanied by a parallel increase in their shielding.[14,15]

3.2. Spectra of charge-transfer complexes

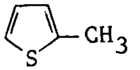
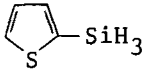
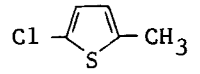
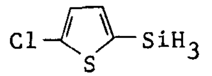
To assess the electron density distribution of thienylsilane, -germane, and -stannane molecules in an excited state their charge-transfer complexes (CTC) were studied using UV-spectroscopy.[167–169]

The CTC frequencies of silyl derivatives of thiophene with tetracyanoethylene are shifted to higher fields[167,168] as compared to the bands of the corresponding carbon analogs (Table II) indicating strongly electron-attracting properties of silyl substituents.

The transition from 2-*t*-butylthiophene to 2-(trimethylsilyl)-thiophene is accompanied by an increase in the ν_{CT} value by 650 cm^{-1}.[168] Upon further transition from silicon-

TABLE II

Frequencies of Charge-Transfer Complexes of Thiophene Derivatives with Tetracyanoethylene

Compounds	ν_I, cm^{-1}	ν_{II}, cm^{-1}
	24400	19600
	24950	21750
	26000	19300
	28400	21650

containing compounds to germanium, tin, and lead derivatives a regular decrease in the ν_{CT} frequencies (Table III)[169] is observed, which is due to stronger electron-donating properties on one hand and diminished p_π–d_π-interaction of the MR_3 substituents with increasing atomic numbers of M on the other.

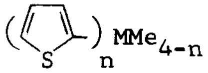
3.3. Infrared spectra

The analysis of the IR spectra of thienylsilanes,[170] -germanes,[171] and -stannanes[171] reveals some characteristic changes in the stretching and deformation frequencies of the C—H bonds of the thiophene ring,[170] the skeleton vibrations of the thiophene ring,[170,171] and the vibrations of the elementorganic substituents.[170,171]

Since the frequency[172,173] and intensity[174,175] of the Si—H bond stretching are essentially determined by the electronic effects of the substituents on the silicon atom the IR

TABLE III

Charge-Transfer Frequencies (ν, cm^{-1}) of Complexes Formed by Thiophene Derivatives



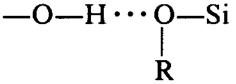
with Tetracyanothylene

M n	C	Si	Ge	Sn	Pb
1	19800	20450	20240	20040	19840
2		20900	20700	20240	
3		21140	20900	20450	
4		21400	21140	20700	

spectra of thienyl substituted hydrosilanes have been studied. In compounds showing no p_π–d_π-interaction the ν_{Si-H} values appear linearly related to the sum of the inductive constants of the substituents. However, in thienylsilane spectra this value is lower than its estimated value, *i.e.* the inductive effects in this case are diminished as a result of the electron donor activity of the thienyl ring towards its silyl substituent. For the same reason the experimentally found intensities of the ν_{Si-H} vibrations exceed their estimated values.[174] The dipole moments and effective charge values on atoms adjoining the Si—H bond have been found on the basis of the intensities of the ν_{Si-H} stretching in the IR spectra.[176]

The thiophene ring acts as a π-acceptor in hydrogen bonding with proton donors.[177,178] The basic properties of the π-system are evident from the shifting of the stretching frequency of the O—H bond of free phenol (3909 cm^{-1}) after hydrogen bonding with thienyl derivatives ($\Delta\nu$). The comparison of $\Delta\nu$ values found for organosilicon compounds and their carbon analogs provides evidence that the electronic effects in thienylsilanes are composed of opposed inductive effects and p_π–d_π-interactions[177,178] (Table IV).

In compounds containing an alkoxy group at the silicon atom a hydrogen bond of the

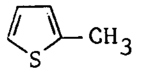
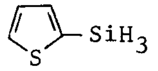
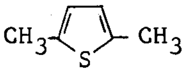
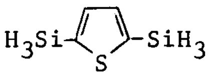


$-O-H\cdots\underset{\displaystyle R}{\underset{|}{O}}-Si$

type is predominantly formed.[178] This property is useful when studying the relative oxygen basicity in the silane $R^1R^2R^3SiOEt$ series and for the determination of the inductive constants σ^* of $R^1R^2R^3Si$ substituents from the $\Delta\nu(OH)$–σ^* relationship.[179] It has been found for the (2-thienyl)-dichlorosilyl group that $\sigma^* = 1.38 \pm 0.12$.

TABLE IV

Shifts of the Phenol ν_{OH} Stretching Frequency upon Hydrogen Bonding with Thiophene Derivatives

Compound	Δv, cm^{-1}
	53
	64
	44
	74
	40

3.4. *Chromatographic behavior*

Thienyl-containing oligocyclosiloxanes[180] and linear siloxanes[181] lend themselves to chromatographic identification and separation despite high boiling points and high molecular mass. It is interesting to study the relationship between the chromatographic parameters and the structure and other properties of thienylsilanes.[182-185] Adsorption gas chromatography can be applied to assess the variation in electron distribution over the thiophene ring upon introduction of silyl substituents,[182] since the heats of adsorption on hydroxylated silochrome (Q ads.) change as a function of the chemical shift of the proton in position 3 of the ring and, consequently, of the electron density.[183]

A chromatographic study of thienylsilatranes[184,185] and 2-thienylgermatrane[185] showed a sufficiently high vapor pressure and thermal stability to allow their chromatographic analysis on polar and nonpolar stationary phases using silanized chromosorb support.

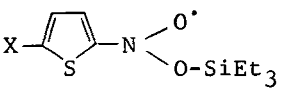
The difference between the retention indices on polar and non-polar phases ΔI amounts to 1200–1500 units for silatranes (Table V) exceeding by far the ΔI values of such chromatographic reference substances as butanol, nitropropane, and pyridine.

The additive scheme used to calculate retention indices for silatranes containing thienyl groups gives values which are by 200–1400 units lower than the experimentally found ones. The observed differences between experimental and calculated retention index values are due to the presence of a silatrane fragment with a transannular bond N → Si and are related to the nature of the substituent R and the element M in $RM(OCH_2CH_2)_3N$.

3.5. *ESR spectra*

The addition of silyl,[186-189] germyl,[188,189] and stannyl[189] radicals $\cdot MR_3$ to the nitro group of nitrothiophenes,[186,187] the pyridine nitrogen atom of 4-(2-thienyl)-pyridine,[188] and the carbonyl group of thienyl ketones[189] results in fairly stable paramagnetic products which have been investigated by means of ESR spectroscopy.

Analysis of the ESR spectra of some 2-thienylnitroxide radicals[186]



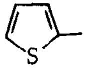
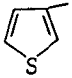
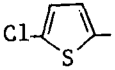
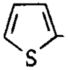
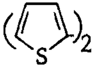
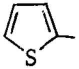
X = H, Me, Ph, Cl, CN, NO_2, Ac, CHO, SMe, CO_2Me

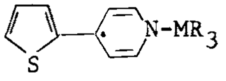
shows that the hyperfine splitting constants are correlated with Hammet's constants σ^- of the substituents X. The splitting is enhanced by electron-donor groups and diminished by electron-acceptor groups. Compounds of this type contain no rotamers at room temperature. However, at lower temperatures the ESR spectra show signals which can be assigned to conformers with the nitroxide oxygen in *cis*- or *trans*-position relative to the sulfur atom of the thiophene ring.[187] The rotational barrier amounts to 11.8 and 9.7 kcal/mole, respectively, in 2- and 3-substituted triethylsiloxynitroxide thiophene radicals.[188]

The replacement of a silyl group by a germyl group in the radical[188]

TABLE V

Retention Indices of Compounds RM$(OCH_2CH_2)_3N$

R	M	I		$\Delta I = {}^{I}OV\text{-}255 - {}^{I}Ap$	$\delta I = I_{found} - I_{calcd.}$	
		Ap	OV-255		Ap	OV-255
	Si	2158	3440	1282	490	960
	Si	2149	3320	1171	480	900
	Si	3386	3918	1532	670	1400
 SiMe$_2$CH$_2$CH$_2$	Si	2396	3327	931	280	460
 SiMeCH$_2$CH$_2$	Si	2946	4136	1190	230	470
	Ge	2299	3606	1307	510	1140



M = Si, Ge

affects only the hyperfine splitting constants of the hydrogen and nitrogen atoms in the pyridine ring whereas the thiophene ring constants remain unchanged.

At the same time dithienyl ketone radicals[189] show decreased hyperfine splitting constants upon transition from silicon to germanium and tin derivatives (Table VI).

3.6. *The ^{35}Cl NQR spectra*

The ^{35}Cl NQR spectra of 5-substituted 2-chlorothiophenes including trimethylsilyl and trichlorosilyl derivatives[190] have been studied. A single narrow band at $\nu^{77} = 36.321$ MHz is observed in 2-chloro-5-trimethylsilylthiophene. The NQR frequencies ν^{77} appear to be correlated with Hammett's σ_p constants:

$$\nu^{77} = 36.872 + 0.878\sigma_p \quad (r = 0.963)$$

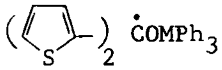
Such a relationship is not observed in the trimethylsilyl derivatives ($\sigma_p = -0.072$) where a significant deviation is evident.

3.7. *The Mössbauer spectra*

The Mössbauer spectra of tetra-(2-thienyl)-stannane[191] show a singlet band with the isomeric shift $\delta = 1.10$ mm • sec^{-1}. The considerably decreased isomeric shift δ, as compared to tetraphenylstannane ($\delta = 1.26$ mm • sec^{-1}), is associated with a greater inductive effect of the heterocycle leading to diminished s-electron density at the tin atom or with increased p-electron density as a result of p_π–d_π-interaction.

TABLE VI

Hyperfine Splitting Constants of Hydrogen Atoms in Thiophene Ring Radicals

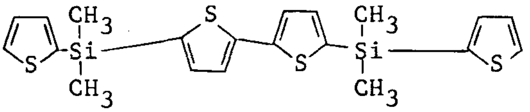


	a, Gs		
M	a(3)	a(4)	a(5)
Si	5.18	1.08	4.34
Ge	5.19	1.08	4.24
Sn	5.03	1.03	4.10

3.8. X-ray studies

The structures of tetra-(2-thienyl)-silane,[192] -germane,[193] -stannane,[193] and -plumbane[193] have been analyzed. These compounds are characterized by identical molecular symmetry and crystal packing. Their structures are orientationally disordered due to the presence of two thiophene ring conformations spaced at 179° relative to the M—C bond. The bond lengths Si—C, Ge—C, Sn—C, Pb—C in tetrathienyl derivatives amount to 1.89 Å, 1.94 Å, 2.15 Å, and 2.20 Å, respectively.

The structure of 5,5′-bis-[dimethyl-(2-thienyl)-silyl]-2,2′-bithienyl:[194]



contains a planar bithienyl moiety. The angles between the thienyl groups and the bithienyl group are about 90°.

The bond lengths Si—C (thienyl) (1.855 Å) and Si—C (bithienyl) (1.852 Å) are somewhat smaller than Si—CH_3 (1.881 Å).

IV. BIOLOGICAL ACTIVITY

Thienyl-containing silatranes,[15,19,135,195,196] germatranes,[19] aminoalkylsilanes,[113,197,198] their hydrochlorides,[15,113,195,197] and methyl-(2-thienyl)-silane[19] have been tested for psychotropic activity and toxicity.

The results of experiments with thienylsilatranes demonstrate that the highest acute toxicity is possessed by compounds with the heterocycle directly associated with the silatrane moiety (Table VII).

The acute toxicity of thienylsilatranes in white mice following intraperitoneal administration[19,135] is comparable to that of 1-phenylsilatrane. Introduction of a methyl group in position 5 on the thiophene ring in 1-(2′-thienyl)-silatrane[135] increases the toxicity whereas the separation of the thienyl group from the silatrane moiety by the Si—C—C group (compound 4 and 5) results in a significant loss of toxicity.

1-(2′-Thienyl)- and 1-(3′-thienyl)-silatranes exert opposite psychotropic effects.[19] The 3′-substituted isomer acts as a sedative agent in animals and inhibits orientational reactions and locomotor activity, the 1-(2′-thienyl)-silatrane eliciting a stimulatory effect. 1-(2′-Thienyl)-germatrane also possesses stimulating properties, but its toxicity is 50 times as low as that of the corresponding silatrane.[19]

It has been found that 1-(2′-thienyl)-silatrane elevates the cycloguanosine monophosphate content in cerebellum whereas the c-AMP concentration in several regions of the rat brain remains unaffected.[196]

The psychotropic activity exhibited by thienyl-containing aminoalkylsilanes[113] and their hydrochlorides[113,195,197] is of the deprimating type. In the α-, β- and γ-substituted perhydroazepinoalkylsilane hydrochlorides[195,197]

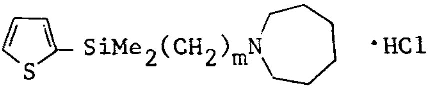
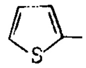
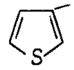
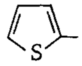
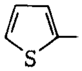
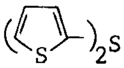


TABLE VII

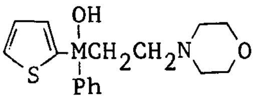
Pharmacological Activity of Thienyl Substituted Silatranes RSi(OCH$_2$CH$_2$)$_3$N

N	R	LD$_{50}$, mg/kg white mice i/p	ED$_{50}$, mg/kg "tube" test	ED$_{50}$, mg/kg hypothermy
1		0.3	0.0016	0.008
2		1.8	0.0016	0.005
3	 *	16.5	1.0	2.7
4	—SiMe$_2$CH$_2$CH$_2$	1650	92	135
5	$_2$SiMeCH$_2$CH$_2$	3900	150	82

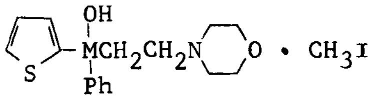
* 1-(2-thienyl)-germatrane.

the largest effect is observed with dimethyl-(2-thienyl)-(β-perhydroazepinoethyl)-silane (m = 2), with a therapeutic index of 23. The above hydrochlorides show a similar toxicity in white mice after intraperitoneal administration (70–78 mg/kg).

The spasmolytic properties of morpholinoethylsilane (I a), its iodomethylate (II a) and their carbon analogs (I b, II b) were compared on isolated guinea pig ileum.[198]



I



II

a, M = Si; b, M = C

At a concentration of 10^{-6} mol/l compound I a was 7 times more effective against carbachol than I b and II a was 6 times more effective than II b.

REFERENCES

1. C. J. Attridge, *Organomet. Chem. Rev. A*, **5**, 323 (1970).
2. T. H. Chan and I. Fleming, *Synthesis*, 761 (1979).
3. D. Habich and F. Effenberger, *Synthesis*, 841 (1979).
4. E. Lukevics and N. P. Erchak, in *Progress in Furan Chemistry* (Zinatne, Riga, 1978), pp. 198–230 (in Russian).
5. E. Lukevics, Organosilicon Derivatives of Furan, Thesis, Riga, 1965.
6. S. N. Borisov, M. G. Voronkov, and E. Ya. Lukevics, *Organosilicon Derivatives of Phosphorus and Sulfur* (Plenum Press, New York, London, 1971), pp. 272–283.
7. S. N. Borisov, M. G. Voronkov, and E. Lukevics, *Organosilicon Derivatives of Phosphorus and Sulfur* (Khimia, Leningrad, 1968), pp. 239–250 (in Russian).
8. V. I. Savushkina, B. M. Tabenko, and Ye. A. Chernishev, *High-Temperature Gas-Phase Methods for the Synthesis of Organosilicon Monomers* (Moscow, 1979), pp. 125–136 (in Russian).
9. C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 4921 (1961).
10. R. A. Benkeser and R. C. Currie, *J. Am. Chem. Soc.*, **70**, 1780 (1948).
11. C. Eaborn and G. Seconi, *J.C.S., Perkin Trans. II*, 925 (1976).
12. D. Häbich, Darstellung von Aryl- and Heteroaryltrimethylsilanen. Anwendung von Desilylierungsreaktionen, Diss., Univ. Stuttgart, 1977.
13. E. Lukevics, O. A. Pudova, and N. P. Erchak, *Zh. Obshch. Khim.*, **50**, 1348 (1980).
14. E. Lukevics, O. A. Pudova, J. Popelis, and N. P. Erchak, *Zh. Obshch. Khim.*, **51**, 115 (1981).
15. O. A. Pudova, Furan and Thiophene Derivatives of IV B Group Elements, Thesis, Riga, 1980.
16. E. Krause and G. Renwanz, *Ber.*, **62**, 1710 (1929).
17. H. Sargent (U.S. Rubber Co.), U.S. Pat. 3,068,241 (1962); C.A., **58**, 10238 (1963).
18. P. D. George (General Electric Co.), U.S. Pat. 2,640,833 (1953); C.A., **48**, 5227 (1954).
19. E. Lukevics, S. Germane, O. A. Pudova, and N. P. Erchak, *Khim. Pharm. Zhurn.*, **13**, N 10, 52 (1979).
20. N. S. Nametkin, T. I. Chernisheva, and L. I. Kartasheva, *Dokl. Akad. Nauk SSSR*, **156**, 608 (1964).
21. L. I. Kartasheva, N. S. Nametkin, and T. I. Chernisheva, *Zh. Obshch. Khim.*, **40**, 1262 (1970).
22. L. I. Kartasheva, N. S. Nametkin, and T. I. Chernisheva, *Dokl. Akad. Nauk SSSR*, **170**, 848 (1966).
23. W. C. Hammann, C. F. Hobbs, and D. J. Bauer, *J. Org. Chem.*, **32**, 2841 (1967).
24. P. D. George (General Electric Co.), U.S. Pat. 2,645,644 (1953); C.A., **48**, 7064 (1954).
25. British Thomson-Houston Co. Ltd., Brit. Pat. 694,440 (1953); C.A., **48**, 10775 (1964).
26. O. G. Yarosh, A. S. Nakhmanovich, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1640 (1977).
27. E. Krause and G. Renwanz, *Ber.*, **65**, 777 (1932).
28. E. Krause and G. Renwanz, *Ber.*, **60**, 1582 (1927).
29. S. Gopinathan, C. Gopinathan, and J. Gupta, *Ind. J. Chem.*, **12**, 623 (1974).
30. H. E. Ramsden (Metal & Thermit Corp.), Brit. Pat. 825,039 (1959); C.A., **54**, 18438 (1960).
31. H. E. Ramsden (Metal & Thermit Corp.), U.S. Pat. 2,965,661 (1960); C.A., **55**, 6377 (1961).

32. H. E. Ramsden (Metal & Thermit Corp.), Brit. Pat. 829,243 (1960); C.A., **54,** 21139 (1960).
33. H. E. Ramsden (Metal & Thermit Corp.), U.S. Pat. 2,873,287 (1959); C.A., **53,** 13108 (1959).
34. H. E. Ramsden (Metal & Thermit Corp.), Brit. Pat. 824,944 (1959); C.A., **54,** 17238 (1960).
35. C. Hoogzand, J. Nielsen, and E. H. Braye, *Chem. Comm.,* 1520 (1971).
36. S. F. Thames and J. E. McCleskey, *J. Heterocycl. Chem.,* **3,** 104 (1966).
37. S. F. Thames and J. E. McCleskey, *J. Heterocycl. Chem.,* **4,** 146 (1967).
38. S. F. Thames and J. E. McCleskey, *J. Heterocycl. Chem.,* **4,** 371 (1967).
39. S. F. Thames, L. H. Edwards, T. N. Jacobs, P. L. Grube, and F. H. Pinkerton, *J. Heterocycl. Chem.,* **9,** 1259 (1972).
40. J.-P. Lampin and F. Mathey, *J. Organomet. Chem.,* **71,** 239 (1974).
41. D. W. Slocum and P. L. Gierer, *J. Org. Chem.,* **41,** 3668 (1976).
42. T. A. Starostina, L. F. Ribakova, and R. R. Shifrina, *Zh. Org. Khim.,* **16,** 1968 (1980).
43. T. Kauffmann, *Angew. Chem.,* **18,** 1 (1979).
44. M. R. Smith, Jr. and H. Gilman, *Organomet. Chem. Synth.,* **1,** 265 (1971); C.A., **76,** 72578 (1972).
45. I. Haiduc and H. Gilman, *Rev. Roum. Chim.,* **16,** 305 (1971).
46. M. T. Rahman and H. Gilman, *J. Ind. Chem. Soc.,* **56,** 346 (1979).
47. M. R. Smith, Jr. and H. Gilman, *J. Organomet. Chem.,* **42,** 1 (1972).
48. M. T. Rahman, M. R. Smith, Jr., A. F. Webb, and H. Gilman, *Organomet. Chem. Synth.,* **1,** 105 (1971); C.A., **74,** 125759 (1971).
49. G. M. Davies and P. S. Davies, *Tetrahedron Lett.,* 3507 (1972).
50. S. Gronowitz, T. Freyd, O. Karlsson, K. Lawitz, P. Pedaja, and K. Pettersson, *Chem. Scripta,* **18,** 192 (1981).
51. D. W. Knight and A. P. Nott, *Tetrahedron Lett.,* **21,** 5051 (1980).
52. Ye. A. Chernishev and N. G. Tolstikova, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1700 (1964).
53. Ye. A. Chernishev, V. I. Savushkina, B. M. Tabenko, N. I. Zaslavskaya, M. M. Serebriannikov, V. Z. Anisimova, and S. G. Yagodina, USSR Author's Certif. 374,318 (1970); *Otkr., Izobr.,* N 15, 51 (1973).
54. D. Mochler and J. E. Sellers (General Electric Co.), U.S. Pat. 2,598,436 (1952); C.A. **47,** 3875 (1952).
55. Ye. A. Chernishev, V. G. Bikovchenko, V. I. Pchelintsev, V. I. Savushkina, A. I. Korshunov, and B. L. Maisuradze, USSR Author's Certif. 455,109 (1972); *Otkr. Izobr.,* N 48, 48 (1974).
56. Ye. A. Chernishev, V. I. Savushkina, A. I. Korshunov, V. G. Bikovchenko, and G. K. Sulzhenko, USSR Author's Certif. 482,457 (1973); *Otkr. Izobr.,* N 32, 67 (1975).
57. Ye. A. Chernishev, V. I. Savushkina, V. Z. Anisimova, G. I. Belik, and D. V. Useinova, USSR Author's Certif. 424,861 (1972); *Otkr., Izobr.,* N 15, 84 (1974).
58. Ye. A. Chernishev and N. G. Tolstikova, USSR Author's Certif. 172,786 (1964); *Bull. Isobr.,* N 14, 24 (1965).
59. Ye. A. Chernishev, V. G. Bikovchenko, V. I. Pchelintsev, V. I. Savushkina, and A. I. Korshunov, USSR Author's Certif. 491,641 (1973); *Otkr., Izobr.,* N 42, 63 (1975).
60. Ye. A. Chernishev, V. G. Bikovchenko, G. I. Sulzhenko, and V. P. Rutkovski, *Kinetika i Kataliz,* **19,** 1100 (1978).
61. V. G. Nosenko, V. G. Lakhtin, V. D. Sheludyakov, and V. F. Mironov, *Zh. Obshch. Khim.,* **50,** 1967 (1980).
62. Ye. A. Chernishev, N. G. Komalenkova, S. A. Bashkirova, and Yu. A. Pazderski, USSR Author's Certif., 739,073 (1980); *Otkr., Izobr.,* N 21, 138 (1980).
63. Ye. A. Chernishev, V. I. Savushkina, Z. V. Belyakova, B. M. Tabenko, A. A. Dmitriev, and V. N. Bochkarev, IXth International Symposium on Organic Sulphur Chemistry, Abstracts, Riga, 1980, p. 162.
64. Ye. A. Chernishev, V. I. Savushkina, T. A. Zhavoronkova, and T. E. Filippova, USSR Author's Certif. 558,920 (1976); *Otkr., Izobr.,* N 9, 63 (1977).
65. Ye. A. Chernishev, N. G. Komalenkova, and S. A. Bashkirova, USSR Author's Certif. 437,769 (1973); *Otkr., Izobr.,* N 28, 54 (1974).
66. Ye. A. Chernishev, N. G. Komalenkova, S. A. Bashkirova, and T. A. Zhavoronkova, *Zh. Obshch. Khim.,* **46,** 1278 (1976).
67. Ye. A. Chernishev, V. I. Savushkina, V. Z. Anisimova, and T. F. Skulkova, USSR Author's Certif. 380,661 (1971); *Otkr., Izobr.,* N 21, 88 (1973).
68. V. F. Mironov and N. S. Fedotov, *Zh. Obshch. Khim.,* **36,** 556 (1966).
69. C. Gopinathan, S. K. Pandit, S. Gopinathan, A. Y. Sonsale, and P. A. Awasarkar, *Ind. J. Chem.,* **13,** 516 (1975).
70. Ye. M. Panov and K. A. Kocheshkov, *Dokl. Akad. Nauk USSR,* **123,** 295 (1958).
71. J. P. Foster and S. B. Soloway (Shell Oil Co.), U.S. Pat. 3,736,333 (1973); C.A., **79,** 42695 (1973).
72. S. Brenner and E. Dunkelblum, *Tetrahedron Lett.,* 2487 (1973).

73. K. Okuhara, *Bull. Chem. Soc. Japan*, **54**, 2045 (1981).
74. R. Oliver and D. R. M. Walton, *Tetrahedron Lett.*, 5209 (1972).
75. M. Bolourtchian and A. Saednya, *Bull. Soc. Chim. Fr.*, II-170 (1978).
76. M. Bolourtchian, M. R. Nouri, and A. Saednya, *Pazhoohandeh* (Tehran), 161 (1978); C.A., **93**, 71843 (1980).
77. O. G. Yarosh, A. S. Nakhmanovich, and N. V. Komarov, *Khim. Geterotsikl. Soedin.*, 642 (1968).
78. E. N. Deryagina, A. S. Nakhmanovich, V. N. Yelokhina, and O. G. Yarosh, *Khim. Geterotsikl. Soedin.*, 891 (1970).
79. M. F. Ford and D. R. M. Walton, *Synthesis*, 47 (1973).
80. E. V. Wilkus and A. Berger (General Electric Co.), U.S. Pat. 3,410,822 (1968); C.A. **70**, 38673 (1969).
81. R. J. Lisanke (Union Carbide Corp.), U.S. Pat. 3,008,922 (1958); C.A., **56**, 8744 (1962).
82. R. J. Lisanke (Union Carbide Corp.), U.S. Pat. 3,008,926 (1958); C.A., **56**, 8745 (1962).
83. I. M. Gverdtsiteli and M. D. Chanturia, *Zh. Obshch. Khim.*, **45**, 2349 (1975).
84. C. Eaborn, G. Pirazzini, G. Seconi, and A. Ricci, *J. Organomet. Chem.*, **192**, 339 (1980).
85. E. Lukevics, *Latv. PSR Zin. Akad. Vestis, Chem. Ser.*, 111 (1963).
86. Yu. K. Yuriev, Z. V. Belyakova, and V. P. Volkov, *Zh. Obshch. Khim.*, **29**, 1463 (1959).
87. S. Weber and E. I. Becker, *J. Org. Chem.*, **27**, 1258 (1962).
88. F. D. King and D. R. M. Walton, *Chem. Comm.*, 256 (1974).
89. Ye. A. Chernishev, Ye. F. Bugerenko, and A. S. Petukhova, *Zh. Obshch. Khim.*, **41**, 2186 (1971).
90. M. G. Voronkov, M. S. Sorokin, and V. M. Dyakov, *Zh. Obshch. Khim.*, **51**, 605 (1981).
91. P. A. Konstantinov and R. I. Shchupik, *Zh. Obshch. Khim.*, **33**, 1251 (1963).
92. J. R. Pratt and S. F. Thames, *J. Org. Chem.*, **38**, 4271 (1973).
93. P. L. Kelly, S. F. Thames, and J. E. McCleskey, *J. Heterocycl. Chem.*, **9**, 141 (1972).
94. H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 1689 (1950).
95. F. H. Pinkerton and S. F. Thames, *J. Heterocycl. Chem.*, **9**, 725 (1972).
96. H. Gilman and M. A. Plunkett, *J. Am. Chem. Soc.*, **71**, 1117 (1949).
97. D. W. Slocum and P. L. Gierer, *J. Org. Chem.*, **38**, 4189 (1973).
98. T. Kaufmann and H.-H. Kniese, *Tetrahedron Lett.*, 4043 (1973).
99. R. A. Benkeser and H. Landesman, *J. Am. Chem. Soc.*, **71**, 1689 (1949).
100. V. F. Mironov, N. S. Fedotov, G. E. Evert, M. G. Kuznetsova, and A. V. Kisin, *Zh. Obshch. Khim.*, **49**, 361 (1979).
101. N. S. Fedotov, G. E. Evert, Vth All-Union Conference on the Chemistry and Application of Organosilicon Compounds, Abstracts, Tbilisi, 1980, p. 43.
102. Ye. A. Chernishev, V. I. Savushkina, and B. M. Tabenko, USSR Author's Certif. 228,685 (1967); *Izobr. Prom. Obr.*, N 32, 13 (1968).
103. Ye. A. Chernishev, V. I. Savushkina, and B. M. Tabenko, USSR Author's Certif. 388,002 (1971); *Otkr., Izobr.*, N 28, 75 (1973).
104. Ye. A. Chernishev, V. I. Savushkina, and V. Z. Anisimova, USSR Author's Certif. 424,862 (1972); *Otkr., Izobr.*, N 15, 84 (1974).
105. Ye. A. Chernishev, Ye. F. Bugerenko, A. S. Petukhova, and G. P. Matveicheva, USSR Author's Certif. 406,837 (1972); *Otkr. Izobr.*, N 46, 69 (1973).
106. L. I. Ignatovich, M. A. Trushule, J. Popelis, and E. Lukevics, Ist All-Union Conference on Organometallic Chemistry, Abstracts, Moscow, 1979, part I, p. 82.
107. M. Dzintara and E. Lukevics, Chemistry and Practical Application of Organosilicon and Organophosphorus Compounds, Leningrad, 1979, p. 29.
108. E. Lukevics, N. P. Erchak, O. A. Pudova, M. Dzintara, and J. Popelis, IXth International Symposium on Organic Sulphur Chemistry, Abstracts, Riga, 1980, p. 179.
109. M. Dzintara, O. A. Pudova, N. P. Erchak, and J. Popelis, Vth All-Union Conference on Chemistry and Application of Organosilicon Compounds, Abstracts, Tbilisi, 1980, p. 166.
110. E. Lukevics and M. Dzintara, *Zh. Obshch. Khim.*, **51**, 2043 (1981).
111. Ye. A. Chernishev, V. I. Savushkina, and V. Z. Anisimova, USSR Author's Certif. 362,019 (1971); *Otkr., Izobr.*, N 2, 54 (1973).
112. N. S. Nametkin, T. I. Chernisheva, N. A. Pritula, M. J. Gevenyan, and L. I. Kartasheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2249 (1969).
113. E. Lukevics, S. Germane, N. P. Erchak, and E. P. Popova, *Khim. Pharm. Zhurn.*, **12,** N 2, 343 (1978).
114. S. R. Nanushyan, Ye. I. Simakovskaya, V. V. Severni, V. I. Savushkina, and Ye. A. Chernishev, USSR Author's Certif. 564,315 (1975); *Otkr., Izobr.*, N 25, 96 (1977).
115. T. I. Tschernyschewa, N. S. Nametkin, N. A. Pritula, and L. I. Kartaschewa, *Plaste Kautschuk*, **10**, 390 (1963).

116. I. A. Vostokov, Yu. I. Dergunov, V. P. Kozyukov, V. D. Sheludyakov, V. F. Mironov, and V. Z. Anisimova, *Zh. Obshch. Khim.*, **43,** 623 (1973).
117. K. I. Kobrakov, T. I. Chernisheva, L. I. Kartasheva, and N. S. Nametkin, *Dokl. Akad. Nauk USSR,* **202,** 343 (1972).
118. Ye. A. Chernishev, V. I. Savushkina, and V. S. Karentnikov, USSR Author's Certif. 241,437 (1967); *Otkr., Izobr.*, N 14, 22 (1969).
119. N. S. Nametkin, O. V. Kuz'min, T. I. Chernisheva, V. I. Savushkina, V. Z. Anisimova, and Ye. A. Chernishev, *Dokl. Akad. Nauk USSR,* **193,** 110 (1970).
120. Ye. A. Chernishev, V. I. Savushkina, T. Ye. Filippova, and T. A. Zhavoronkova, USSR Author's Certif. 595,323 (1976); *Otkr., Izobr.*, N 8, 98 (1978).
121. V. F. Mironov, V. D. Sheludyakov, and V. G. Nosenko, *Dokl. Akad. Nauk SSSR,* **224,** 600 (1975).
122. N. R. Nanushyan, Ye. I. Simakovskaya, V. V. Severni, V. I. Savushkina, Ye. A. Chernishev, and B. M. Tabenko, USSR Author's Certif. 556,157 (1975); *Otkr., Izobr.*, N 16, 70 (1977).
123. M. L. Galashina, G. A. Matveeva, M. V. Sobolevski, Ye. A. Chernishev, and N. G. Tolstikova, USSR Author's Certif. 190,571 (1965); *Bull. Izobr.*, N 2, 88 (1967).
124. M. V. Sobolevski, D. V. Nazarova, G. V. Voropaeva, A. A. Kuznetsova, M. L. Galashina, V. I. Savushkina, Ye. A. Chernishev, and G. A. Matveeva, USSR Author's Certif. 265,445 (1968); *Otkr., Izobr.*, N 10, 104 (1970).
125. Yu. A. Yuzhelevski, T. V. Kurlova, and O. N. Larionova, *Zh. Obshch. Khim.*, **39,** 2372 (1969).
126. P. D. George (General Electric Co.), U.S. Pat. 2,640,818 (1953); C.A., **47,** 9055 (1953).
127. S. Nitzsche and R. Riedle (Wacker Chemie G.m.b.H.), U.S. Pat. 2,770,611 (1956); C.A., **51,** 7761 (1957).
128. K. Olsson and C. Axén, *Ark. Kemi,* **22,** 237 (1964).
129. P. D. George (General Electric Co.), U.S. Pat. 2,640,833 (1953); C.A., **48,** 5227 (1954).
130. Yu. Ye. Raskin, G. P. Kvitnitskaya, and L. V. Gornets, *Khim. i Tekhnol. Topliv i Masel,* **15,** N 12, 42 (1970).
131. B. A. Orkin (Secony-Vacuum Oil Co.), U.S. Pat. 2,701,803 (1955); C.A., **49,** 7236 (1955).
132. N. P. Sluchevskaya, V. A. Yablokov, N. V. Yablokova, V. I. Savushkina, and Ye. A. Chernishev, *Zh. Obshch. Khim.*, **47,** 229 (1977).
133. Yu. K. Yuriev, Z. V. Belyakova, and V. P. Volkov, *Zh. Obshch. Khim.*, **29,** 3652 (1959).
134. M. G. Voronkov, G. I. Zelchan, Ye. A. Chernishev, B. M. Tabenko, and V. I. Savushkina, USSR Author's Certif. 364,621 (1971); *Otkr., Izobr.*, N 5, 76 (1973).
135. M. G. Voronkov, G. I. Zelchan, V. I. Savushkina, B. M. Tabenko, and Ye. A. Chernishev, *Khim. Geterotsikl. Soed.*, 772 (1976).
136. E. Lukevics, O. A. Pudova, J. Popelis, and N. P. Erchak, *Zh. Obshch. Khim.*, **51,** 369 (1981).
137. N. P. Sluchevskaya, N. V. Yablokova, V. A. Yablokov, and Yu. A. Aleksandrov, *Zh. Obshch. Khim.* **48,** 1136 (1978).
138. C. Eaborn and P. M. Jackson, *J. Chem. Soc.*, B, 21 (1969).
139. G. Seconi and C. Eaborn, *J.C.S., Perkin Trans II,* 931 (1981).
140. F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2299 (1959).
141. F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2303 (1959).
142. H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71,** 2066 (1949).
143. R. A. Benkeser and A. Torkelson, *J. Am. Chem. Soc.*, **76,** 1252 (1954).
144. J. P. Pratt, F. H. Pinkerton, and S. F. Thames, *J. Organomet. Chem.*, **38,** 29 (1972).
145. K. Dey, C. Eaborn, and D. R. M. Walton, *Organomet. Chem. Synth.*, **1,** 151 (1971); C.A., **75,** 48618 (1971).
146. F. Montoro, J. Calatayud, and A. Vilar (Especialidades Latinas Medicamentos Universales S.A.), Span. Pat. 486,730 (1979); C.A., **94,** 47128 (1981).
147. S. F. Thames, J. E. McClesky, and P. L. Kelly, *J. Heterocycl. Chem.*, **5,** 749 (1968).
148. R. Tacke, E. Zimonyi-Hegedüs, and U. Wannagat, *J. Organomet. Chem.*, **173,** 21 (1979).
149. M. R. Smith, Jr. and H. Gilman, *J. Organomet. Chem.*, **37,** 35 (1972).
150. F. H. Pinkerton and S. F. Thames, *J. Organomet. Chem.*, **27,** C4 (1971).
151. R. D. Howells and H. Gilman, *J. Organomet. Chem.*, **77,** 177 (1974).
152. G. R. John, L. A. P. Kane-Maguire, and C. Eaborn, *Chem. Comm.*, 481 (1975).
153. C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S., Dalton Trans.*, 357 (1978).
154. C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S., Dalton Trans.*, 1288 (1978).
155. C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S., Dalton Trans.*, 134 (1979).
156. C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S., Dalton Trans.*, 758 (1979).
157. C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organomet. Chem.*, **146,** 17 (1978).

158. C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organomet. Chem.*, **96,** C38 (1975).
159. A. N. Egorochkin, A. I. Burov, N. S. Vyazankin, V. I. Savushkina, V. Z. Anisimova, and Ye. A. Chernishev, *Dokl. Akad. Nauk SSSR,* **184,** 351 (1969).
160. A. N. Egorochkin, N. S. Vyazankin, A. I. Burov, Ye. A. Chernishev, V. I. Savushkina, and B. M. Tabenko, *Khim. Geterotsikl. Soed.*, 911 (1972).
161. A. N. Egorochkin, N. S. Vyazankin, A. I. Burov, Ye. A. Chernishev, V. I. Savushkina, and O. V. Kuz'min, *Khim. Geterotsikl. Soed.*, 1483 (1972).
162. G. Barbieri and F. Taddei, *J. Chem. Soc., B,* **1971,** 1903.
163. A. P. Ebdon, T. N. Huckerby, and F. G. Thorpe, *Tetrahedron Lett.*, 2921 (1971).
164. M. J. Bulman, *Tetrahedron,* **25,** 1433 (1969).
165. D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching, and M. Bullpitt, *Aust. J. Chem.*, **27,** 417 (1974).
166. B. Wrackmeyer, *Z. Naturforsch,* **34b,** 325 (1979).
167. V. A. Kuznetsov, A. N. Egorochkin, Ye. A. Chernishev, V. I. Savushkina, and V. Z. Anisimova, *Dokl. Akad. Nauk SSSR,* **214,** 346 (1974).
168. V. A. Kuznetsov, A. N. Egorochkin, A. I. Burov, Ye. A. Chernishev, V. I. Savushkina, V. Z. Anisimova, and O. V. Kuz'min, *Dokl. Akad. Nauk SSSR,* **216,** 1062 (1974).
169. M. A. Lopatin, V. A. Kuznetsov, A. N. Egorochkin, O. A. Pudova, N. P. Erchak, and E. Lukevics, *Dokl. Akad. Nauk SSSR,* **246,** 379 (1979).
170. S. Ya. Khorshev, N. S. Vyazankin, A. N. Egorochkin, Ye. A. Chernishev, V. I. Savushkina, O. V. Kuz'min, and V. Z. Anisimova, *Khim. Geterotsikl. Soed.*, 477 (1974).
171. A. K. Kozirev and I. F. Kovalev, Ist All-Union Conference on Organometallic Chemistry, Abstracts, Moscow, 1979, p. 97.
172. A. N. Egorochkin, S. Ya. Khorshev, N. S. Vyazankin, T. I. Chernisheva, and O. V. Kuz'min, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 544 (1971).
173. A. N. Egorochkin, S. Ya. Khorshev, N. S. Vyazankin, T. I. Chernisheva, and O. V. Kuz'min, *Izv, Akad. Nauk SSSR, Ser. Khim.*, 776 (1971).
174. A. N. Egorochkin, N. S. Vyazankin, S. Ya. Khorshev, N. S. Ostasheva, O. V. Kuz'min, N. S. Nametkin, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR,* **211,** 337 (1973).
175. A. N. Egorochkin, S. Ya. Khorshev, N. S. Ostasheva, M. G. Voronkov, N. S. Vyazankin, T. V. Kashik, O. V. Kuz'min, N. S. Nametkin, and N. A. Pritula, *J. Organomet. Chem.*, **99,** 47 (1975).
176. A. N. Egorochkin, N. S. Vyazankin, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR,* **211,** 859 (1973).
177. A. N. Egorochkin and S. E. Skobeleva, *Usp. Khim.*, **48,** 2216 (1979).
178. A. N. Egorochkin, N. S. Vyazankin, S. E. Skobeleva, S. Ya. Khorshev, Ye. A. Chernishev, V. I. Savushkina, and O. V. Kuz'min, *Khim. Geterotsikl. Soed.,* 1057 (1972).
179. J. Pola and V. Chvalovský, *Coll. Czech. Chem. Comm.*, **43,** 746 (1978).
180. B. M. Luskina and N. N. Troitskaya, *Zh. Anal. Khim.*, **33,** 1435 (1978).
181. G. N. Turkeltaub, V. N. Bochkarev, M. L. Galashina, and Ye. I. Golisheva, *Zavodskaya Lab.*, **44,** 278 (1978).
182. G. N. Bortnikov, A. V. Kiselev, N. S. Vyazankin, and Ya. I. Yashin, *Chromatographia,* **4,** 14 (1971); C.A., **74,** 112,148 (1971).
183. G. N. Bortnikov, A. N. Egorochkin, N. S. Vyazankin, Ye. A. Chernishev, and Ya. I. Yashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1402 (1970).
184. V. D. Shatz, N. P. Erchak, V. A. Belikov, O. A. Pudova, and E. Lukevics, *Zh. Obshch. Khim.*, **48,** 1661 (1978).
185. V. D. Shatz, V. A. Belikov, G. I. Zelchan, I. I. Solomennikova, N. P. Erchak, O. A. Pudova, and E. Lukevics, *J. Chrom.*, **200,** 105 (1980).
186. C. M. Camaggi, R. Leardini, and G. Placucci, *J.C.S., Perkin Trans.* II, 1195 (1974).
187. C. M. Camaggi, L. Linazzi, G. F. Pedulli, G. Placucci, and M. Tiecco, *J.C.S., Perkin Trans.* II, 1226 (1974).
188. A. Alberti and G. F. Pedulli, *Tetrahedron Lett.*, 3283 (1978).
189. A. Alberti, M. Guerra, and G. F. Pedulli, *J.C.S., Perkin Trans.* II, 1568 (1979).
190. M. G. Voronkov, V. P. Feshin, Ye. A. Chernishev, V. I. Savushkina, P. A. Nikitin, and V. A. Kotikov, *Dokl. Akad. Nauk SSSR,* **212,** 395 (1973).
191. D. W. Allen, J. S. Brooks, and R. Formstone, *J. Organomet. Chem.*, **172,** 299 (1979).
192. A. Karipides, A. T. Reed, and R. H. P. Thomas, *Acta Cryst.*, **B30,** 1372 (1974).
193. A. Karipides, A. T. Reed, D. A. Haller, and F. Heyes, *Acta Cryst.*, **B33,** 950 (1977).
194. A. Lipka and H. G. von Schnering, *Chem. Ber.*, **110,** 1377 (1977).
195. E. Lukevics, S. Germane, O. A. Pudova, and N. P. Erchak, Vth All-Union Conference on Chemistry and Application of Organosilicon Compounds, Abstracts, Tbilisi, 1980, p. 363.

196. K. Brandt, H. Mattsson, and E. Heilbronn, *Acta Pharmacol. Toxicol.*, **41,** 42 (1977).
197. E. Lukevics, S. Germane, N. P. Erchak, and O. A. Pudova, *Khim. Pharm. Zhurn.*, **15,** N 4, 42 (1981).
198. R. Tacke, E. Zimonyi-Hegedüs, M. Strecker, E. Heeg, B. Berndt, and R. Langner, *Arch. Pharm.*, **313,** 515 (1980).