SILICON - APPLICATION TO ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1974

STEPHEN S. WASHBURNE

Department of Chemistry, Temple University,
Philadelphia, Pennsylvania 19122 (USA)

CONTENTS

Silicon - Application to organic synthesis; Annual Survey covering the year 1973 see J.Organometal. Chem., 83(1974)155-211.

I. GENERAL COMMENTS

The use of silicon compounds in organic synthesis continues to be a vital area. The guiding principal of this survey continues to be that expressed in the 1973 survey(1): The final reaction product must not contain silicon at the reaction center, and that the reaction in question be synthetically useful (or have potential utility), rather than produce a product available at low expense from commercial sources.

Again, papers in this survey are grouped by reaction type rather than by silicon reagent, and excluded are references to silylation as a derivitization procedure for chromatography or mass spectrometry, use of silicon fluids or resins in coatings, stationary phases, and heat transfer media (except where such silanized surface is used as a reagent in organic synthesis), and references to the patent literature (which is unlikely to contain sufficient experimental detail). Usual abbreviations for organic groups and solvents are used——DME = dimethoxyethane, HMPT = hexamethylphosphortriamide, Pyr = pyridine, etc.

Appreciation is expressed to those who were kind enough to send preprints and reprints of work in this widely-scattered field for inclusion in this survey, and the hope is expressed that more preprints will be sent for inclusion in future surveys.

Two significant reviews appeared during 1974 of interest to synthetic chemists: The Si-H/CF_3CO_2H system for ionic hydrogenation, e.g. eq. 1, largely explored by Russian workers and ill-appreciated in the West, has been the subject of an exhaustive

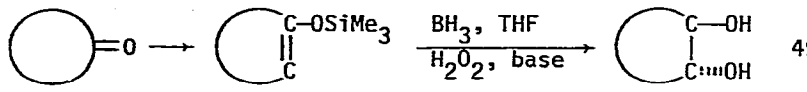
$$Et_3Si{-}H + CF_3CO_2H + X{=}Y \longrightarrow H{-}X{-}Y{-}H + Et_3SiO_2CCF_3 \qquad (1)$$

review with experimental detail (2). This process should be

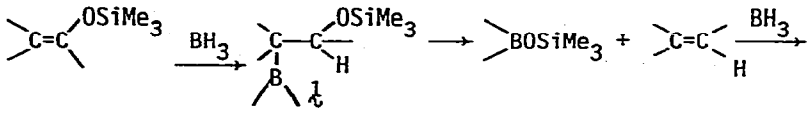
considered as an alternative to traditional hydrogenation. Brook has summarized work from his laboratory on molecular rearrangements of organosilicon compounds (3) with emphasis on the mechanistic aspects, but generates much synthetic food for thought—"organosilicon compounds having adjacent functional groups on carbon are a fertile source of molecular rearrangements, which frequently involve silicon-oxygen bond formation and concomitant silicon-carbon bond cleavage." (3)

II. OXIDATION AND REDUCTION

Specific oxidation of the ketone function is a common synthetic goal which silicon reagents can effectuate in various ways (4–9). Conversion of cyclic (but not acyclic) ketones to trans-1,2-diols is achieved by hydroboration-oxidation of silyl enol ethers (4,5), eq. 2. Presumably, in the acyclic series, an intermediate β-trimethylsilyloxyborane 1 suffers elimination to an alkene, which is further hydroborated, the overall result being carbonyl reduction, eq. 3 (4).



(2)

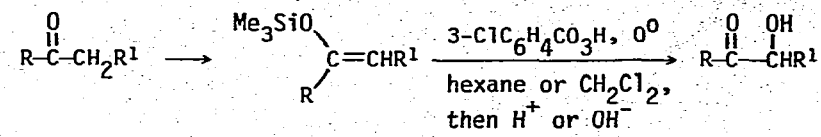


(3)

Hydroxylation of ketones in the α position is efficaceously achieved with m-chloroperbenzoic acid treatment of the corresponding trimethylsilyl enol ether followed by hydrolysis (6,7), eq. 4. A mechanism involving silyloxy epoxide 2 seems most plausible. Anomalously, the silyl enol ether of phenyl acetone gave a 70% yield of hydroxyacetophenone 3 on hydrolysis, probably

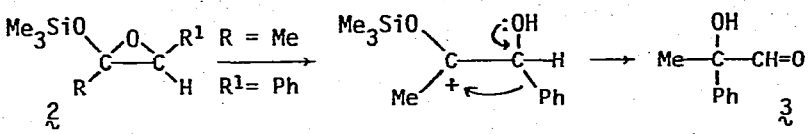
References p. 61

via a mechanism of eq. 5. The generality of this oxidation remains to be explored (7).



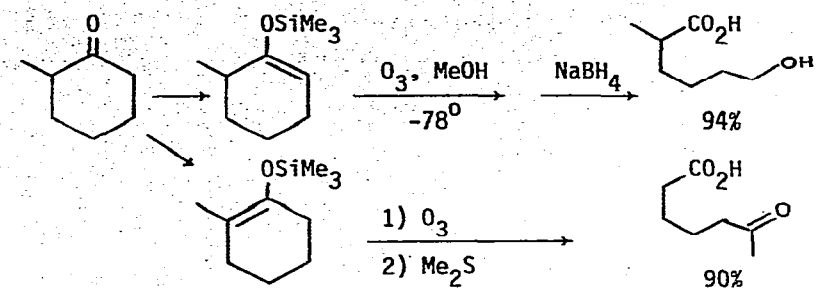
(4)

R, R^1 = -$(CH_2)_4$-; -$(CH_2)_3$-; Ph, Me; Ph, H 60-80%



(5)

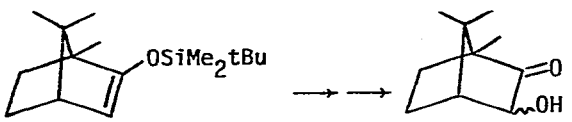
Ozonolysis of ketone trimethylsilyl enol ethers provides a method for cleaving a ketone on the less alkylated side, i.e. in opposite sense to the Baeyer-Villiger oxidation, when the kinetic (less substituted) silyloxy alkene is treated with ozone in methanol (8). Cyclic and acyclic ketones react smoothly according to eq. 6, but ketene acetals and camphor gave α-hydroxylated products similar to those noted above as well as cleavage, eq. 7. Noteworthy is the great nucleophilicity of the silyl enol ether function which allows it to trap ozone in the presence of a vinyl group. This cleavage reaction figured prominently in an elegant synthesis of a model 4 of the A & B rings of the anti-tumor sesquiterpene vernolepin, eq. 8 (9). Noteworthy in this sequence is the trapping of an enolate generated by 1,4-addition of an organocuprate to a conjugated carbonyl [AS, 1973, p. 165, and III-B below] as a route to silyl enol ethers.

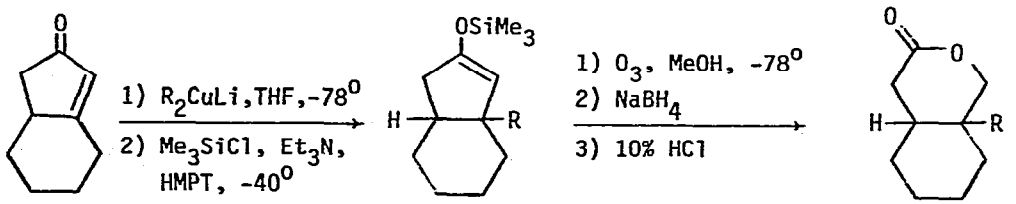


(6)

$MeCO(CH_2)_5CH_3 \longrightarrow\longrightarrow CH_3(CH_2)_5CO_2H$ 90%

$nC_6H_{13}CH{=}C(OMe)OSiMe_2tBu \longrightarrow\longrightarrow nC_6H_{13}CH{=}O$ (50%) + $nC_6H_{13}CHOH{-}CO_2Me$ (50%) (7)





$R = CH_2{=}CH$, 68% overall $R = CH_3$, 63% overall

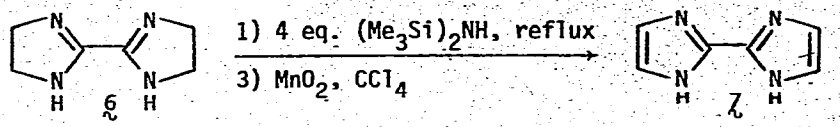
4 (8)

Reaction of imines with O-trialkyl silyl hydroxylamines affords an alternate route to oximes 5 according to eq. 9. 5 can be easily desilylated or used as a subsequent synthon (10). Oxidation of 2,2'-di(2-imidazoline) 6 to 2,2'-biimidazole 7 is facilitated by conversion of 6 to the bis(silylamine) before treatment with MnO_2, eq. 10 (11).

$$R_2C{=}NR' + R''_3SiO{-}NH_2 \longrightarrow \underset{5}{R_2C{=}N{-}OSiR''_3} + R'NH_2 \qquad (9)$$

R' = Ph, H, Et_3Si ; R" = Me, Et 80-95%

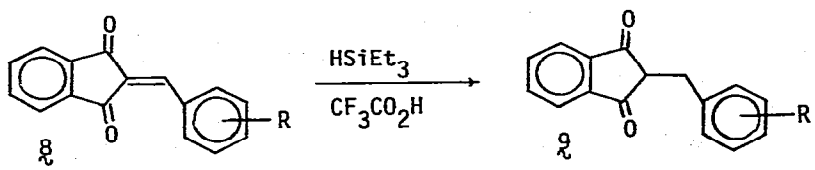
References p. 61.



70% (10)

Many synthetic applications of organosilyl peroxides are potentiated in a review article (12) on R_3SiOOR, R = H, $SiMe_3$, ML_x, compounds. A recent finding is that bis(trimethylsilyl)-peroxide oxidizes a variety of organo-element functionality in petroleum ether solution: $R_2S \rightarrow R_2SO_2$ 76-87%; $P(OEt)_3 \rightarrow OP(OEt)_3$ 98%; $Ph_3E \rightarrow Ph_3E{\rightarrow}O$ (E = P, As, Sb) 77-100% (13). It is noteworthy that triphenyl stibine is not oxidized by $(tBuO)_2$ under similar conditions.

Silicon-aided reduction continues active. Some reports on ionic hydrogenation (2) have appeared (14-16). Benzylidene indandiones 8 are reduced to 2-benzylindandiones 9 by Et_3SiH/CF_3CO_2H (14), eq. 11. Details of the ionic reduction of acyl-



(11)

R = H, p-Me, p-Et, o-Me, p-OMe, p-Cl 53-78%

methylidene tricobalt clusters $RCOC-Co_3(CO)_9$ to alkylidene derivative $RCH_2C-Co_3(CO)_9$ with Et_3SiH/CF_3CO_2H, and reduction of the former to secondary alcohols $RCHOHC-Co_3(CO)_9$ with Et_3SiH followed by sulfuric acid, have been published (15). Surprisingly, attempted reduction of tricobaltcarbon decacarbonyl hexafluorophosphate 10 with triethylsilane gave a mixture of 11 and 12 rather than desired aldehyde 13, eq. 12. When three equivalents of aluminum chloride were added to the reaction mixture 13 was obtained in 74% yield (16).

$$[(CO)_3Co]_3C\text{–}CO^+\ PF_6^- \ (10) + 3\ Et_3SiH \longrightarrow [(CO)_3Co]_3CH\ (11) + [(CO)_3Co]_3CCH_3\ (12) \qquad (12)$$
$$\text{"} \qquad \text{"} \qquad + 3\ AlCl_3 \longrightarrow [(CO)_3Co]_3CH{=}O\ (13)$$

In a mechanistically obscure reaction probably related to ionic hydrogenation, the combination of silanes with alkyl iodides reduced carbonyls to methylenes, e.g. 2-nonanone $\longrightarrow$ nonane (Ph_2SiH_2, $n\text{-}C_6H_{13}I$, 190°)(17). Closely related is the conversion of nitriles to aldehydes by triethylsilane reduction of the corresponding nitrilium fluoborate (18). N-alkylnitrilium ions 14 are converted to secondary amines with borohydride, but the milder reductant Et_3SiH stops at the imine stage, and hydrolysis gives the aldehyde, eq. 13. The important advantages cited for this procedure include mild

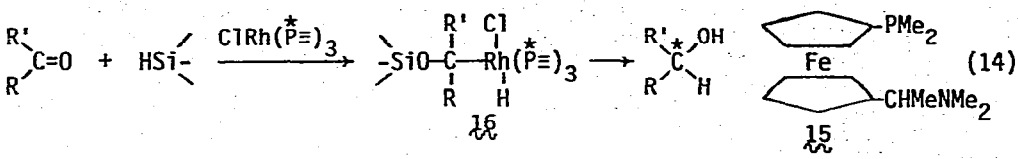
$$RC{\equiv}N \xrightarrow[CH_2Cl_2]{Et_3O^+BF_4^-} RC{\equiv}\overset{+}{N}(Et)\ BF_4^- \ (14) \xrightarrow[CH_2Cl_2]{Et_3SiH} \xrightarrow{H_2O} RCH{=}O + Et_3SiF \qquad (13)$$

conditions and no need for careful temperature control. The Et_3OBF_4/Et_3SiH combination also converts tertiary amides to ethyl esters, e.g. $PhCONEt_2 \rightarrow PhCO_2Et$, 84%. Di- or tributylsilane is an effective reducing agent for gem-bromofluoro- and dibromo-cyclopropanes, giving good yields of fluorocyclopropanes of variable stereochemistry. The reactivity of metal hydrides toward dihalocyclopropanes is $Bu_3SnH > Bu_2SiH_2 > Bu_3SiH$ (19).

Hydrosilylative reduction of ketones [AS, 1973, p. 157] continues active (20-24). Use of chiral ferrocenylphosphine ligands, e.g. 15 in asymmetric hydrosilylation of ketones under Rh^I catalysis affords chemical yields of 40-88% and

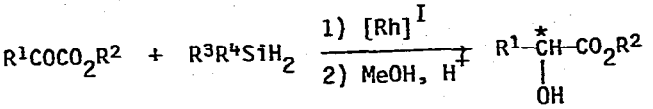
References p. 61.

optical yields of up to 49%, better than that observed with chiral benzylmethylphenylphosphine or DIOP (20). Interestingly, asymmetric induction during hydrosilylation of benzophenone with Rh^{I}BzMePhP: catalysis allowed partial resolution of a silicon-hydride species (21). The mechanism of hydrosilylation using BzMePhP: as ligand has been shown to proceed via intermediate complex 16 (22), eq. 14.



(14)

Ketoesters yield chiral α-hydroxyacids upon hydrosilylation (23), best results being obtained with a chiral rhodium complex of commercially available (+)-DIOP and diphenylsilane. Significantly, (+)-benzylmethylphenylphosphine afforded hydroxy acids of opposite configuration. Optical yields in the range of 30-80% were obtained, eq. 15.



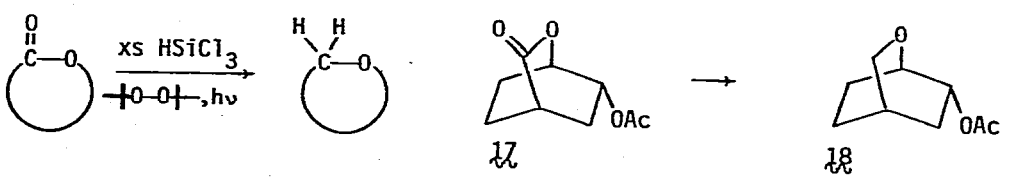
(15)

Modest optical yields (6-7%) of chiral alcohols are reported to be obtained in the hydrogenation of silyl enol ethers catalysed by $Rh^{I}(DIOP)_2$(24), but this procedure appears to offer no advantage over direct asymmetric reduction of the corresponding ketone. Symmetrical formamidines R-NH-CH=N-R, R = iPr, cC_6H_{11}, are conveniently prepared by hydrolysis (H_2O or MeOH) of silylformamidines R-N($SiMe_3$)CH=NR generated from carbodiimide and silane (Et_3SiH or $PhMe_2SiH$) in the presence of $PdCl_2$ or $(Ph_3P)_3RhCl$ at 140-200° in an extension

of ketone hydrosilylation (25). Similarly, although less advantageous synthetically, formamides result from treatment of isocyanates under hydrosilylation, e.g. nBu-N=C=O $\longrightarrow$ nBu-NH-CH=O (26). A brief survey of silanes in reduction precedes a detailed study of the reduction of aldehydes and ketones by Et_3SiH and $nBuSiH_3$ (27). Although the emphasis is mechanistic, some synthetic techniques are presented. Depending on conditions, alcohols, ethers, esters, and acetamides can be formed by silane reduction (eq. 16)

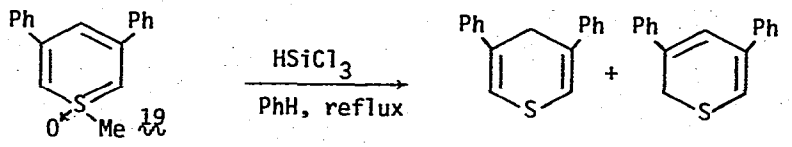
$$\begin{aligned} R_2C{=}O \;+\; Et_3Si{-}H \;&\xrightarrow{H^+,\ H_2O}\; R_2CHOH \;+\; Et_3SiOH \\ \text{"} \qquad\quad \text{"} \;&\xrightarrow{R'CO_2H}\; R_2CH{-}O{-}CHR_2 \;+\; R_2CH{-}O_2CR' \\ \text{"} \qquad\quad \text{"} \;&\xrightarrow[H_3O^+]{MeC{\equiv}N}\; R_2CH{-}NH{-}COCH_3 \end{aligned} \qquad (16)$$

Besides the extensive use of trichlorosilane in conversion of phosphine oxides to phosphines (see Section VIII below), this reagent continues to find simple applications in organic chemistry (28-31). Use of $HSiCl_3$ in photolytic reduction of lactones to ethers has been commented on [AS, 1973, p. 161] but the precedure of eq. 17 (28) appears cumbersome, particularly in requiring several freeze-thaw cycles. Noteworthy, however, is the specificity by which lactones are reduced in the presence of esters, e.g. 17 $\longrightarrow$ 18 (28). Further investigation here is clearly desirable.



17 18 (17)

The reduction of aromatic carboxylic acids to methyl groups, e.g. 2-carboxy-biphenyl → 2-methylbiphenyl, 74%; with the trichlorosilane/tri-n-propylamine system has appeared as an Organic Syntheses procedure (29). Upon reaction with 1,10-phenanthroline in benzene, trichlorosilane gives (in addition to the molecular complex $HSiCl_3.C_{12}H_8N_2$) a small amount of 1,2,3,4-tetrahydro-1,10-phenanthroline dihydrochloride (30), while thiabenzene oxides 19 are converted to thiapyrans by the agency of trichlorosilane in benzene, eq. 18 (31).

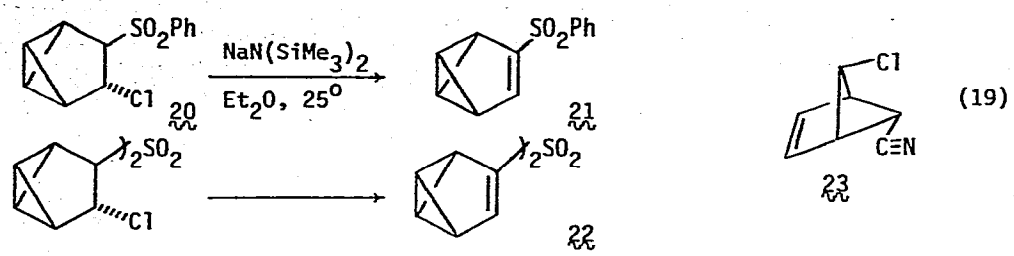


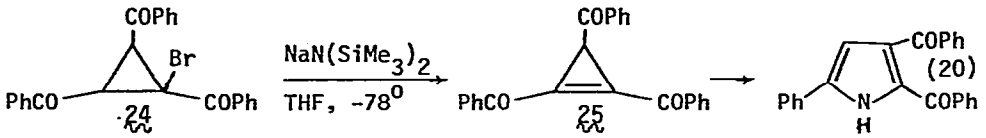
(18)

III. CARBON-CARBON BOND FORMATION AND RUPTURE

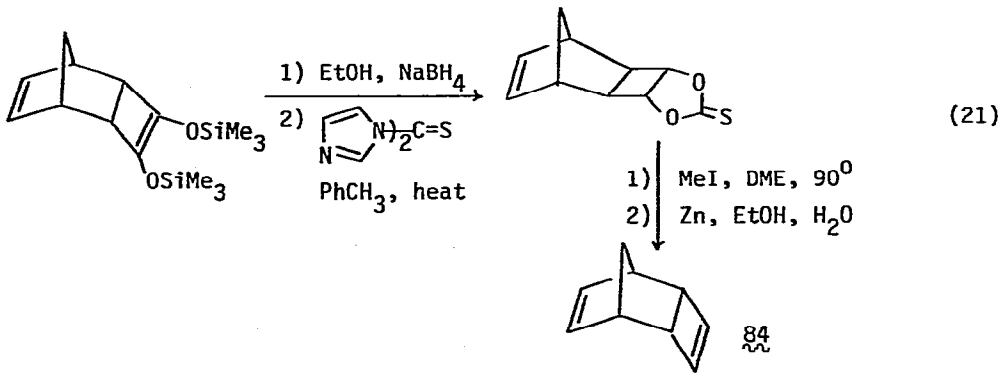
A. Elimination Reactions

Olefin synthesis with silicon reagents should be vigorously exploited as a consequence of several reports on its generality. Sodium bis(trimethylsilyl)-amide is a dehydrohalogenating agent (32-33). In ethereal solution, it dehydrochlorinates sulfone 20 to the first reported benzvalone 21. Distaurophenylsulfone 22 is prepared analogously, eq. 19 (32). But failures occur also: none of the metallo-silyl amides were capable of dehydrochlorinating 23 to cyanoprismane (32), and sodium bis-(trimethylsilyl)amide did not generate the exquisitely sensitive tribenzoylcyclopropene 25 from bromide 24, as $NaN(SiMe_3)_2$ apparently attacks 25 faster than it reacts with 24, eq. 20 (33).

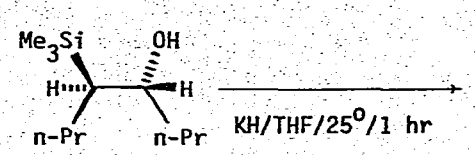




Vedejš has outlined a superior olefin synthesis via thionocarbonates which illustrates the versatility of siloxy enediols, eq. 21 (34).



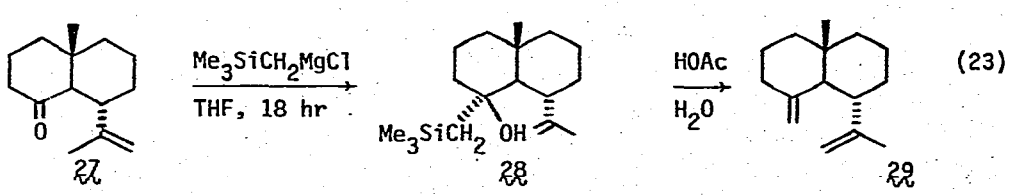
Related olefin synthesis by elimination from β-hydroxysilanes has been made more versatile by Hudrlik's observation that stereospecificity in elimination is possible, as the results of eq. 22 demonstrate (35). The threo alcohol 26 is



		%	%	total yield %
26	KH/THF/25°/1 hr	5	95	96 (22)
	$MeSO_2Cl$, Et_3N/ pentane/0°/15 min	89	11	90
	$BF_3 \cdot Et_2O/CH_2Cl_2$/ 0°/ 1 hr	94	6	99

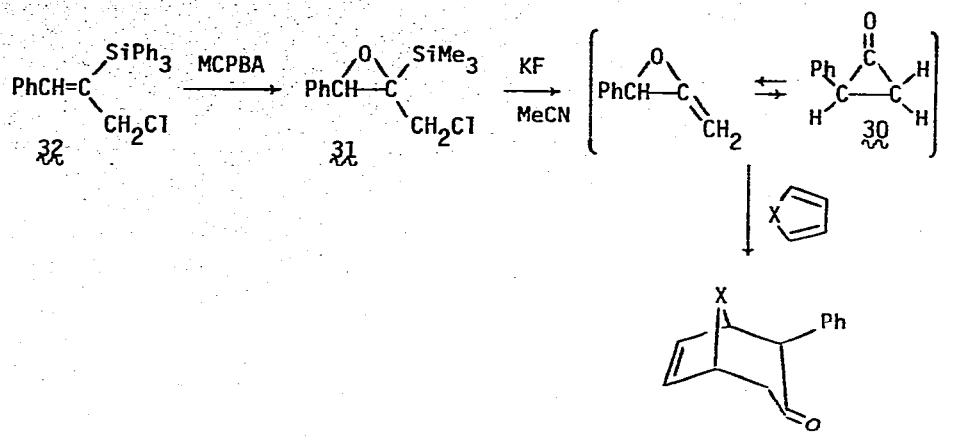
conveniently generated by iBu_2AlH reduction of the corresponding β-ketosilane. Despite the selectivity, the combination of circuitous routes to β-ketosilanes and a plethora of excellent olefin syntheses by classical routes make this a less than eximious procedure.

A related route to β-hydroxysilanes is illustrated in eq. 23. Whereas peri-hindered decalone 27 was unreactive toward $Ph_3P{=}CH_2$ in DMSO, it reacted smoothly with Me_3SiCH_2MgCl, giving carbinol 28 which underwent smooth β-elimination of trimethylsilanol upon acid treatment, affording (±)-β-gorgonene 29 (36). The cis-fused isomer was similarly prepared.



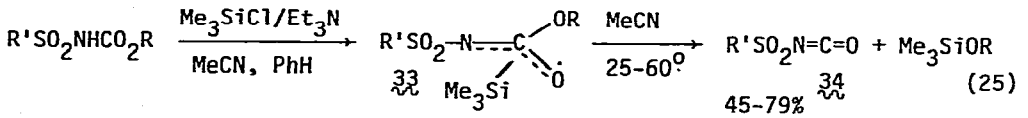
(23)

A related elimination of Me_3SiCl is involved in a novel route to generation of 2-phenylcyclopropanone 30 (37). Fluoride ion promotes elimination from epoxysilane 31, prepared from α-chloromethylvinylsilane 32. Treatment of 31 with the alternative source of F^-, Et_4NF in DMSO, produced $PhCH_2CH_2CO_2CH(Ph)$-$COCH_3$ rather than cyclopropanone, eq. 24 (38).



(24)

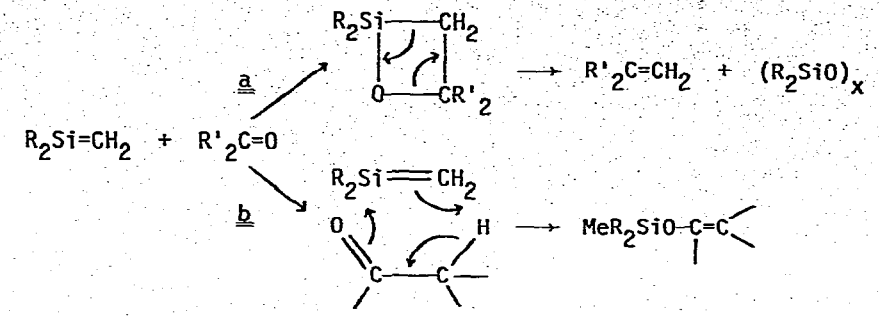
Related is a thermolysis reaction undergone by silylated O-alkyl-N-alkyl-sulfonylcarbamates 33 in polar solvents to give alkylsulfonylisocyanates 34 and alkoxy silane. As 34 can not be readily prepared by direct phosgenation of sulfonamides, this procedure is of general applicability, eq. 25 (39).



(25)

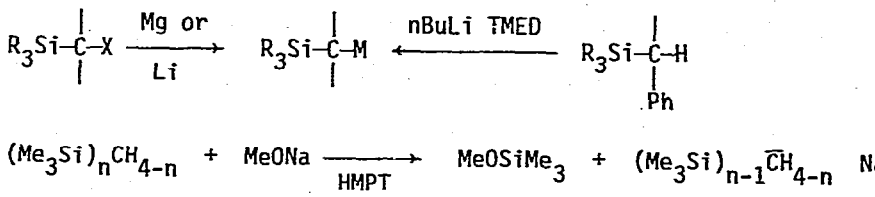
Olefin synthesis by the silicon equivalent of the Wittig Reaction: $R_3Si-C^{\diagup}_{\diagdown}$ + $R_2C{=}O \rightarrow R_2C{=}C^{\diagup}_{\diagdown}$, continues to be investigated (40-45). The fundamental silicon species would be equivalent to $Si{=}C^{\diagup}_{\diagdown}$ in this synthesis, and to that end the scope and nature of the reaction of $R_2Si{=}CH_2$, generated by pyrolysis of the corresponding silacyclobutane at 611°, with carbonyl compounds has been reported by Sommer's group (40). Both pseudo-Wittig (route a), and silylenol ether (route b) pathways occur, eq. 26, but synthetic utility remains to be maximized.

References p. 61.



(26)

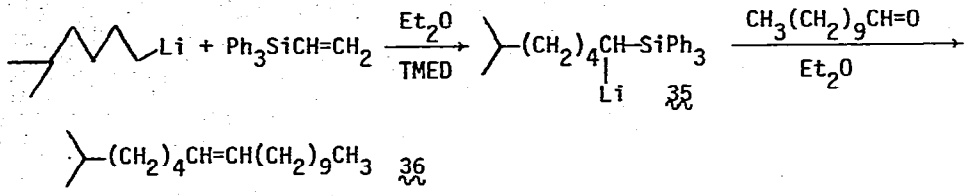
Due to the lessened ability (relative to phosphorus) of silicon to stabilize an adjacent carbanionic center, the silicon equivalent of $Ph_3P=CH_2$ and its homologues is of little synthetic advantage, despite ease of generation of α-metallosilanes from e.g. α-halo (41), α-protio (41), or α-trialkylsilanes (42), eq. 27.



(27)

Chan and Chang have presented details of a synthetically interesting modification of this method for carbon-chain elaboration, using silyl carbanions generated by addition of alkyllithiums to vinylsilanes, e.g. 35. Eq. 28 shows the synthesis of disparlure 36 by this method (41), and other silyl-Wittig reactions (42). The geometrical isomer ratios formed in these reactions imply that Me_3SiO^- is eliminated in a cis fashion from intermediate $RCH(SiMe_3)CR_2O^-$ adducts (42).

Both t-butyltrimethylsilyl acetate 37 [AS, 1973, p. 170] and ethyl trimethylsilylacetate are useful reagents for conversion of carbonyl compounds to α,β-unsaturated esters



$$Me_3SiCH_2Na + Ph_2C{=}O \xrightarrow[HMPT]{} Ph_2{=}CH_2 \quad 53\% \qquad (28)$$

$$Me_3SiCH(Na)Ph + \text{"} \longrightarrow Ph_2C{=}CHPh \quad 79\%$$

$$\text{"} + PhCOtBu \longrightarrow tBu{-}\underset{\displaystyle Ph}{\overset{|}{C}}{=}CHPh \quad 26\%$$

(43,44). Lithiation of 37 with lithium diisopropylamide (43), or of $Me_3SiCH_2CO_2Et$ with lithium dicyclohexylamide (44) generates an enolate which undergoes reaction at -78° with aldehydes and ketones, eq. 29. Elimination of lithium trimethylsilanoate yielding the homologated ester is suggested to precede workup (43). The advantages of this procedure over phosphorus ylid-based conversions are claimed to be mildness of conditions, high yield, avoidance of competing enolate formation from the carbonyl compound, and in the case of unsaturated carbonyls, avoidance of Michael addition products.

The silyl-Wittig synthesis has been used by Seebach and co-workers in a general synthesis of the synthetically useful ketene thioacetal series (45). Alkylation of $(RS)_2CHSiMe_3$ 38 proceeds smoothly, eq. 30, affording thioacetals 39 in high isolated yield, even in the preparation of sensitive α,β-unsaturated, $(RS)_2C{=}CH{-}CH{=}CR_2$, and heteroatom substituted,

$$Me_3SiCH_2CO_2tBu \;(37) \xrightarrow[THF,\ -78^{o}]{LiN(iPr)_2} Me_3SiCHLiCO_2tBu \xrightarrow[-78^{o}]{R^1R^2C=O} \xrightarrow[HCl]{3\ N} R^1R^2C=CHCO_2tBu$$

isol. 53-93%

R^1,R^2= $-(CH_2)_5$; Me,H; iPr,H; Ph,H; MeCH=CH-,H; PhCH=CH-,H; Me,Me (29)

$$Me_3SiCH_2CO_2Et \xrightarrow[THF,\ -78^{o}]{LiN\langle\bigcirc\rangle_2} Me_3SiCHLiCO_2Et \xrightarrow[-78\ to\ -25^{o}]{R_2C=O} R_2C=CHCO_2Et$$

81-95%

$R_2C=O$ = PhCH=O, $nC_8H_{17}CH=O$, $(CH_2)_4C=O$, $(CH_2)_5C=O$, $(CH_2)_{11}C=O$, PhCH=CHCOPh

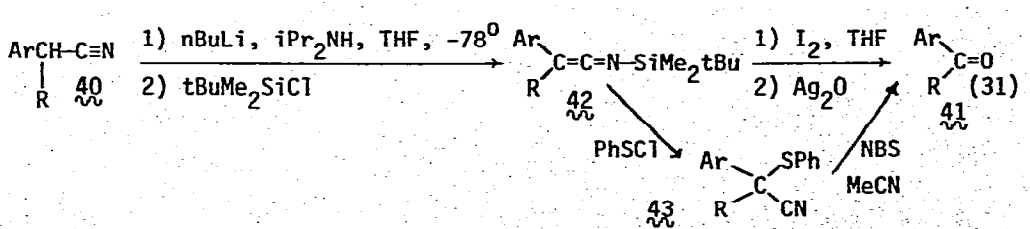
$$(RS)_2CH_2 \xrightarrow[2)\ 2\ eq.\ Me_3SiCl,\ -60\ to\ 0^{o}]{1)\ nBuLi,\ THF} (RS)_2CHSiMe_3\ (38)\ >90\% \xrightarrow[2)\ R^1R^2C=O,\ -80^{o}]{1)\ nBuLi,\ THF}$$

$$(RS)_2C(SiMe_3)(O^-)CR^1R^2 \xrightarrow[0^{o}]{H_2O} (RS)_2C=CR^1R^2\ (39)\ 60-95\% \quad (30)$$

R = ½-$(CH_2)_3$, Me, Ph R^1 = H, Alkyl, Aryl R^2 = H, Alkyl, NR_2, Alkenyl

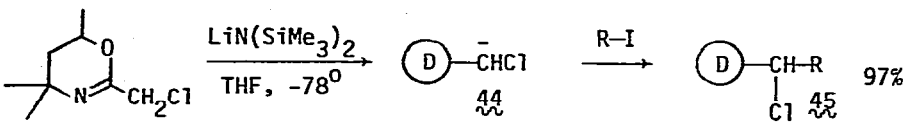
$(RS)_2C=CH-NR_2$, thioacetals. As enolizable carbonyls reacted without complication, this procedure seems more versatile than traditional ketenethioacetal syntheses.

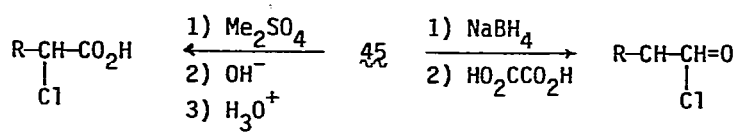
Carbon-carbon bond cleavage reactions with silicon reagents is less prominent than olefin synthesis above, but ketone synthesis by decyanation is the subject of reports by Watt (46,47). Secondary arylacetonitriles 40 are converted to ketones 41 in 61-82% yield by the two-step process of eq. 31 (46). Alternatively, silylketenimine 42 can be sulfenylated to 43, which is then cleaved by N-bromosuccinimide in acetonitrile to 41 in 64-100% yield (47).



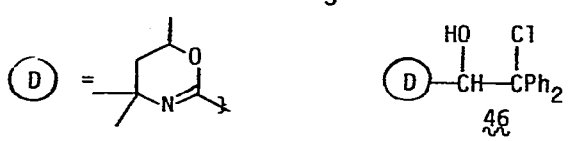
B. Alkylation of Carbon

The most modest use of silicon reagents in alkylation is as a hindered base. N-lithio hexamethyldisilazane (lithium bis-(trimethylsilyl)amide, LiBSA) is the base of choice for formation of the carbanion of 2-chloromethyloxazine 44, which can be alkylated, eq. 32, to 45. Elaborated oxazine 45 car be reduced and hydrolysed to α-chloroaldehydes, or alternatively to α-chloroacids (48). Chlorohydrin 46 of reversed orientation was formed when 44 was treated with benzophenone.

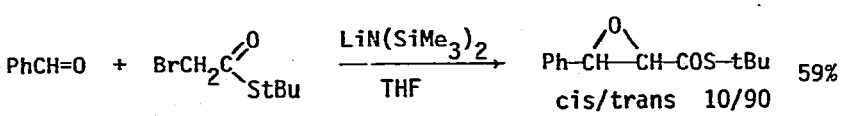




(32)



It is claimed that LiBSA can be used to good advantage as the base in a Darzens-type glycidic thiol ester synthesis, eq. 33 (49), giving an isomer distribution inverse to that of a reaction where sodium hydride was the base. A conflicting report finds

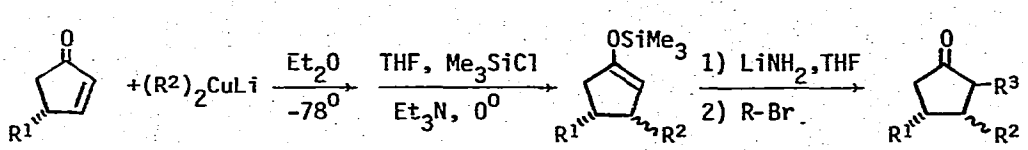


(33)

use of $NaN(SiMe_3)_2$ or $LiN(SiMe_3)_2$ in the Darzens glycidic

ester synthesis offers no advantages, either in stereospecificity, yield, or convenience (50). Similarly, these bases were ineffective in the deprotonation-protonation sequence to effect transformation of prostaglandin A_2 to C_2 (51).

Trimethylsilylenol ethers as enolate equivalents is an active area (52-58). Z- and E-silyl enol ethers of 3-methyl-2-heptanone, separable by glpc, can be stereospecifically cleaved to enolates of known configuration by CH_3Li in DME, with only a few percent of starting ketone as by-product (52). This stereospecific cleavage has been exploited in prostaglandin synthesis (53), as copper enolates derived by addition of alkylcuprates to cyclopentenones could not be directly alkylated. They were, however, trapped and purified as silyl enol ethers cleavable to alkylatable lithium enolates, e.g. eq. 34 (53).

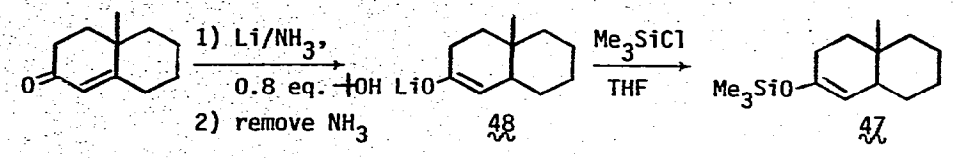


(34)

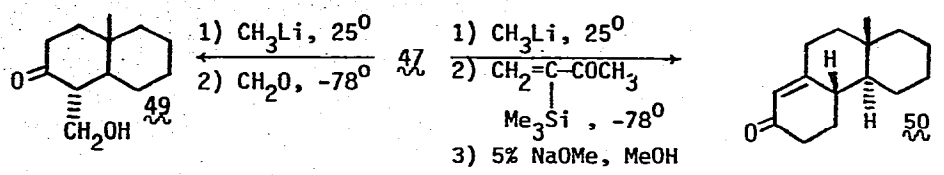
R^2 = trans-1-octenyl ; trans -CH=CH-CH(O-C(CH$_3$)$_2$OCH$_3$)-C_5H_{11}

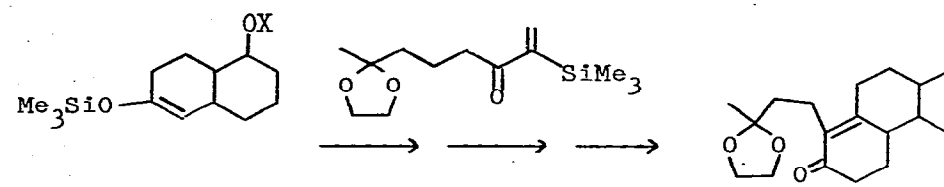
R^3 = trans $-CH_2CH=CH(CH_2)_3CO_2Me$

Similarly, in the octalone series, where tBuOH or even NH_3 appeared sufficiently acidic to cause regio-isomerization of enolate 48, silyl enol ether 47 was isolated by chlorosilane treatment of 48, then cleaved and alkylated with formaldehyde to give exclusively ketol 49 in 90% yield, eq. 35 (54). Of more generality is the use of α-trimethylsilyl vinylketones in a modified Robinson Annelation [AS, 1973, p. 165], e.g. 47 → 50, which can provide intermediates capable of ready elaboration to steroids, eq. 36 [55,56].



48 47 (35)

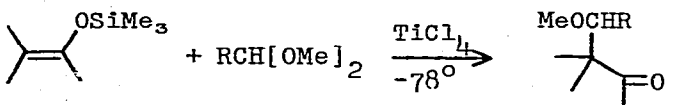




[36]

X = tBu, 74%, ref. 55 ; X = THP, 50%, ref. 56

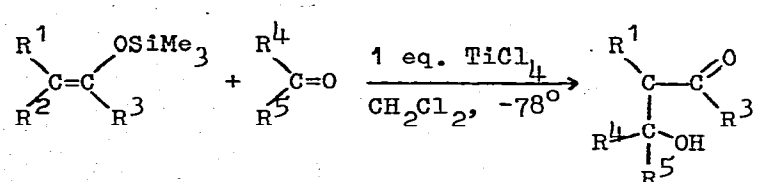
For introduction of an alkoxyalkyl function α to a carbonyl, silyl enol ethers are reported to react with dimethyl or diethyl acetals at -78° in the presence of $TiCl_4$, giving 60 to 98% yields of β-alkoxy ketones, eq. 37 [57]. Silyl enol ethers of acetophenone, isobutyraldehyde, cyclohexanone, and phenyl acetone were employed.



[37]

R = Ph, OMe, $PhCH_2CH_2$–, $N{\equiv}CCH_2CH_2$–

Likewise, in crossed aldol condensations, trimethylsilyl enol ethers are general enol partners with $TiCl_4$ catalysis. The general reaction, eq. 38, proceeds with a wide variety of substrates in commonly 60-90% yield. In the majority of cases, aldol 51 was accompanied by only a few percent of dehydration product. Other Lewis



[38]

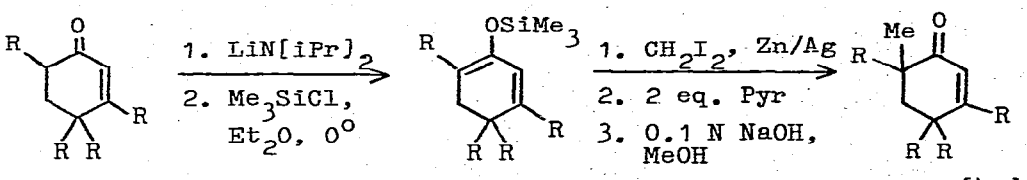
51

acids were less effective catalysts. As aldehydes reacted faster than ketones, specific attack, e. g. eq. 39 is possible [58].

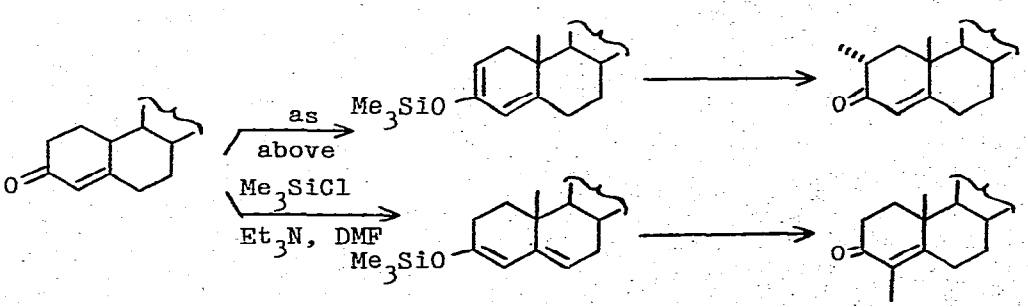
$$PhCH{=}C[CH_3]OSiMe_3 + PhCOCH{=}O \xrightarrow[-78^{\circ}]{TiCl_4,\ H_2O} \begin{matrix} Ph{-}CH{-}COCH_3 \\ | \\ HO{-}CH{-}COC_6H_5 \end{matrix} \quad 83\% \qquad [39]$$

Hydroxymethylation can be achieved with trioxane as carbonyl partner, e. g. $PhCH{=}C[CH_3]OSiMe_3 \longrightarrow PhCH[CH_2OH]COCH_3$, 64%. Regiospecificity in alkylation of the olefinic position derived from the enol ether was observed for reaction of benzaldehyde with 2- and 6-methyl-1-trimethylsiloxycyclohexenes, showing another advantage of this aldol condensation technique, which should be vigorously followed up [58].

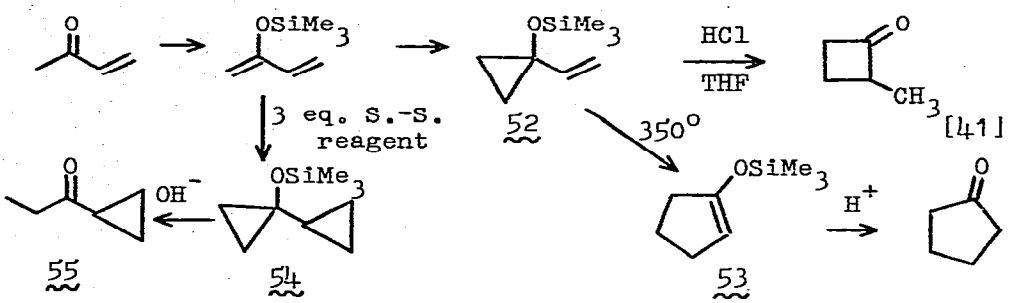
Methylation of cyclohexenones in the α' position [eq. 40] is facilely carried out via the 'improved' Simmons-Smith procedure [AS, 1973, p. 166-7] applied to siloxy-dienes, and subsequent methanolysis [59]. In the steroid series, testosterone can be specific α' or α-monomethylated [eq. 40] in a reaction claimed to be more specific than classical routes [59]. Yields exceed 80%.



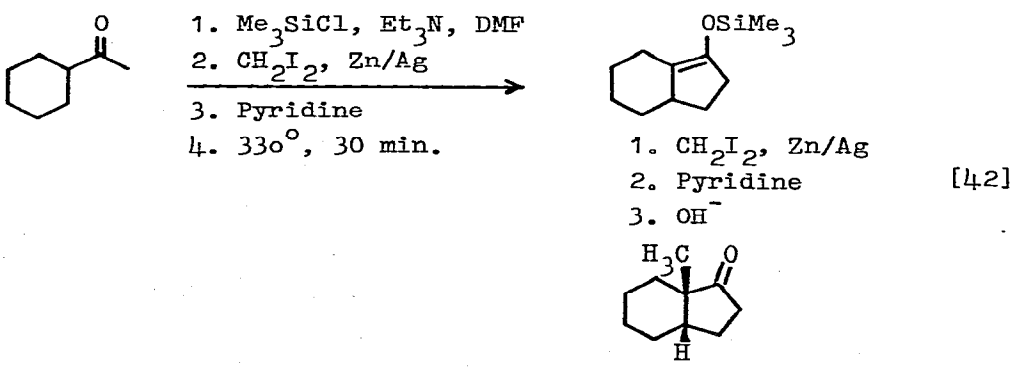
[40]



In the acyclic series, such cyclopropanations afford [after pyridine treatment] siloxyvinyl cyclopropanes 52 convertible to [AS, 1973, p. 176] cyclobutanones by acid-catalysed rearrangement, or to cyclopentanones via vinylcyclopropane rearrangement, eq. 41, [60].



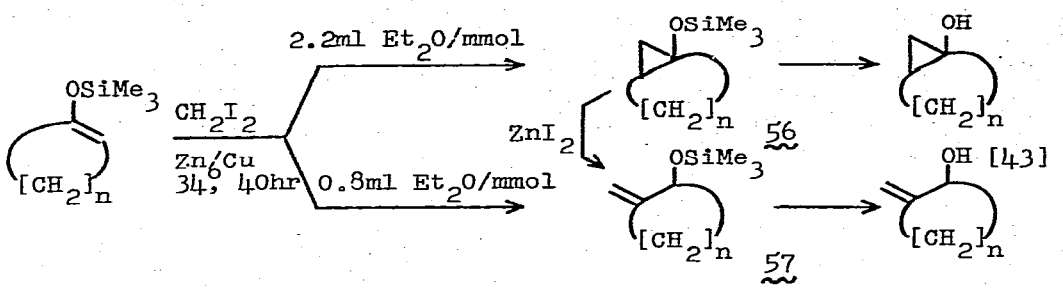
Siloxycyclopentenes, e. g. 53 can be further cyclopropanated as the stereoselective hydrindanone synthesis of eq. 42 demonstrates [60]. Under forcing conditions, i. e. 3 equivalents CH_2I_2, Zn/Ag, bicyclo propyls will be formed, e. g. 54, which can be converted to either cyclopropanols or to ring-opened cyclopropyl ketones 55 [61].



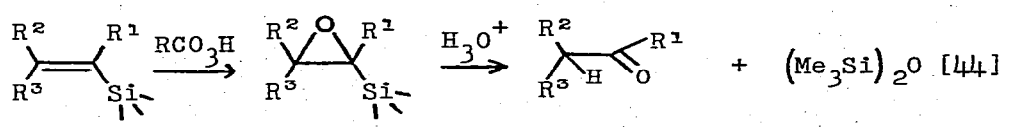
[42]

While the Simmons-Smith Reaction applied to silyl enol ethers gives cyclopropanols, a slight change in reaction parameters, namely de-

crease in solvent concentration, gives 2-methylenecycloalkan-1-ols [62] as illustrated by equation 43. The isomerization of 56 to 57 is mediated by zinc iodide, as shown by control experiments. Interestingly, no 57 is formed from cycloheptyl [n = 5] systems. This opens a route to 2-methylene-1-cyclopent- and -hexanols, hitherto difficultly accessible, but conversely, care must be taken in structural assignments of products derived from the Simmons-Smith reaction of silyl enol ethers.

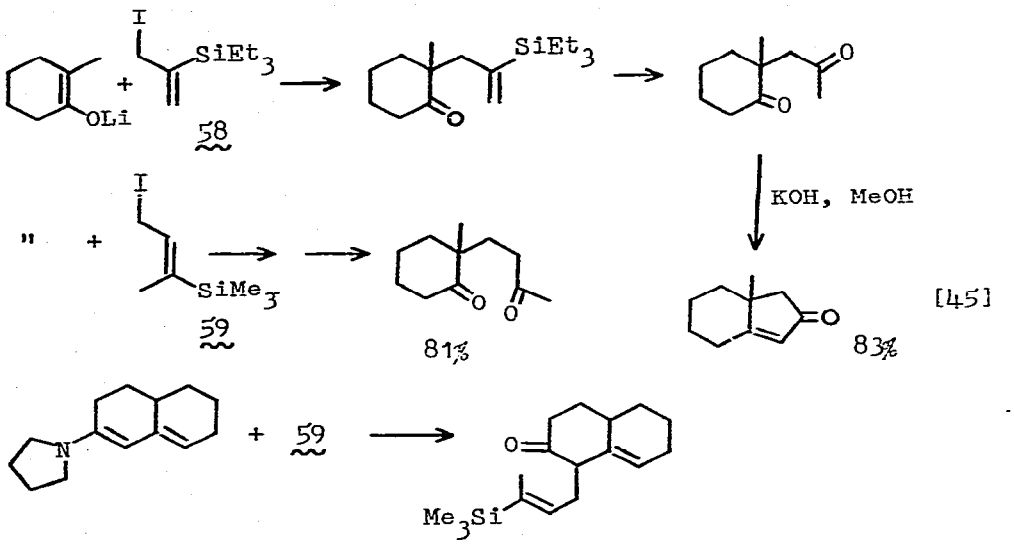


The oxidation-hydrolysis sequence for conversion of vinyl silanes to carbonyls [G. Stork and E. Colvin, JACS, 93 (1971) 2080], eq. 44, has hitherto been of limited synthetic utility due to the inaccessibility of these silanes. Gröbel and Seebach have reviewed and generalized vinyl silane synthesis [63] in a useful article.

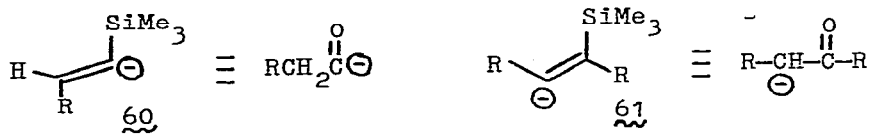


The Stork group has exploited this conversion by utilizing halomethyl vinyl silanes as ketoalkyl halide equivalents in annelation reactions [64,65], while Boeckman has carried out conversions in the reverse sense using trimethylsilylvinyl cuprates as masked acyl

anions in Michael Additions [66,67]. The sequences of eq. 45 show the versatility of silanes 58 and 59 [65], which synthons would be more generally used, were they less cumbersomely accessible. They are effective trappers of regiospecifically generated enolates [vide Sect. II infra].

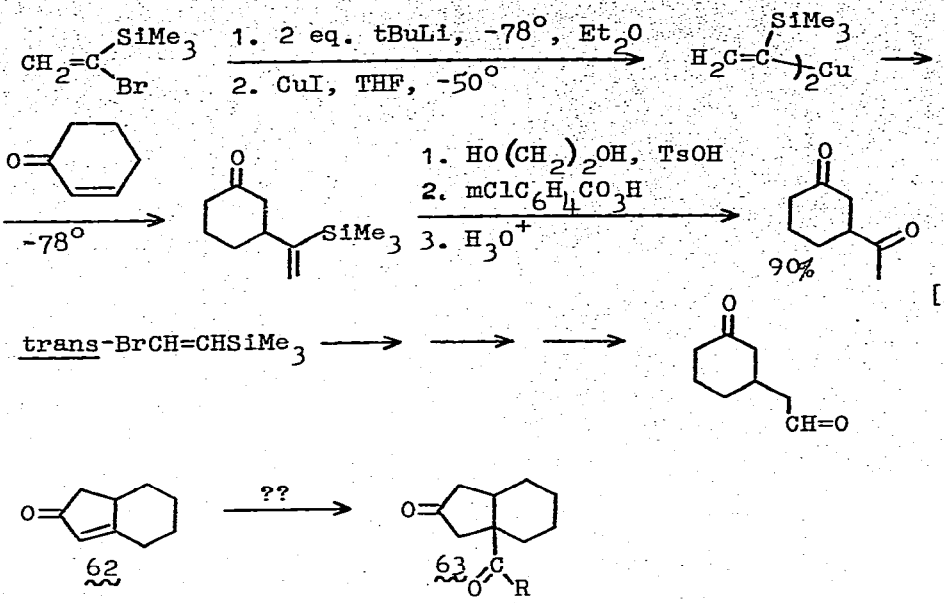


The equivalence of 60 to an acyl anion and 61 to an enolate was exploited in the sequences of eq. 46 [66,67]. In contrast to known acyl anion equivalents, which do not undergo conjugate addition, 60 does. The utilization of 60 and 61 for angular functionalization, e. g. 62 → 63, is a promising synthetic tool.



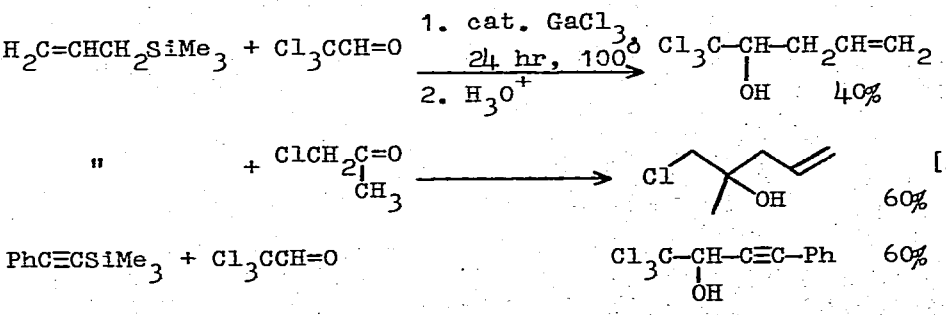
Vinylsilanes such as 60 and 61 may become more accessible through the observation of Kumada [68] that mixtures of cis- and trans-1,2-bistrimethylsilyl olefins are formed by reaction of acetylenes with $Ni[bipy][SiCl_3]_2$ followed by exhaustive methylation with MeMgBr.

References p. 61.



[46]

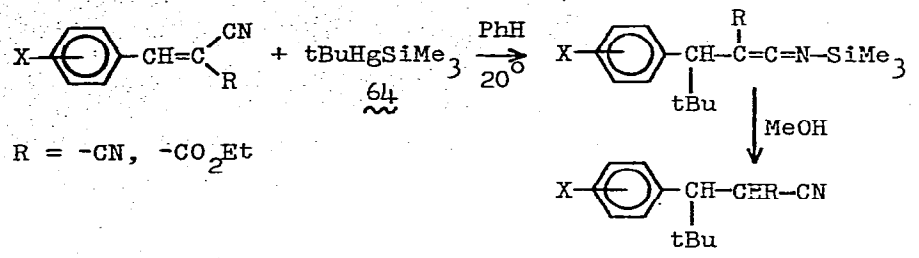
The first Grignard-type reactions of organosilanes [$R\overset{|}{\underset{|}{Si}}-$ + $R_2C{=}O$ → → $R'R_2C{-}OSi\overset{|}{\underset{|}{}}$] have been reported [69]. An active C–Si bond, an electron deficient carbonyl, and a Lewis acid catalyst are required to effect good yields. As a Group IV alternative to grignard synthesis, these reports should be vigorously pursued. A related rea-



[47]

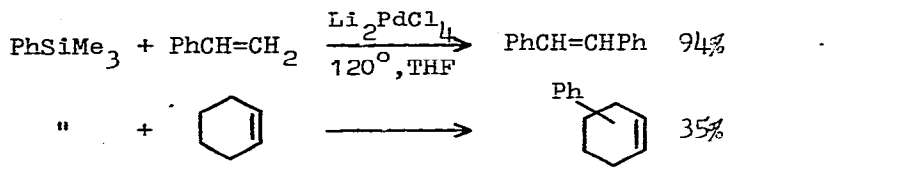
gent is t-butyltrimethylsilylmercury, 64, which alkylates benzylidenemalononitriles and cyanoacetates, eq. 48 [70], at the β-carbon atom to give net addition of isobutane across the olefinic linkage. A simple preparation of 64 [71] implies considerable synthetic

utility for this novel organosilicon reagent.



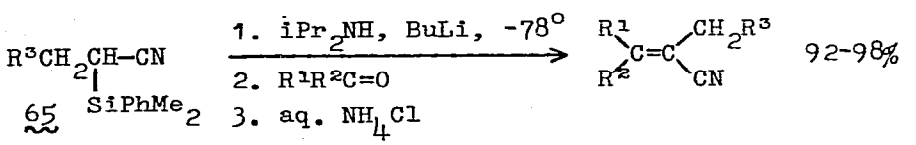
R = -CN, $-CO_2Et$ [48]

Related is the observation that various palladium compounds can cleave Me–Si and Ph–Si bonds; when olefins are included in the reaction mixture, alkylation or arylation can occur via intermediate alkylpalladium species, e. g. eq. 49[72]. Further study of this reaction should uncover some useful synthetic applications.



[49]

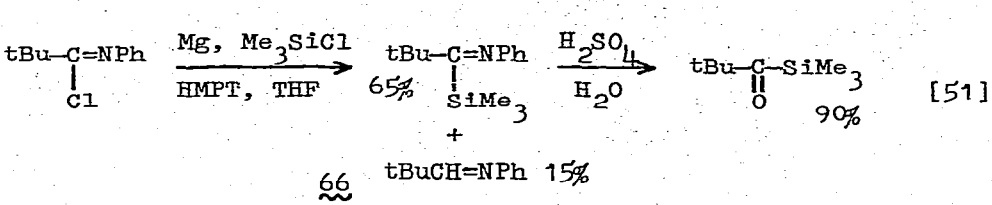
Related to these is a Knoevenagel-type synthesis of α,β-unsaturated nitriles by the addition of a carbonyl compound to the α-carbon of a silylated nitrile. $R'CH(SiX_3)CN + R_2C{=}O \rightarrow R_2C{=}C(CN)CH_2R' + 1/2\ X_3SiOSiX_3$ can be effected by the sequence of eq. 50 [73]. The



R^1,R^2 = H, Ph; Me,Me; Et,Me; $-(CH_2)_4-$; Ph,Me; MeCH=CH-,Me; etc.
R^3 = H, Me, Ph [50]

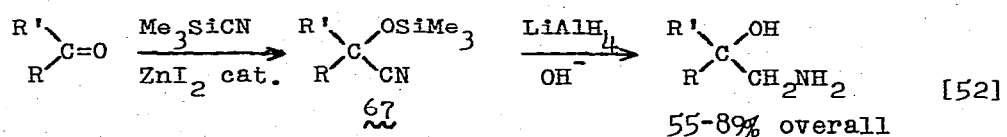
requisite α-silylpropionitriles 65 can be prepared in 55-75% yield by Rh^I-catalysed hydrosilylation of substituted acrylonitriles. The condensation proceeds exclusively at the C=O bond of the substrate, even with crotonaldehyde and β-ionone.

Use of the 2-silyl-1,3-dithiane anion $S[CH_2]_3\overline{C}-SiMe_3$ in homologative conversion of carbonyls to α,β-unsaturated ketones has been expanded upon by Seebach [74]. An alternative to silylation of dithiane derivatives for synthesis of α-ketosilanes, eq. 51, is silylation of an imidoyl chloride with Me_3SiCl/Mg/THF followed by acid hydrolysis [75]. The aldimine 66 was a minor byproduct.



[51]

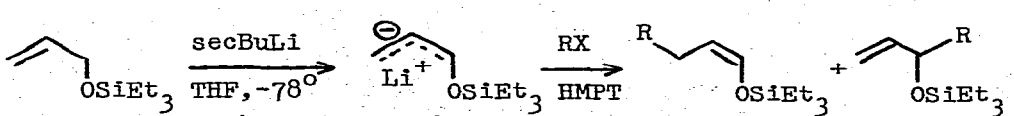
A reliable preparation of β-aminomethyl alcohols by net addition of $H-CH_2NH_2$ across a carbonyl is reduction of stable trimethylsilylcyanohydrins 67, which can be formed from ketones resistant to cyanohydrin formation, e. g. camphor and α-tetralone, eq. 52 [76].



[52]

R,R' = $-(CH_2)_n-$ n = 5, 7, 11; Ph, Me; 2-butenyl, Me, etc.

Metallated allyloxysilanes 68 are β-acylcarbanion equivalents, as demonstrated by an ingenious sequence worthy of further investigation, eq. 53 [77]. Total isolated yields of 69 and 70 were in



[53]

R = Me, Et, nPr, iPr, $CH_2=CHCH_2$, c-C_6H_{11}

X = Br, I

excess of 95% except for R = cyclohexyl. The predominant product

69, being a silyl enol ether, is a useful synthon in its own right or, it may be hydrolysed to an aldehyde. Interestingly, trimethyl- and t-butyldimethyl-silyl ethers gave lower yields and/or byproducts.

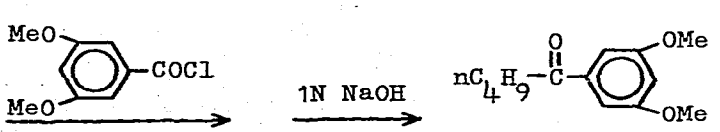
C. Acylation of Carbon

Direct acylation of an anion is the subject of several reports [78-82]. A key intermediate, 71, for synthesis of methyl acryloylacetate [viz. AS, 1973, p. 170] was prepared by condensation of the anion of trimethylsilyl 2-methoxycarbonylacetate 72 with 3-phenylthiopropanoyl chloride, eq. 54 [78]. Relatedly, the lithium salt

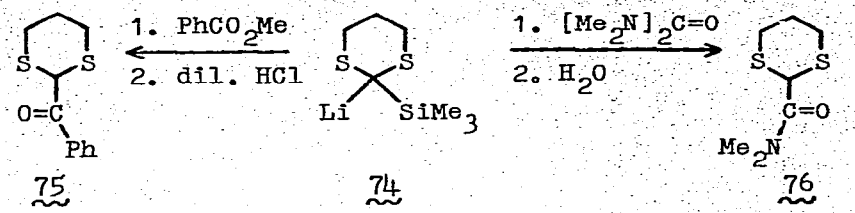
$$Me_3SiO{-}\overset{O}{\overset{\|}{C}}{-}CH_2CO_2Me \quad (72) \xrightarrow[2.\ PhSCH_2CH_2COCl,\ DME \quad 3.\ 1N\ HCl]{1.\ BuLi,\ Et_2O,\ -78^\circ} PhSCH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2CO_2Me \quad (71,\ 93\%) \qquad [54]$$

of bis[trimethylsilyl]malonate 73 found application in an olivetol synthesis, eq. 55 [79]. And a rather cumbersome synthesis of ketones RCOR' from esters RCO_2Et [80], with application to a jasmone synthesis [81], has been reported, but despite use of silicon reagents, seems unattractive. The reaction of 2-lithio-2-trimethyl silyl-1,3-dithiane 74 with methyl benzoate to give 75 and with tetramethylurea to give 76 appears to offer a general route to acyl dithianes, eq. 56 [45].

$$nC_3H_7CH[CO_2H]_2 \xrightarrow[2.\ nBuLi,\ -60^\circ]{1.\ Me_3SiN{=}C(Me)OSiMe_3,\ Et_2O} nC_3H_7{-}\overset{CO_2SiMe_3}{\underset{CO_2SiMe_3}{C}}{-}Li \quad (73) \longrightarrow$$

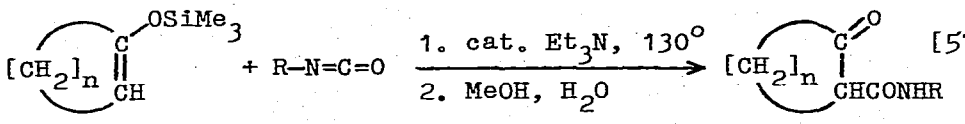


[55]



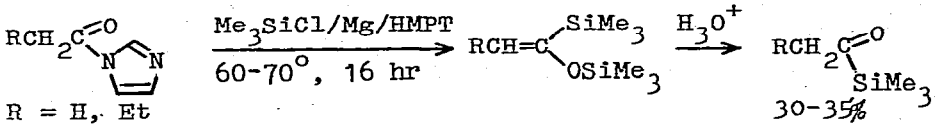
75 74 76 [56]

Silyl enol ethers of cyclopent- and -hex-anone react with aryl [82] and tosyl [83] isocyanates to give, after hydrolysis, excellent yields of 2-carboxamidoketones 77, eq. 57. Acyclic silyl enol ethers react analogously via an intermediate azetidinone [83].



n = 3,4 R = Ph, αNp, SO2Tol 77 72-97% [57]

The Bordeaux group has reported a new synthesis of acylsilanes by direct silylation of acylimidazoles, eq. 58 [84], potentially of great synthetic interest. This group has further found that vinylsilanes can transfer the vinyl group to acid chlorides in an attractive synthesis of α,β-unsaturated ketones [85], the synthetic possibilities of which deserve to be explored further, eq. 58.



R = H, Et [58]

$H_2C{=}CH{-}SiMe_3$ + MeCOCl ⟶ $MeCOCH{=}CH_2$

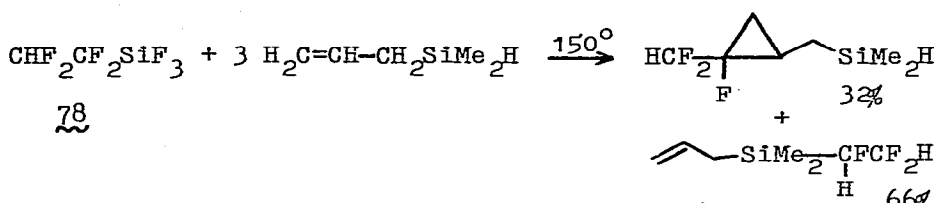
$Me_3SiCH{=}CHSiMe_3$ + RCOCl ⟶ $Me_3SiCH{=}CH{-}C(=O)R$

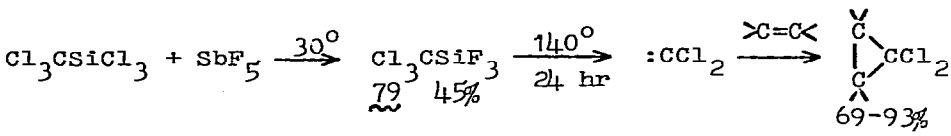
R = Me, tBu, Ph

D. Cyclization and Ring-forming Reactions

Considering carbene + olefin reactions to be the simplest type

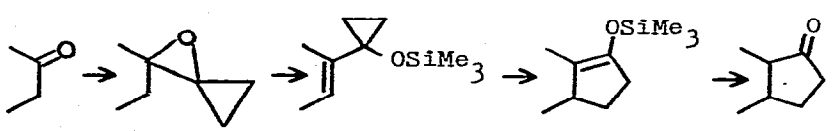
of cyclization, silicon reagents have figured in three communications by Haszeldine [86-88]. 1,2,2-Trifluoroethylidene, generated by thermolysis of 1,1,2,2-tetrafluoroethyltrifluorosilane 78 at 150°, previously shown to insert into C=C and C–H bonds [Haszeldine 1967], inserts into Si–H, Si–Br, and Si–Cl bonds [86], eq. 59. The order of reactivity is Si–H > C=C > Si–Cl for this carbene. Tri-





fluoro[trichloromethyl]silane 79, bp 45°, generated by fluorination of Cl_3CSiCl_3, undergoes vapor-phase decomposition at 100-140° to singlet dichlorocarbene, which reacts smoothly with olefins to generate dichlorocyclopropanes [87], eq. 59. Trimethylsilylcarbene, Me_3SiCH:, formed by photolysis of trimethylsilyldiazomethane, forms cyclopropanes in low yield with 2-butene, ethylene, and also inserted into Si–H and C–H bonds [88].

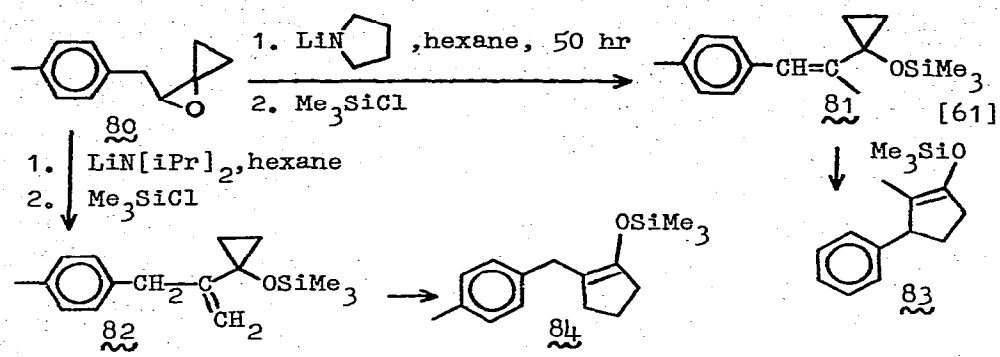
The cyclopentanone annelation sequence of eq. 60 [AS, 1973, p. 178] has been the subject of further investigation by the Trost



[60]

group [89]. For an oxospiropentane which can eliminate in two ways, e. g. 80, use of a sterically-hindered base affords mostly

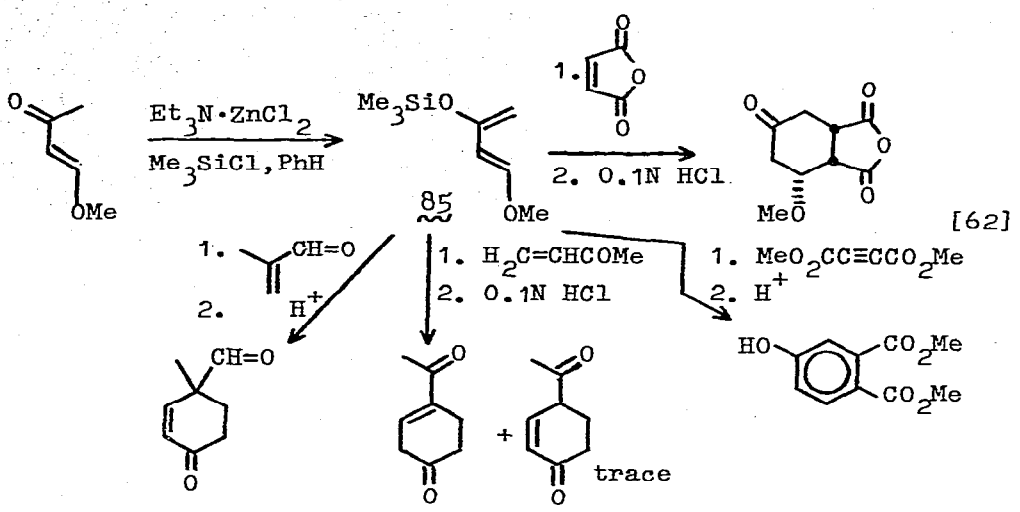
the less-substituted vinylcyclopropane 82, while a sterically less demanding base utilized under conditions of thermodynamic control produces the other regio-isomer 81. Bromination-dehydrobromination of these regio-selectively produced siloxycyclopentenes 83 and 84 affords a good route to cyclopentenones valued as prostaglandin intermediates.

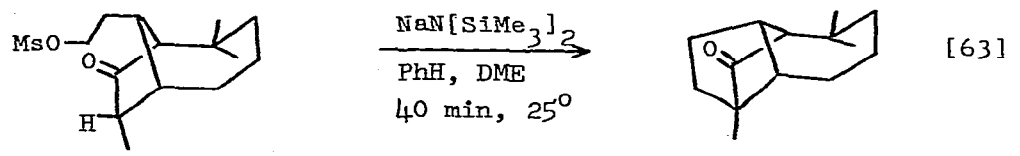


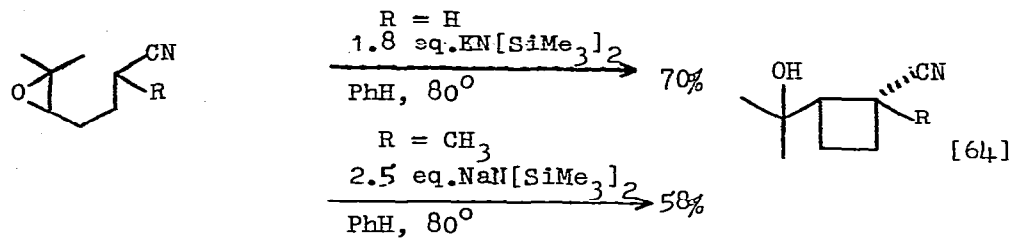
However, to catalyse the rearrangement of oxaspiropentane itself to cyclobutanone, lithium iodide or bromide in methylene chloride is superior to trimethylchlorosilane [90].

A useful diene synthon for Diels-Alder reactions in which a 2-oxo function is desired is Danishefsky's 1-methoxy-3-trimethylsiloxy-1,3-butadiene 85. It is easier to prepare, and more amenable to subsequent transformation than 1,3-dimethoxybutadiene [91]. The examples of eq. 62 show some intriguing possibilities. Use of benzoquinone as dienophile offers an entry to the 1,4,6-trioxygenated naphthalene system, while methacrolein hints at routes to prephenic and trisporic acids.

Use of N-metallo-bis[trimethylsilyl]amines as bases in enolate alkylative cyclizations has continued, e. g. eq. 63 [92], and more spectacularly in the conversion of epoxynitriles to cyclobutanes, eq. 64 [93].



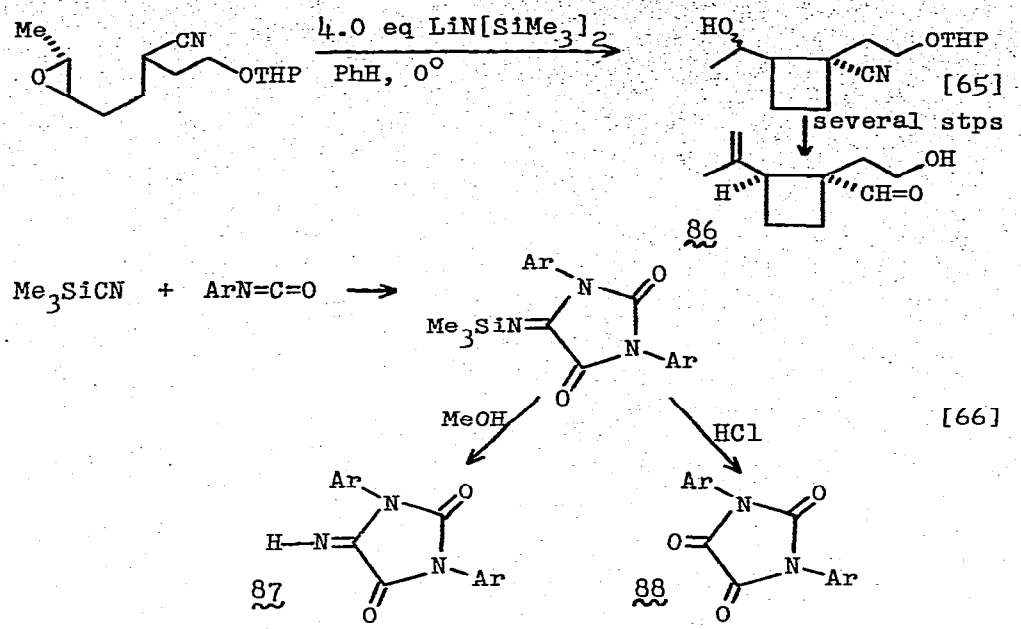




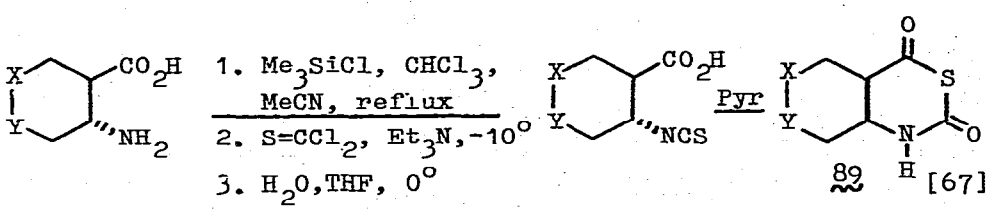
A particular feature of this cyclization is the stereochemical control, in that a single stereoisomer was obtained, which allowed synthesis of grandisol 86, eq. 65, contaminated with only 5% of epigrandisol [93].

Silicon reagents have been used to form heterocyclic rings as well [94,95]. 5-Iminodiazolidinediones 87 and diazolidinetriones 88 are formed by desilylation of the adducts of trimethylsilylcyanide and aromatic isocyanates, eq. 66 [94].

References p. 61.



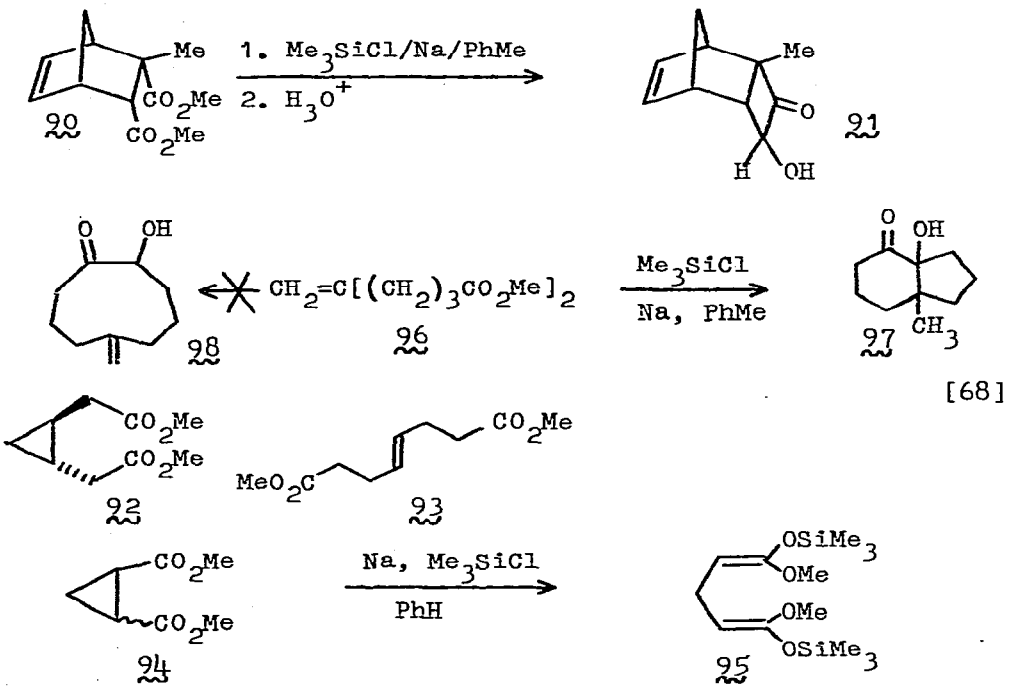
β-Isothiocyanatocarboxylic acids are best prepared by the sequence of eq. 67. Dihydrothiazinediones 89, formed by isomerization of initially cyclized oxazine-2-thione-6-ones, can be polymerized to novel polyamides [95].



In a ring-opening reaction, pyrolysis [420°] of the disilylester of cyclobutene-1,2-dicarboxylic acid followed by hydrolysis affords an elegant synthesis of the previously elusive butadiene-2,3-dicarboxylic acid [96].

The Ruhlmann modification of the acyloin condensation [AS, 1973, p. 174] continues to be actively employed in synthesis [97-

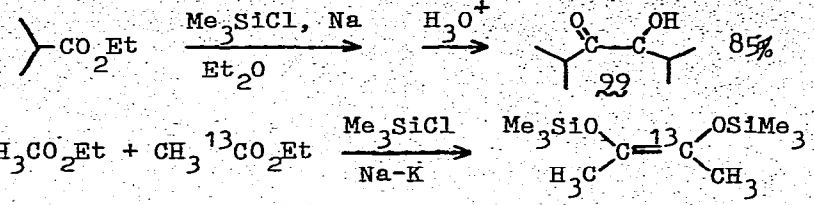
-102]. Details of the practical preparation of cyclobutanedione [97], cyclobutane-1,2-diol [98], and cyclopropane carboxaldehyde [98] are available. Conversion of 90 to acyloin 91 was routine, eq. 68 [99], but the Na/PhH/Me_3SiCl reagent failed with 92 and 93, apparently for reasons of strain [100], and with cis or trans 94 gave mixed ketene acetal 95 rather than a bicyclo[2.1.0]pentane, eq. 68 [100]. Unexpectedly, condensation of diester 96 led to hydroxyketone 97 rather than azeloin 98, eq. 68. A mechanism involving transannular interaction of the terminal olefin and a semidione intermediate was proposed [101].



[68]

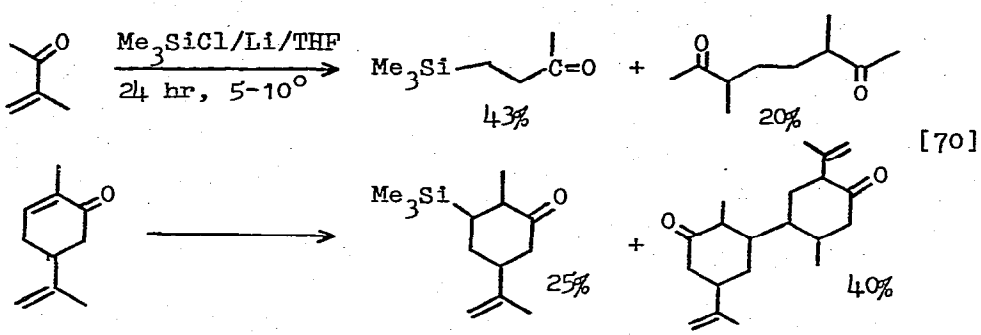
E. Dimerization and Other Coupling Reactions

The acyloin coupling above works equally well in acyclic systems, as shown by Russell's preparation of isobutyroin 99 and a ^{13}C-labelled bis[trimethylsilyl]enediol, eq. 69 [102].

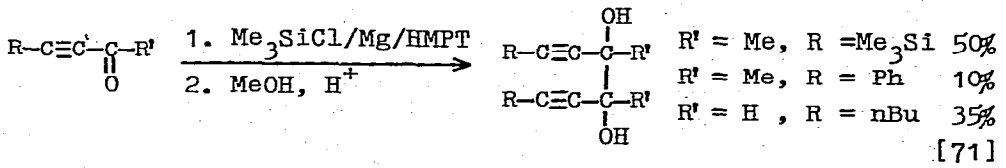


[69]

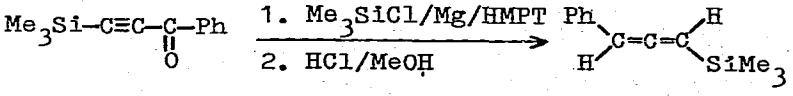
French work on reductive dimerization with chlorosilane/metal systems has continued [103-105]. Reaction of α,β-unsaturated ketones with Me_3SiCl/THF/Li differs from that with Me_3SiCl/HMPT/Mg [AS, 1973, p. 169]. Synthetically useful reductive dimerization is much less prevalent with the former system, as the examples of eq. 70 demonstrate [103]. Acetylen c ketones react with the Mg/HMPT pair in a variety of modes [104], of which pinacolization, eq. 71, and deoxygenation, eq. 72, are synthetically intriguing.



[70]



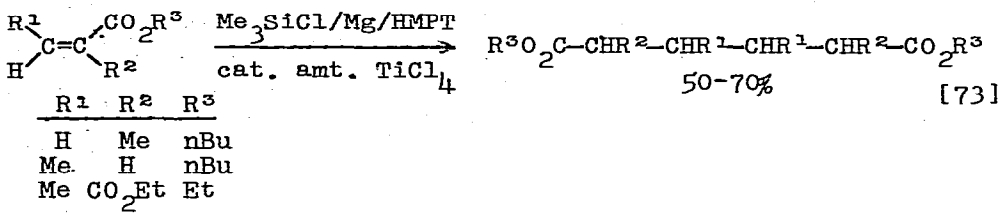
[71]



[72]

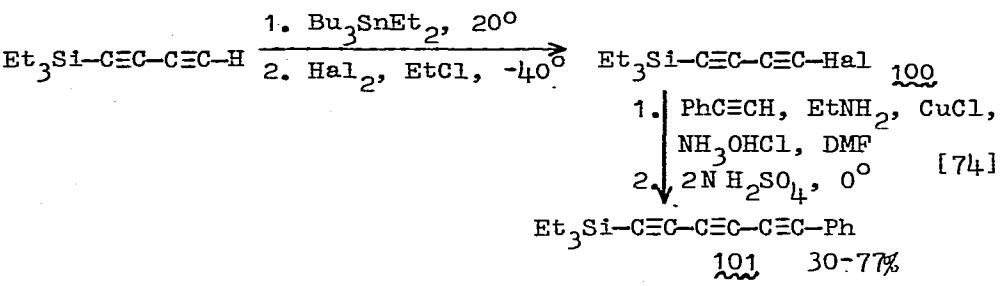
Reductive dimerization is the major course of reaction of butyl acrylate and diethyl ethylidenemalonate derivatives with the Me_3SiCl/Mg/HMPT system [105], eq. 73. A few drops of titanium

tetrachloride was used as catalyst. With other esters [cinnamic, maleic, fumaric] simple reduction or C-silylation intervened. Further study of the scope of this synthesis of adipic acid derivatives is to be awaited.

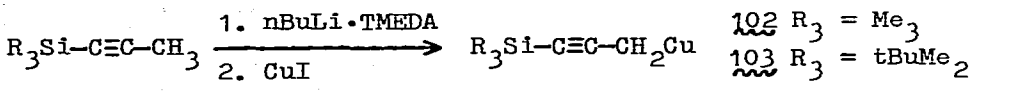


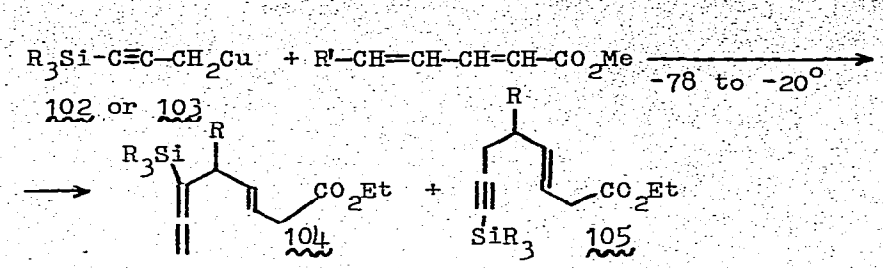
R^1	R^2	R^3
H	Me	nBu
Me	H	nBu
Me	CO_2Et	Et

A key synthon in polyacetylene synthesis, 1-halo-4-trimethylsilylbutadiyne 100, can be prepared by stannylation followed by halodestannylation, then used in synthesis of 101, eq. 74 [106].



Trialkylsilylpropynylcopper reagents 102 and 103 add in 1,6-fashion to dienoates to give mixtures of allenic 104 and acetylenic 105 esters which can be desilylated to 1,5-enynes and 1,4,5-trienes, eq. 75 [107]. For high overall yields 3.5 eq. of the organocopper reagent are preferred. 1,4-Addition of 102 to e. g. 2-cyclohexenone or ethyl acrylate does not proceed well.





[75]

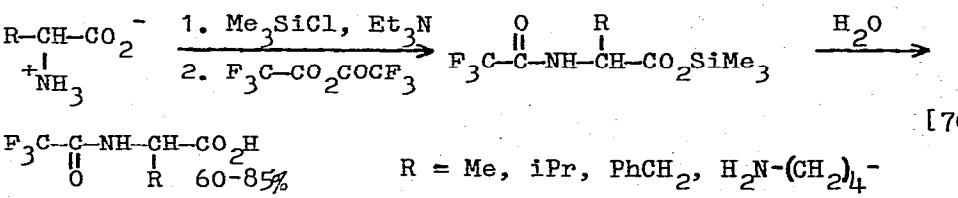
Ratio of 104:105 [total yield]

Cuprate	R' = H	R' = CH_3	
102	80:20 [80%]	18:82 [70%]	$R_3 = Me_3$
103	95:5 [36%]	3:97 [25%]	$R_3 = tBuMe_2$

IV. FORMATION OF BONDS TO HETEROATOMS

A. Acylation and Alkylation of Nitrogen

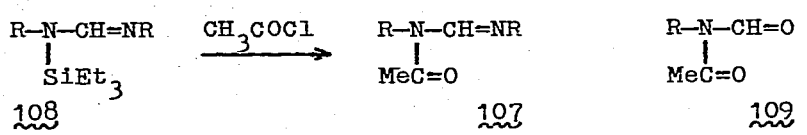
Silicon reagents function for the conversion of N–H to N–COR, inter alia the key reaction in peptide synthesis [108-114]. For example, protected N-trifluoroacetyl-amino acids are best prepared by treatment of N,O-bis[trimethylsilyl]amino acids with trifluoro acetic anhydride. The sequence of eq. 76 is fast, applicable to a variety of amino acids, and proceeds with little racemization. Glycyl-glycine reacts similarly [82% overall], while aspartic and glutamic acids formed trifluoroacetaminoanhydrides [108].



[76]

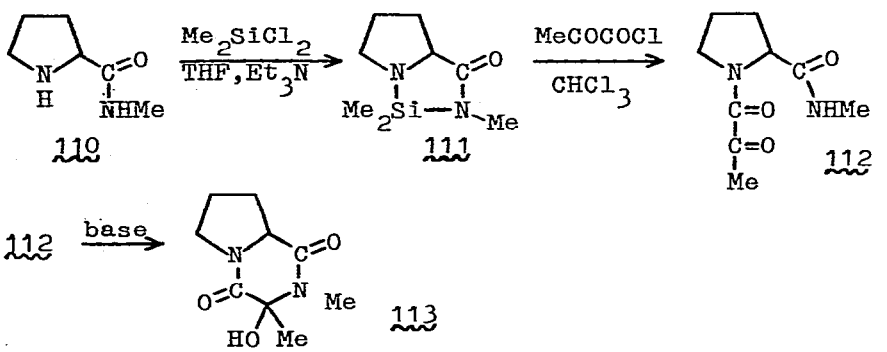
Trimethylsilylimino-methyldiphenylphosphorane 106 reacts with acid anhydrides to afford excellent yields of acyliminophosphoranes and with alkyl isocyanates to give alkylcarbamoyliminophosphoranes [109]. Reactions of 106 with phenyl isocyanate, phenyl isothiocyanate, and carbon disulfide were more complicated.

Acylformamidines 107 can be prepared in nearly quantitative yield by treatment of silylformamidines 108 with acetyl chloride [25], and in related vein isocyanates are converted [via silylformamides, see. sect. II above] into N-acylformamides 109 [26], eq. 77



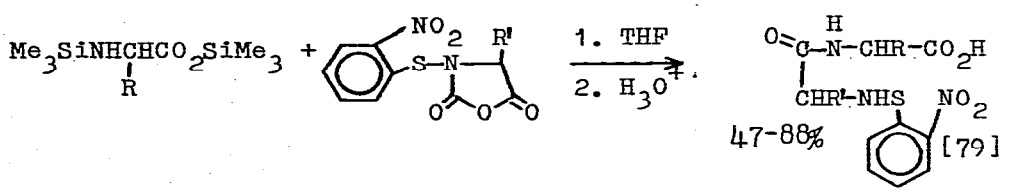
[77]

In an interesting conversion, l-proline methylamide 110 can be converted, via diazasilole 111, to N-pyruvoylproline 112. The latter readily cyclizes to 113 [110], eq. 78. The alternative reaction of 110 with hydroxymaleic anhydride proceeded in lower yield, and isolation of 112 was impossible.



[78]

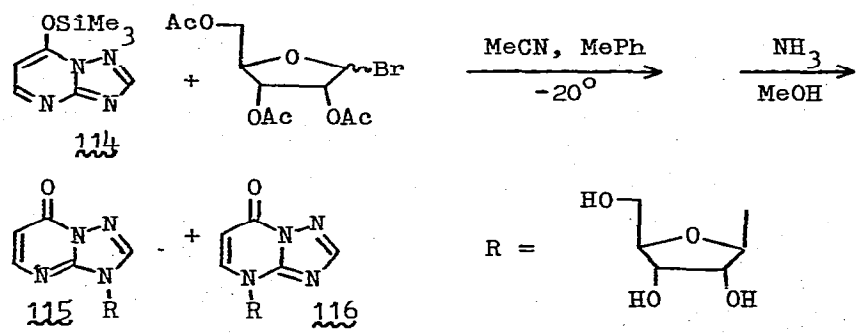
In direct peptide synthesis, N-[2-nitrobenzenesulfenyl]-N-carboxyanhydrides of amino acids couple readily with bis[trimethylsilyl]-aminoacids to afford, after hydrolysis, good yields of dipeptides [111], eq. 79. The sulfenyl group can be removed by exchange with mercaptoethanol.



47-88% [79]

Isocyanates can be prepared from amines without the use of phosgene in a sequence utilizing a silylamine [112]; $RNHSiMe_3$ sequentially treated with CO_2 at 20-50°, Me_3SiCl/Et_3N, and heated at 140-180°, gives 22-83% yields of RN=C=O, R = Me, nBu, allyl, Me_3Si.

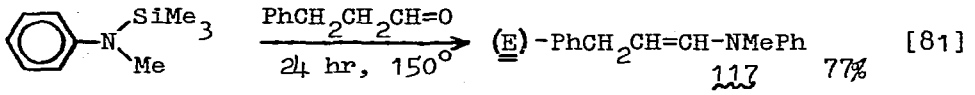
The production of nucleoside analogs by condensation of a silylated nucleobase and an activated sugar [AS, 1973, p. 185-6] continues to be active [113-128]. Among the structural types preparable by this route are pteridine ribosides [113], isopteridine ribosides and deoxyribosides [114], isoxanthopterin ribosides [115] lumazine ribosides [116] and glucosides [117], 3-oxauracil riboside [118], cytosine riboside [119], as well as several un-natural nucleosides [120-121]. A detailed survey of the silyl-method for nucleoside synthesis has been made by Vorbrüggen [122-127]. It was claimed that with $SnCl_4$ catalysis, only the β-anomers of uracil and cytosine ribosides were obtained [119], in contrast with previous reports of anomer mixtures. For un-natural nucleosides, structure proofs have often been non-rigorous, and Tolman has cautioned glib assignment of structure to reaction products where there are multiple sites of glycosylation, as in the case of 114, where both 115 and 116 were obtained [120], eq. 80.



[80]

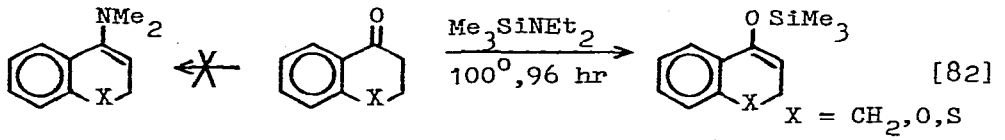
Alkylation of nitrogen has been well represented [129-132]. The

silylamine route to enamines [AS, 1973, p. 186] is preferred for preparation of 117, eq. 81, the synthetic equivalent of a 3-oxo-carbanion [129].



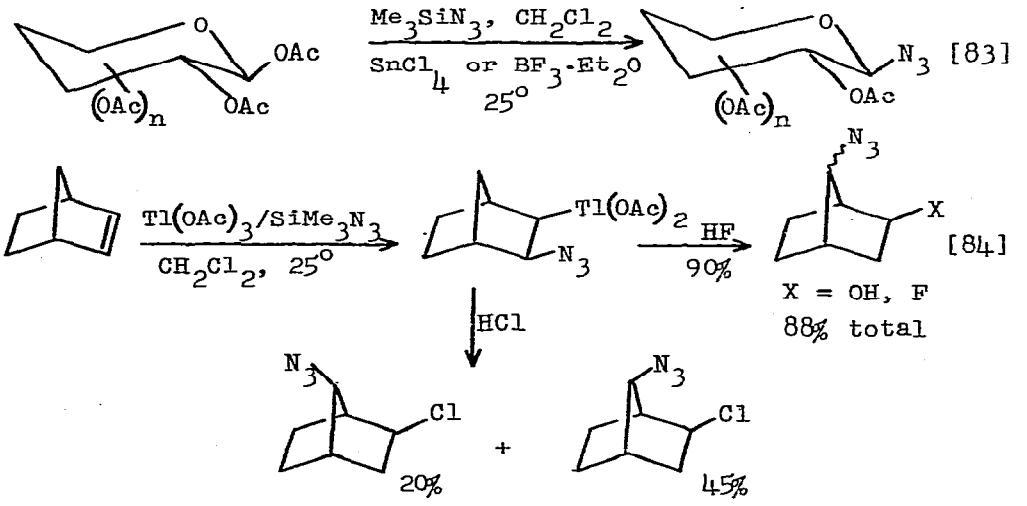
[81]

But the ketone plus trimethylsilyldimethylamine synthesis is not general. Analogs of tetralone give silyl encl ethers instead, eq. 82 [130].



[82]

In a mechanistically intriguing reaction, trimethylsilyl azide converts glucopyranosyl halides and acetates to azides with retention of configuration, eq. 83 [131]. A controlling effect by the 2-acetoxy group is suggested to explain the stereochemical results. The same reagent, in combination with thallium(III) acetate, adds to norbornene type olefins [132], eq. 84.



[83]

[84]

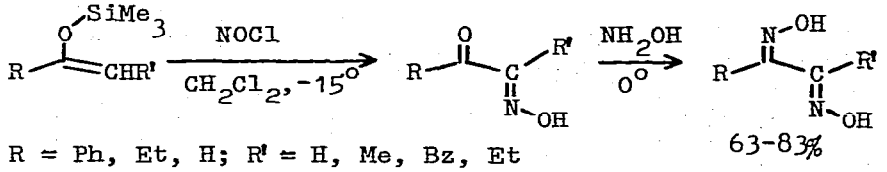
A direct process for conversion of Ar-Hal to $Ar-NH_2$ would be of great interest. An approach is found in the reaction of N-cupro bis[trimethylsilyl]amide 118 with aryl iodides which gives modest yields of aryl amines [133], eq. 85. The synthetically more advantageous process using Ar-Br gives only meager yields of amine.

$$[Me_3Si]_2NH \xrightarrow[CuI]{nBuLi} \underset{118}{[Me_3Si]_2NCu} \xrightarrow[18\ hr]{ArI,Pyr} \xrightarrow{MeOH} \underset{30\text{-}60\%}{Ar\text{-}NH_2} \qquad [85]$$

Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 2-C_4H_3S, etc.

N,O-bis[trimethylsilyl]hydroxylamines, e. g. $PhN(SiMe_3)OSiMe_3$, undergo thermal or photochemical fragmentation to nitrenoid species and hexamethyldisiloxane, as shown by trapping experiments [134], but the synthetic advantages of this method remain to be explored..

Addition of nitrosyl chloride to trimethylsilyl enol ethers and silyl ketene acetals constitutes a convenient lab-scale synthesis of α-oximinocarbonyl compounds [135], and is particularly valuable for conversion of aldehydes to glyoximes, eq. 86. A scheme involving addition of NOCl to the double bond, Me_3SiCl elimination, and tautomerization was proposed. The potential for regiospecific nitrosation [from regiospecifically generated silyl enol ethers] is especially noteworthy.



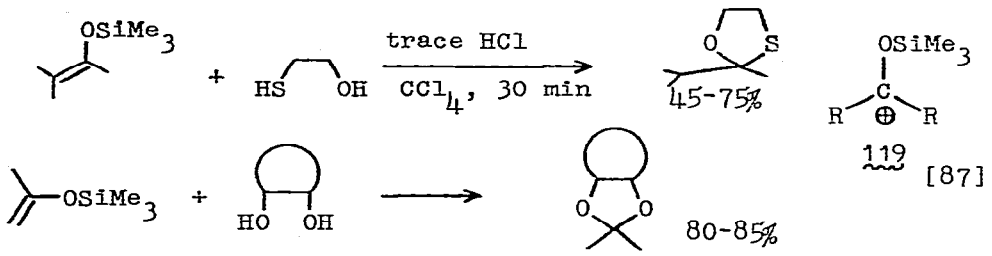
[86]

R = Ph, Et, H; R' = H, Me, Bz, Et

B. Acylation and Alkylation of Oxygen

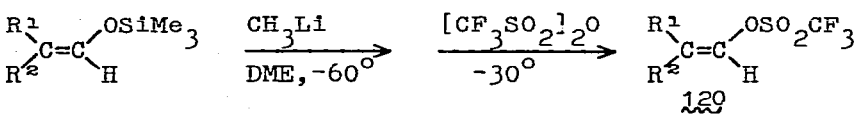
Two reports on the conversion of carbonyls to acetals and ketals have appeared [136,137]. Hemiacetals of trifluoroacetaldehyde are preparable in 65-92% yields by treatment of $CF_3CH{=}O{\cdot}HF$ with

$Si[OR]_4$, R = Me, Et, iPr, n-amyl [136]. Good yields of hemithioketals are obtained by reaction of trimethylsilyl enol ethers with mercaptoethanol, eq. 87 [137]. Analogously, acetonides [including the previously unknown acetonide of trans-1,2-cyclohexanediol] are formed from trimethylsiloxy propene and vic-diols. With scant justification, siloxy carbonium ion 119 is proposed as an intermediate [137].



[87]

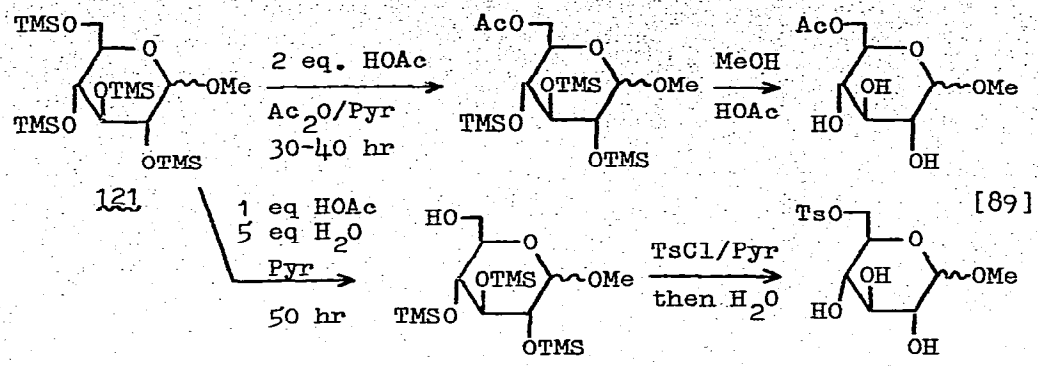
Aldehyde silylenol ethers are precursors to vinyl triflates 120, ten of which were prepared as precursors of unsaturated carbenes by the route of eq. 88 [138].



[88]

For rationally designed carbohydrate synthesis, specifically acetylated or tosylated primary hydroxyl functions in monosaccharides are required. Fuchs and Lehmann have elegantly achieved this by treating a persilylated saccharide 121 [from e. g. 1-methyl β-D-glucopyranose] with acetic acid, specifically desilylating the primary C-O-Si function and acetylating the CH_2OH generated [139], eq. 89. Tosylation proceeds analogously, although secondary silyl groups disappear in the work-up stage. Finally, aryl trifluoroacetates [AS, 1973, p. 188] are generated by plumbation of aryltrimethylsilanes [140].

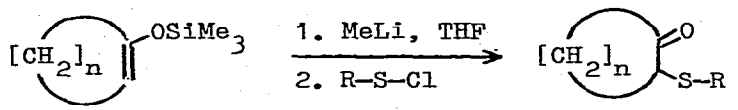
References p. 61.



[89]

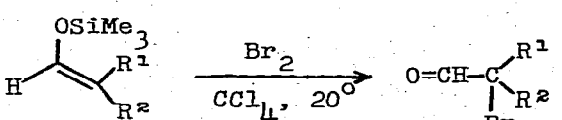
C. Formation of Other C-Heteroatom Bonds

Three papers [137, 141,142] have mentioned formation of bonds to sulfur. Ethyl esters react with S-trimethylsilyl thioethanol or thiophenol to afford high yields of the corresponding thioesters, $RCO_2Et + Me_3SiSR' \rightarrow RCOSR'$, 72-89%, R = alkyl, aryl; R' = Et, Ph [141]. The reaction of trimethylsilylenol ether-derived enolates with sulfenyl halides is the preferred route to α-thiolated carbonyl compounds, eq. 90 [142].



n = 3,4,5,6 R = Me, Ph [90]

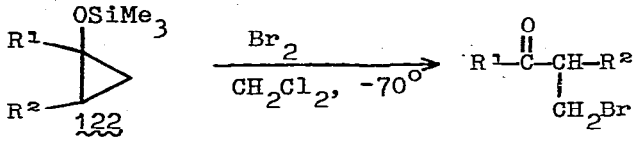
Halogenation has been the subject of five reports [143-147]. Synthetically useful, but difficultly accessible α-bromoaldehydes are obtained by simple halogenation of silylenol ethers, eq. 91, [143]. α-Chloro, but not α-iodo-aldehydes were similarly prepared.



R^1,R^2 = Bz,H; Ph,Me; Me_2; $n\text{-}C_8H_{17}$,H; H,$[CH_2]_4CN$

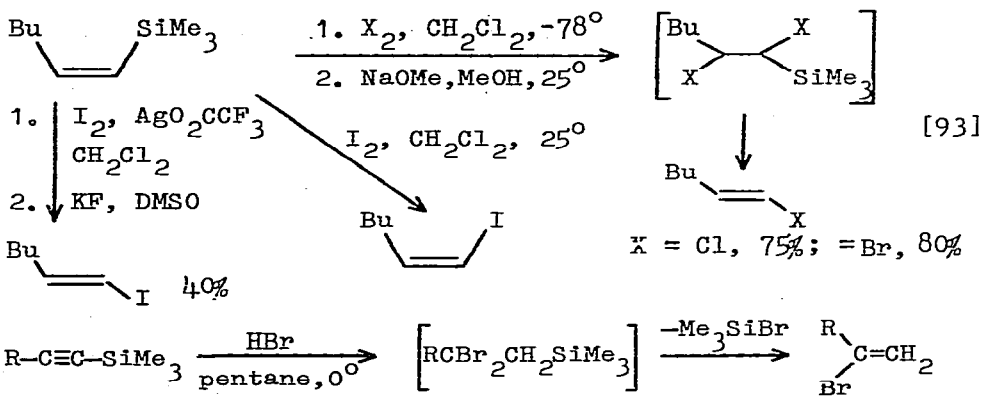
51-94% [91]

An α-bromomethyl group can be introduced into silyl enol ethers by the sequence ketone → silyl enol ether → siloxycyclopropanol 122 [62] → α-bromomethyl ketone, eq. 92 [144]. Yields are reportedly quantitative.



[92]

Alkenyl and alkynyl silanes find utility in the stereospecific synthesis of vinyl halides [67, 145] useful in cuprate preparation. Various halogenation procedures convert cis-1-trimethylsilyl-1-hexene into cis- or trans-1-iodo-1-hexene or trans-1-bromo[chloro]-1-hexene [145], eq. 93; while HBr in pentane, which adds sluggishly to terminal alkynes giving meager yields of 2-bromo-1-alkene, reacts smoothly with trimethylsilyl acetylenes to give desired bromide in 60-94% yield [67], eq. 93.



[93]

R = alkyl, carboxyalkyl, ketoalkyl, etc.

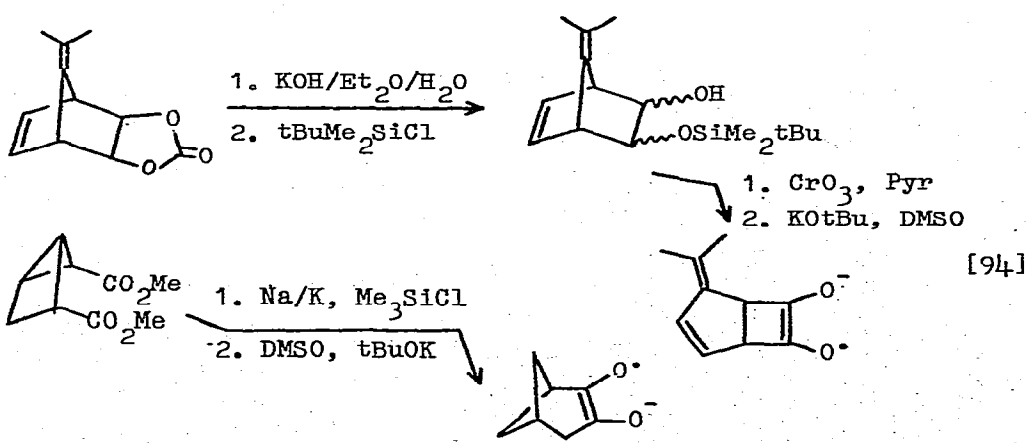
An extremely mild route for preparation of sensitive acyl halides is illustrated by the conversion of pyruvic acid to pyruvoyl chloride [146]. The silyl ester $MeCOCO_2SiMe_3$, prepared in the usual

fashion, is exchanged with oxalyl chloride containing a trace of DMF, at 25°, producing MeCOCOCl.

A convenient alternative to direct thallation of arenes for preparation of arylthallium bistrifluoroacetates $XC_6H_4Tl[O_2CCF_3]_2$ consists of treatment of the corresponding aryltrimethylsilane with thallium[III]trifluoroacetate in nitromethane-trifluoroacetic acid [147]; yields range from 60-95% isolated.

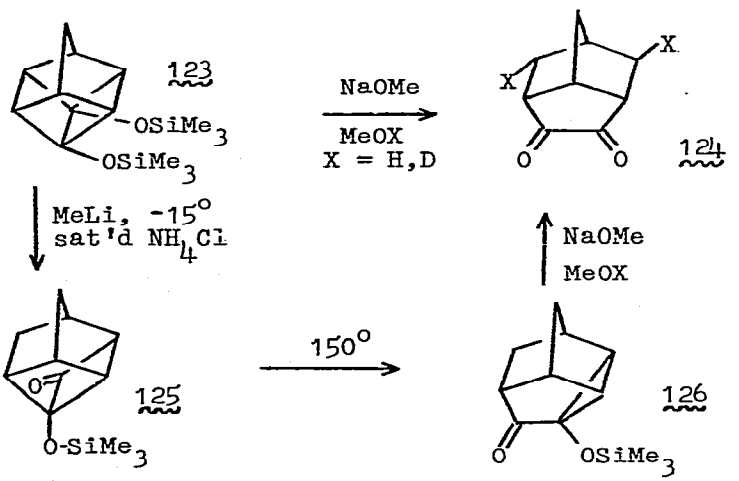
V. REARRANGEMENTS

Molecular rearrangements of the C–O–Si ⇔ ?? type are well-known collectively as the Brook Rearrangement [see e. g. [148]]. Extensive study of this rearrangement in the benzyloxy- and benzylthio-silane series, which has synthetic ramifications, has been reported by Wright and West [149,150]. The ozonolysis of silyl enol ethers [9], sect. II above, is a further example. That these rearrangements can occur unpredictably is shown by two examples [151,152]. Russell's group observed rearrangements in two instances during the straightforward preparation of semidiones from siloxy alkenes [151], eq. 94, see also sect. X below.



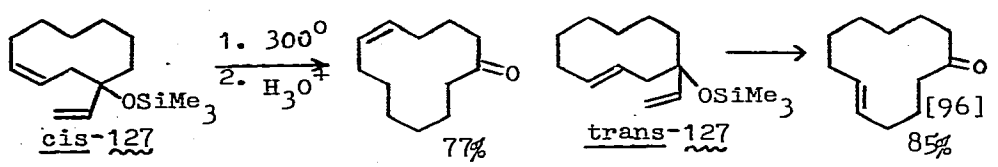
[94]

The previously reported bis[siloxy]homocubane 123 [AS,1973, p. 174] undergoes a novel rearrangement to brendadione 124 in the presence of base. Clarification of this [152] has shown the presence of two unprecedented steps, eq. 95: formation of a ketone by fragmentation of a tertiary silyl ether [H–C–C–O–$SiMe_3$ + MeLi → Me_4Si + >C=O + –C–H] and a silyl-acyloin rearrangement [RCO–CR'_2–$OSiMe_3$ → $Me_3SiOCRR'$–COR'] . Both are probably mediated by relief of strain, although interestingly, the ethyl analog of 125 [Me_3Si = Et] does not thermally rearrange to 126.



[95]

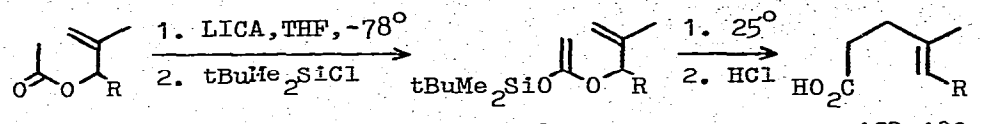
Electrocyclic rearrangement of siloxy compounds are more predictable [153-155]. Siloxy-Cope rearrangement of 1-trimethylsiloxy-1-vinyl-3-cyclodecene 127 and subsequent hydrolysis gave the results indicated in eq. 96 [153].



[96]

References p. 61.

Related to this is [3,3]-Claisen-type rearrangement of allyl silyloxyvinyl ethers 128, which proceeds smoothly at 70° to afford γ,δ-unsaturated acids with >98% stereoselectivity [154]. t-Butyldimethylsilyl ethers gave yields of 70% or better, and were useful in synthesis of a queen-bee phemerone 129, eq. 97.



128

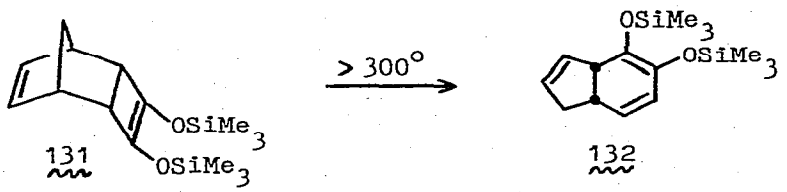
129, 130

98% (E)-olefin

129 R = $CH_2CH_2C(Me)=CHCH_2O_2CAr$, 70%
130 R = $n\text{-}C_6H_{13}$, 80%

[97]

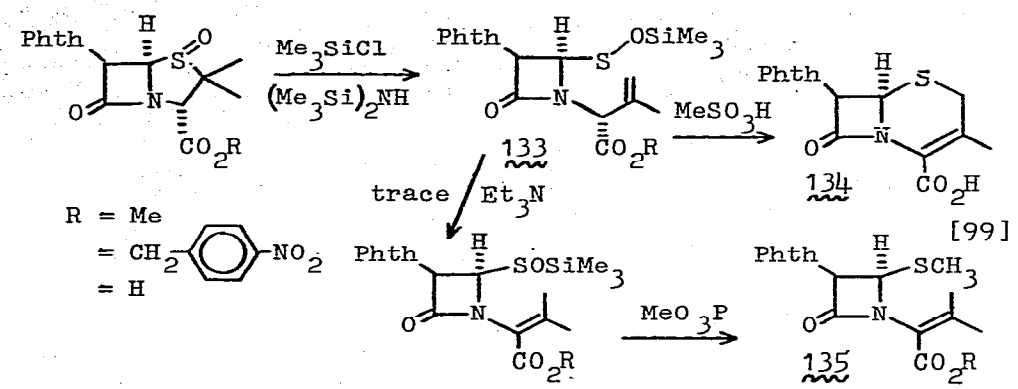
An entry into the cis-8,9-dihydroindene system is provided by the quantitative rearrangement of 131, in a flow system at 350-450°, to 132 [155], eq. 98. 131 is readily accessible from the cyclopentadiene-maleic anhydride adduct.



131 132

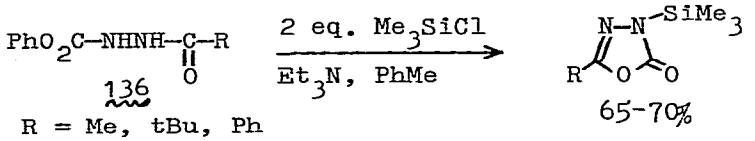
[98]

A further, and promising, rearrangement of X-O-Si moieties is the transformation of penicillin sulfoxide to desacetoxycephalosporin, mediated by trimethylsilylsulfenic acids R-S-O-$SiMe_3$ [156,157]. The R-S-OH fragment, potentially of great versatility, has formerly been known only as a transient species, but stabilization of it as the trimethylsilyl ester allows the transformations diagrammed in eq. 99 [157]. Silyl sulfenate 133 functions as a masked positive sulfur RS^+, as the acid-catalysed cyclization to 134, and the Arbusov reaction leading to 135 indicate.



[99]

Rearrangement in molecules with Si-N bonds has been less studied, but a novel synthesis of aryl cyanates and thiocyanates reported by Kricheldorf should be mentioned. O- and S-Aryl-thiocarbonic acid chlorides react with trimethylsilyl azide in refluxing benzene to afford 80-90% of cyanate or thiocyanate, presumably via elimination of N_2 and 1/8 S_8 from an intermediate 5-aryloxy- or thio-1,2,3,4-thiatriazole [158]. Likewise, phenyl 3-acylcarbazates 136 rearrange to 5-substituted-1,3,4-oxadiazoline-2-ones in the presence of trimethylchlorosilane [159], eq. 100.

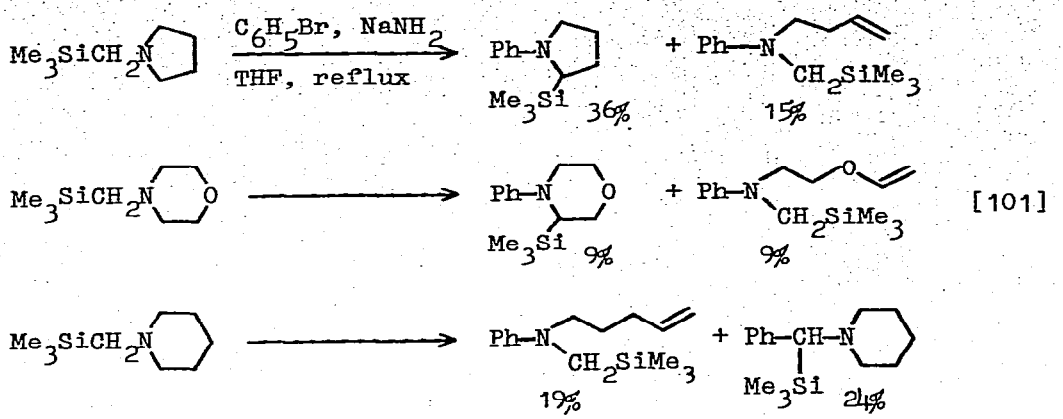


[100]

Reaction of dialkylaminomethyltrimethylsilanes with sodamide/bromobenzene affords some interesting ring expansion and cleavage products, eq. 101 [160]. Speculative mechanisms are presented.

VI. SILICON AS A PROTECTING GROUP

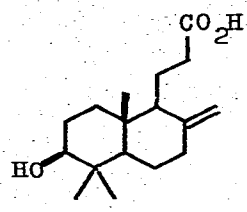
The principal use of silicon reagents in protection continues the tieing-up of OH functions as R_3SiO groups, but there has app-



eared a report of silicon as a deblocking reagent [161]. Some, but not all, benzyl esters of amino acids suffer hydrogenolysis with the $Et_3SiH/[Ph_3P]_3RhCl/MeOH$ 'ionic hydrogenation' system [2]. Future study is suggested [161].

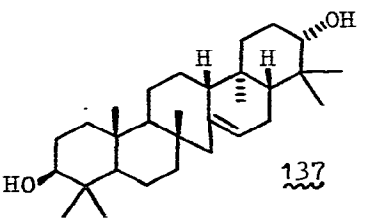
Two requisites of any successful protecting group are selective formation, and easy deblocking. That rates of silylation of secondary alcohols by $[Me_3Si]_2NH$ in pyridine at 25° vary over a factor of 1000 from endo-fenchol to exo-norborneol [162], suggests that selective protection with Me_3Si is possible. Another deblocking agent for t-butyldimethylsilyl ethers, which converts R-O-Si to R-O-Ac, has been developed [163]: A catalytic amount of anhydrous $FeCl_3$ in acetic anhydride converts (+)-2-octyl silylether to (+)-2-octyl acetate with 88% retention of configuration.

R_3Si-, principally Me_3Si- and $tBuMe_2Si$, groups are used to great extent in protection of OH functions, a particularly spectacular example of which protection is shown in eq. 102 [164]. That the silylated -OH survived the ten steps indicated leading to serratenediol 137 is indicative of the versatility and stability of the $tBuMe_2Si$- function.



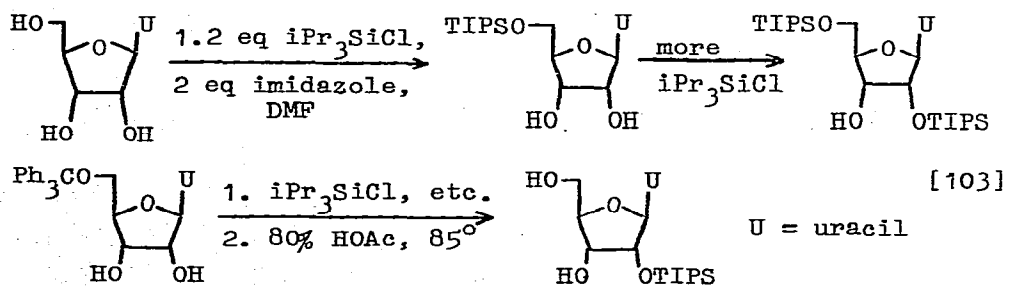
1. 8 $tBuMe_2SiCl$, 17 imidazole, DMF, 25°
2. CrO_3 following reduction of $CO_2H \rightarrow CH_2OH$
3. $H_2C{=}C(Me){-}MgBr$
4. $CH_3C(OMe)_3$, trace $EtCO_2H$, 105°
5. $NaAlH_2(OCH_2CH_2OMe)_2$
6. CrO_3
7. $H_2C{=}C(Me)Li$, -78°; 3 eq. $MeC(OMe)_2CMe_2Cl$, xylene, 120°
8. EtOH, -25°, 1 hr, then 7.
9. $Li/NH_3/Et_2O$, 1 hr
10. 5 eq. CF_3CO_2H, -78°
11. RuO_4, -25°, then 9.
12. Bu_4NF, THF, 70°

[102]



137

Table I gives an indication of the inertness of the R_3Si function to reagents in recently reported applications [165-180]. Of particular import is the work of Ogilvie in developing t-butyldimethylsilyl[TBDMS] and triisopropylsilyl[TIPS] groups for protection of ribonucleoside hydroxyl functions in oligonucleotide synthesis [180]. Differing rates of hydroxyl silylation, and inertness of TBDMS-O bonds to 80% acetic acid allow selective synthesis of 2'- or 5'-silylated uridines, eq. 103. After phosphorylation, coupling, and deblocking with Bu_4NF, a uridylyl-uridine was obtained.



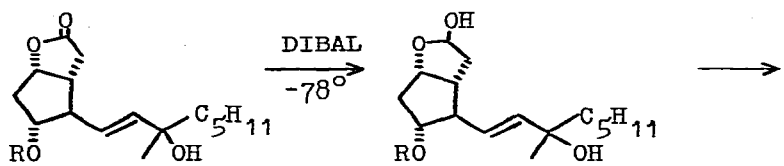
[103]

Table I

Trialkylsilyl Groups as Protecting Agents for Alcohol Functions

Alcohol type, [ref.]	R_3Si	Reagent(s) Protected Against	Deblocking Agent
2β-hydroxysteroid[165]	$tBuMe_2$	CrO_3/Pyr	HOAc/THF/H_2O
11β-hydroxysteroid[166]	Me_3	HNO_3/Ac_2O/-10°; KOAc/DMF	1% $HClO_4$/HOAc
serine or threonine[167]	Me_3	Cl_2CO/THF/20°	- - -
haloallylic[65]	Me_3	Wurtz coupling	5% K_2CO_3/MeOH
secondarycyclohexyl[168]	Me_3	$Me_2S{=}CH_2$/THF/HMPT/-20 Jones oxid./$BF_3{\cdot}Et_2O$	TsOH
ω-cyclopropylalkyl[169]	Me_3	n-BuLi, -40°	HCl/EtOH/45°
3',5'-deoxyribonucleoside, nucleosidephosphate, or ribonucleoside[170-175]	Me_3	n-BuLi/HMPT/-45°; then various alkylating agents	MeOH/H_2O
3',5'-deoxyribo-cycloazauridine[176]	$tBuMe_2$	KOtBu, DMF	Et_4NF/Pyr
ribosyl-heterocyclic-phosphonium salt[177]	Me_3	Wittig reaction	- - -
5'-deoxynucleoside with free 3'-OH[178]	$tBuMe_2$	- - -	Bu_4NF/THF/20°
ditto [179]	iPr_3	- - -	"
[179]	tBu-$[CH_2]_4$	- - -	"
3'-deoxynucleoside with free 5'-OH[179]	xs $tBuMe_2$	5'-OH freed with 80% HOAc, 10 min, 90°	"
ribonucleosides and nucleotides[180]	$tBuMe_2$ iPr_3	oligonucleotide synth.	see text

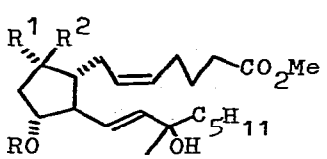
Silyl protecting functions continue to be prominent in prostaglandin synthesis [AS,1973,p. 200-201]. Silylation of intermediate 138 with Me_3SiNEt_2 in acetone at -78° gave 139, which survived iBu_2AlH treatment at -78°, affording 140. The silyl function was cleaved by NaH in DMSO during a Wittig reaction [compare with ref. 177, Table I] giving 141, but was easily resilylated [Me_3SiNEt_2, -45°] to 142. 142 survived oxidation [Collins reagent] to 143, which was desilylated conventionally with aqueous methanol acetic acid [181], eq. 104. Similar results obtained in the PGE_1 series [no 5,6-double bond] and the PGF series [11-hydroxyl β rather than α][182]. A related entry to the 140 system is found in the reaction of t-butyldimethylsilyl- and tribenzylsilyl-acetals of epoxide 145 with divinylcopperlithium, which introduced the vinylic side chain with the desired regioselectivity [183].



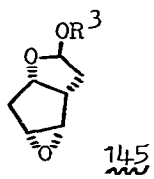
[104]

138 R = H
139 R = Me_3Si

140 R = Me_3Si



141 R=R^2 = H; R^1 = OH
142 R = Me_3Si; R^1 = OH; R^2 = H
143 R = Me_3Si; R^1=R^2 = =O
144 R = H, R^1=R^2 = =O

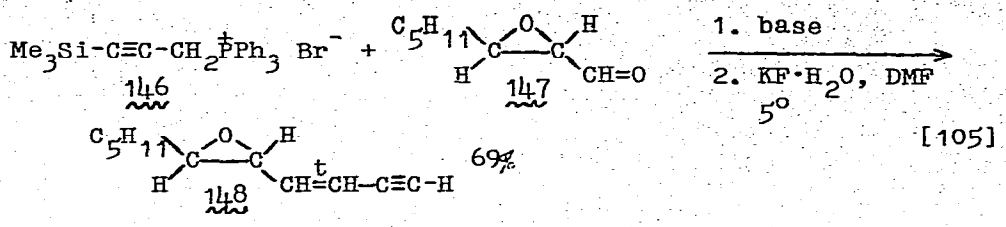


145

R^3= $tBuMe_2Si$ or Bz_3Si

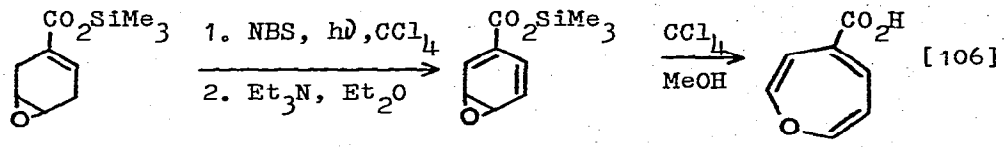
In contrast to Me_3Si-O cleaved during the Wittig Reaction, the Me_3Si-C≡C- bond of 146 [prepared from propargyl alcohol in 34% yield by sequential treatment with 2 eq. nBuLi, 2 eq. Me_3SiCl, dilute HCl, $[PhO]_3PBr_2$ in pyridine, and Ph_3P in dioxane] was coupled

with epoxy aldehyde 147 giving, after cleavage, prostanoid intermediate 148 in good yield, eq. 105 [184].



[105]

The trimethylsilyl function was chosen, eq. 106, to tie up a carboxylic acid function during synthesis of 4-carboxybenzene oxide, and survived two steps, before deblocking with methanol [185].



[106]

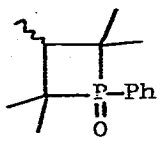
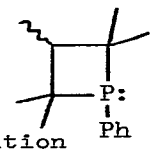
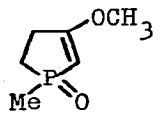
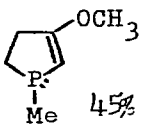
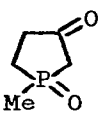
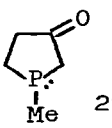
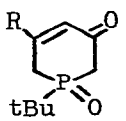
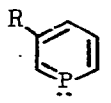
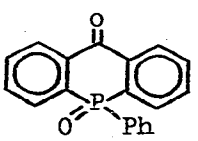
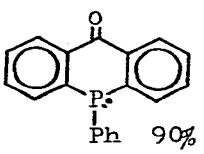
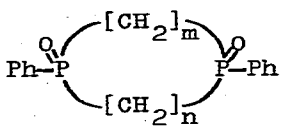
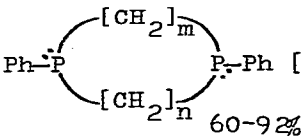
Although silylation of nitrogen functionality has not been widely investigated for protection, it should be noted that silylated intermediates increase the yield over more customary 'Schotten Baumann' conditions in the synthesis of N-sulfenyl-aminoacids and -oligopeptides [186], and the combination of β-mercaptoethanol with trimethylsilylthiocyanate de-sulfenylates oligopeptides in 69-95% yield [186]. Since the $RMe_2SiCH_2-\overset{|}{\underset{|}{N}}^{+}$ bond is cleaved by $LiAlH_4$ in preference to $CH_3-\overset{|}{\underset{|}{N}}^{+}$ or $PhCH_2-\overset{|}{\underset{|}{N}}^{+}$ [187], it may be implied that Me_3SiCH_2Cl could protect a tertiary amine as a quarternary salt.

VII. PHOSPHORUS CHEMISTRY

Several further examples of reduction of phosphine oxides to phosphines by Si–H bonds [AS, 1973, p. 196-7] have been reported [188-193] and are summarized in Table II.

Table II

Silanes For Conversion of $R_3P{=}O$ to R_3P:

Phosphine Oxide	Silane, conditions	Phosphine	Ref.
(+)(R) MePhnPrP=O	$PhSiH_3$	(-)(S) nPrMePhP: 100% retention 96% yield	[188]
	$HSiCl_3$, Et_3N	 retention	[189]
	$HSiCl_3$, Et_3N; then 10 N NaOH	 45%	[190]
	ditto	 21%	[190]
	$HSiCl_3$, PhH reflux	 30%	[191]
	ditto	 90%	[192]
 cis- or trans-	xs $HSiCl_3$, PhH, 60-70%	 60-92% stereospecific	[193]

References p. 61.

In contrast, silicon reagents can carry out a formal oxidation of phosphorus(III) to phosphorus(V), often by the agency of a silyl azide, i. e. $X_3P + R_3SiN_3 \rightarrow X_3P{=}N{-}SiR_3 + N_2$. Some examples of this process are shown in eq. 107 [194-195].

$$Me_3SiN_3 + P[NMe_2]_3 \longrightarrow Me_3SiN{=}P[NMe_2]_3 \xrightarrow[iPrOH]{H_2SO_4} HN{=}P[NMe_2]_3$$

$$\xrightarrow{MeHgN[SiMe_3]_2} MeHgN{=}P[NMe_2]_3 \quad ; \text{ ref. [194]}$$

[107]

$$R_2P{-}PR_2 + Me_3SiN_3 \xrightarrow{100^\circ} R_2P(S)\text{-}PR_2(N\text{-}SiMe_3) \xrightarrow[PhH]{S_8} R_2P(S)\text{-}PR_2(N\text{-}SiMe_3)$$

R = Me, Et, nPr

$$\xrightarrow{H_2O} \left[R_2P(S)\text{-}PR_2(O)\right] \longrightarrow R_2PSH + R_2PO_2H \quad ; \text{ ref. [195]}$$

$$R_2P{-}PR_2 + 2 \text{ eq. } Me_3SiN_3 \longrightarrow R_2P(N\text{-}SiMe_3)\text{-}PR_2(N\text{-}SiMe_3) \quad ; \text{ ref. [195]}$$

Oxidation of monophosphites, especially those of nucleosides, by conversion to the disilylphosphite and treatment with disulfides can afford phosphates or thiophosphates [196] or S-phenylphosphorothioates [197], eq. 108. Thymidine-5'-phosphite was converted to thymidine phosphate.

$$RO{-}P(H)(O)OH \xrightarrow[Et_3N,\ Pyr]{3 \text{ eq. } Me_3SiCl} RO{-}P(OSiMe_3)_2 \quad (149) \xrightarrow[25^\circ,4 \text{ hr}]{PhSSPh} RO{-}P(O)(SPh)OH$$

70-99%

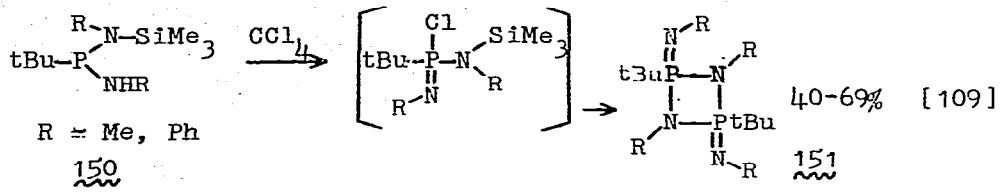
[108]

$$149 + PyrS{-}SPyr \longrightarrow \left[RO{-}P^{+}[OSiMe_3]_2(SPyr)\ \ {}^{-}SPyr\right] \xrightarrow{-PyrSSiMe_3} RO{-}P(O)(SPyr)OSiMe_3$$

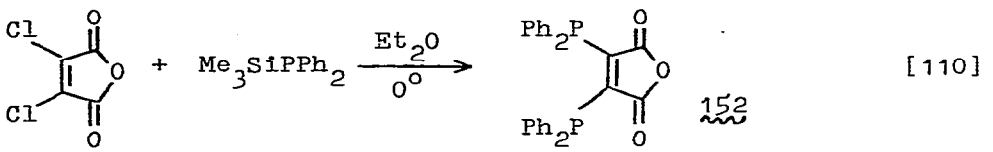
$$149 \xrightarrow[2.\ H_2O]{1.\ S_8} RO{-}P(S)(OH)OH$$

$$RO{-}P(O)(SPyr)OSiMe_3 \xrightarrow{H_2O} RO{-}P(O)(OH)_2$$

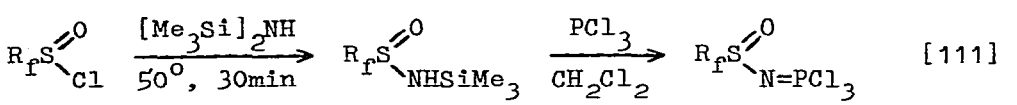
Oxidation by carbon tetrachloride [a novelty] converts silylated diaminophosphine 150 to diazadiphosphetidine 151 [198], eq. 109.



In organophosphorus synthesis, the reaction of trimethylsilyldiphenylphosphine with acid chlorides [AS, 1973, p. 195] has been extended to the synthesis of substituted maleic anhydride 152, a novel bidentate ligand, eq. 110 [199]. A variety of silyl phosph-



ines $tBu_nP[SiMe_3]_{3-n}$, prepared from the chlorides, undergo reaction with Me_3MCl, M = Ge, Sn, affording the element-phosphines $tBu_nP[MMe_3]_{3-n}$, n = 0, 1, or 2, in 93-96% yield [200]. A variety of novel ylides, of potential interest as unusual olefinating species, are produced by the action of heterocumulenes such as PhNCO, MeNCS and CS_2 on $PhMe_2P{=}CHSiMe_3$ [201]. Insertion into the =C—Si bond is the usual reaction path. Some unusual phosphineimines, eq. 111, result from reaction of sulfinyl chlorides with hexamethyldisilazane and phosphorus trichloride [202]. Extrusion of Me_3SiH seems to be occuring in the second step.



N-trialkylsilylphosphinimines react with S_4N_4 to form an intriguing series of trithiatriazines $R_3P{=}N{-}S_3N_3$ [203], and an unusual cyclization-oxidation occurs in the reaction of $[Me_3Si]_2NPF_2$ with hexafluoroacetone and then PF_5 giving F_3P[perfluoropinacol] [204].

The reaction of $R_2N{-}Si$ with Cl–P bonds, yielding $R_2N{-}P$ and Si–Cl, is a common use of silylamines [205-210], examples of which are shown in eq. 112.

$$PF_5 + Me_3SiNMe_2 \longrightarrow [Me_2N]_2PF_3 \qquad \text{ref. [205]}$$

$$Me_3SiN{=}S{=}NSiMe_3 + PF_4X \longrightarrow \text{(cyclic)} \qquad \text{ref. [206]}$$

X = F, Ph; 25%

$$Cl_2\overset{\overset{O}{\|}}{P}{-}N(Me){-}PCl_2 + Me_3SiNMe_2 \longrightarrow Cl_2\overset{\overset{O}{\|}}{P}{-}N(Me){-}P[NMe_2]_2 \qquad \text{ref. [207]}$$

87%

[112]

$$\text{(cyclic)} + [Me_3Si]_2NMe \xrightarrow[3\text{ days}]{PhH} \text{(cyclic)} \qquad \text{ref. [208]}$$

72%

$$2\,[RO]_2PCl + [Me_3Si]_2NMe \xrightarrow[3\text{ hr}]{} [RO]_2P{-}N(Me){-}P[OR]_2 \qquad 43\text{-}46\%$$

R = Me, Et; ref. [209]

$$\text{(cyclic)} + R^1R^2NSiMe_3 \xrightarrow[2\text{ hr}]{80^\circ} \text{(cyclic)} \qquad \text{ref. [210]}$$

R^1R^2 = H,Me; H,Et; Me,Me; Et,Et

78-85%

VIII. INORGANIC SYNTHESES

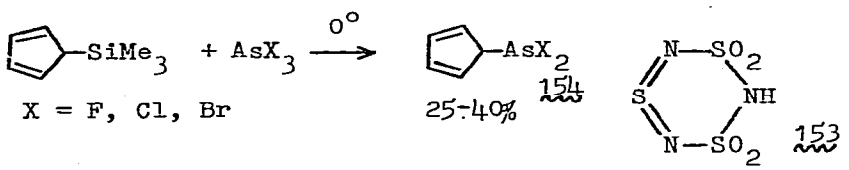
Although no attempt at completeness has been made in this section, the following illustrate novel uses for silicon reagents in inorganic synthesis, an area of great future promise.

SULFUR: Bis[trimethylsilyl]sulfur diimide reacts with $[ClSO_2]_2NH$ to afford the novel heterocycle 153 [211]. See also [218-219].

SELENIUM: Reaction of Ph_2SeCl_2 with Me_3SiNMe_2 gives 30% of $Ph_2Se(Cl)NMe_2$, but with $[Me_3Si]_2NH$ gives 85% of the novel salt $[Ph_2Se{=}N{=}SePh_2]^+Cl^-$ [212].

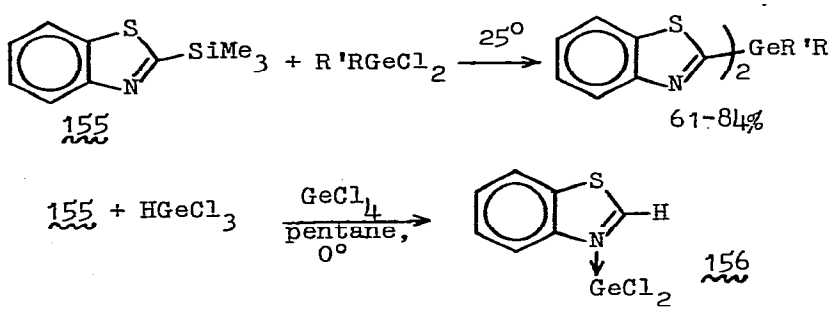
BORON: Reaction of phenyldichloroborane with hexamethylcyclotrisilazane in 5:6 molar ration gives a 30% yield of $[Ph{-}B{-}NH]_3$ together with other Si–B compounds [213]. See also [220-222].

ARSENIC: σ-Bonded, fluxional, cyclopentadienyldihaloarsines 154 are best synthesized by metathesis of cyclopentadienyltrimethylsilane and an arsenic trihalide, eq. 113 [214].



[113]

GERMANIUM: While treatment of 155 with dichlorogermanes gives straightforward transsilylation, eq. 114, with trichlorogermane, the stabilized germylene complex 156 is obtained [215,216]. Similar results obtained in the benzimidazole series [-S- replaced by -NMe-] where a similar germylene was isolated and characterized by



[114]

X-ray diffraction [217]. Trimethylsilylselenomethane [223] is an efficient reagent for transfer of the $SeCH_3$ moiety to germanium, e. g. $Me_nH_{3-n}GeCl + Me_3SiSeMe \rightarrow Me_nH_{3-n}GeSeMe$, n = 0,1,2; 90-95% [224].

IODINE: Sequential replacement of fluoride by methoxide in the trifluoromethyliodine(V) series is achieved by trimethylmethoxysilane or dimethyldimethoxysilane [225] which function as methoxide transfer reagents, e. g. $CF_3IF_4 + n\ Me_3SiOMe \rightarrow CF_3IF_{4-n}OMe_n$.

MAGNESIUM: Triphenylfluorosilane is neither as efficient nor as convenient as SiF_4 or $BF_3 \cdot Et_2O$ for effecting the cleavage of dialkylmagnesiums: $R_2Mg + M\text{-}F \rightarrow RMgF + M\text{-}R$ [226].

TRANSITION METALS: Silicon reagents figure prominently in transition metal synthesis [227-238]. Common are reactions in which a $Si\text{-}ML_n$ bond is broken by E-X, yielding $Si\text{-}X + E\text{-}ML_n$, eq. 115.

$h^5\text{-}CpM(CO)_xSiMe_3 + Me_2AsCl \longrightarrow h^5\text{-}CpM(CO)_xAsMe_2$

$M(CO)_x = Fe(CO)_2$, $Cr(CO)_3$, $Mo(CO)_3$, $W(CO)_3$ ref. [227]

$h^5\text{-}CpM(CO)_3SiMe_3 + ClPMe_2 \longrightarrow h^5\text{-}CpM(CO)_3PMe_2 \longrightarrow$

$\left[h^5\text{-}CpM(CO)_3\overset{+}{P}Me_2PMe_2\right]Cl^-$ M = Mo, W ref. [228]

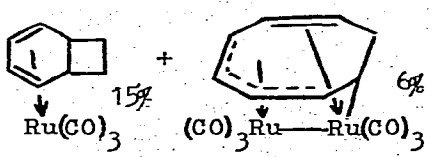
$h^5\text{-}CpM(CO)_3SiMe_3 + Me_3M'OSiMe_3 \longrightarrow h^5\text{-}CpM(CO)_3M'Me_3$, 35-74%

M = Mo, W; M' = Sn, Ge ref. [229]

$(CO)_4Co\text{-}SiMe_3 + Me_3MH \xrightarrow[PhH]{20^\circ} Me_3MCo(CO)_4$

M = Sn, Ge ref. [230]

[115]

$[SiMe_3]_2Ru(CO)_4 + C_8H_{10} \longrightarrow$  +

15% 6%

$Ru(CO)_3$ $(CO)_3Ru\text{—}Ru(CO)_3$

ref. [231]

Alternatively, transfer of a ligand from silicon to a metal can occur: $Si\text{-}N< + ML_n \rightarrow >NML_{n-1} + SiL$ [232-234], eq. 116.

$$PhN{=}NSiMe_3 + Mn(CO)_5Br \xrightarrow[6\ days]{25^\circ} (CO)_4Mn\langle \overset{N\text{-}Ph}{\underset{Ph\text{-}N}{N}} \rangle Mn(CO)_4 \quad \text{ref. [232]}$$

$$MoO_2[S_2CNMe_2]_2 \xrightarrow[[Me_2NCS_2]_2]{Me_3SiN_3} Mo[NS][S_2CNMe_2]_3 \ 50\% \quad \text{ref. [233]}$$

$$MoCl_4[MeCN]_2 \xrightarrow[2.\ ligand]{1.\ Me_3SiN_3} MoCl_3N[ligand]_2$$

ligand = 1/2 bipy, Ph_3PO, Cl^-

$$\xrightarrow[2.\ Ph_3P]{} MoCl_2N[PPh_3]_2 \qquad [116]$$

$$\xrightarrow[2.\ Me_3SiSCSNEt_2]{} MoN[S_2CNEt_2]_3 \quad \text{ref. [234]}$$

Or, ligand modification such as replacement of -F by $-NH_2$, eq. 117.

$$Ni[PF_3]_4 + NaN[SiMe_3]_2 \xrightarrow[5^\circ]{PhH} [PF_3]_3Ni\text{-}PF_2N[SiMe_3]_2 \xrightarrow{H_2O} \qquad [117]$$

$$\longrightarrow [PF_3]_3Ni\text{-}PF_2NH_2 \quad \text{ref. [235]}$$

Less well understood are reorganization reactions [236-238] of complexes mediated by chlorosilanes, eq. 118. These may involve complex series of oxidative addition-elimination reactions with Si-H and Si-Cl bonds.

$$NaCo(CO)_4 + MeSiCl_3 \xrightarrow{THF} HO(CH_2)_4CCo_3CO_9 \ 20\% \quad \text{ref. [236]}$$

$$[PPh_3]_4Ni + Ph_nSiCl_{4-n} \rightarrow [(Ph_3P)_2NiCl]_m \quad \text{ref. [237]}$$

$$[diphos]_2CoH + xs\ HSiCl_3 \longrightarrow [(diphos)_2CoClH]Cl + H_2SiCl_2 \qquad [118]$$

ref. [238]

References p. 61.

IX. MISCELLANEOUS REACTIONS

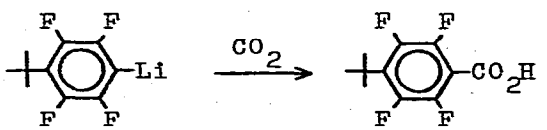
Although organosilicon reagents can be used to prepare carbanions [239-241], free radicals [151,242-245], and solid-phase synthesis polymers [246], it is best to start a miscellaneous section with a caveat: $[H_2C{=}CH]_2PtCl_4$ has been added to the select list of reagents that catalyse cleavage of methyl groups from Me_4Si [247].

A general preparation of benzyl anions of Na, K, Rb, and Cs, eq. 119, is suitable for making nmr samples [239].

$$[Me_3SiCH_2]_2Hg + 2\,M \xrightarrow[C_6H_{12}]{} 2\,Me_3SiCH_2M + Hg\downarrow$$
$$Me_3SiCH_2M + Ar{-}\overset{|}{\underset{|}{C}}{-}H \longrightarrow Me_4Si + Ar{-}\overset{/}{C}^{-}\ M^{+} \qquad [119]$$

Bis[perhaloaryl]methylsilanes Ar_2SiMeH, and tris[perhaloaryl]silanes Ar_3SiH, Ar = 2-Cl_3C_4S, 4-C_5Cl_4N, C_6F_5, C_6Cl_5, are cleaved by butyl- or methyl-lithium under mild conditions [Et_2O, -30 to -75°] to perhaloaryllithium reagents in a surprisingly facile metal-metal exchange [240]. In contrast, alkyllithium cleavage of perfluorophenylsilanes Ar_fSiR_3 is generally synthetically useless, as Ar_fLi is more conveniently prepared by direct halogen-metal exchange. However, eq. 120 demonstrates a sequence leading to previously unknown 4-t-butyltetrafluorobenzoic acid [241]. Apparently t-BuLi is too bulky to attack at silicon.

$$[C_6F_5]_2SiMeH + 2\ t\text{-}BuLi \xrightarrow[-78^\circ]{Et_2O} [4\text{-}tBuC_6F_4]_2SiMeH \xrightarrow[-50^\circ]{MeLi}$$



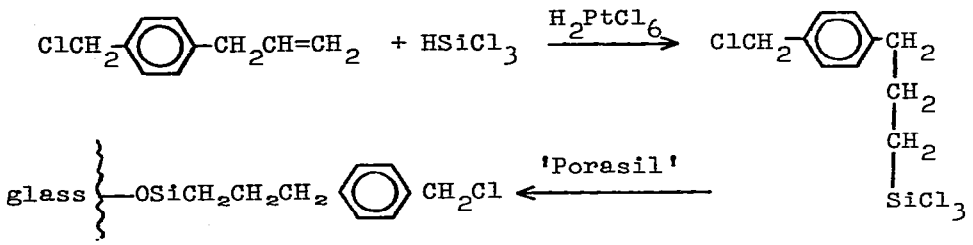
[120]

In the radical generation area, the Russell Iowa State group has continued the study of semidione generation by anionic cleavage

of α-trimethylsiloxy ketones [151] or bis[siloxy]alkenes [151,242], e. g. $Me_3SiO-CR=CR-OSiMe_3$ or $Me_3SiOCHR-COR + KOtBu/DMSO \longrightarrow RC(O\cdot)-C(O^-)R$. Generally, organic free radicals for epr analysis are generated by photolysis of a mixture of tBuOOtBu, Me_3SiH, and RCl; or of 2-nitrofuran and Et_3SiH [243-245]. A process such as that of eq. 121 is postulated.

$$[tBuO]_2 \xrightarrow{h\nu} 2\ tBuO\cdot \xrightarrow{Me_3SiH} tBuOH + Me_3Si\cdot$$
$$Me_3Si\cdot + RCl \longrightarrow Me_3SiCl + R\cdot \qquad [121]$$

A final exciting development of silicon compounds in synthesis has been the development of a porous glass with pendant chlorobenzyl groups suitable for Merrifield solid-phase peptide synthesis.



Whether these glass beads [246] have an advantage over traditional macroreticular polystyrene beads remains to be seen.

X. REFERENCES

Note: [AS, 1973, p.---] refers to pages in ref. [1]

1. S. S. Washburne, J. Organometal. Chem.,83 [1974] 155.
2. D. N. Kursanov, Z. N. Parnes, and N. M. Loim, Synthesis, [1974] 633.
3. A. G. Brook, Acct. Chem. Res., 7 [1974] 77.
4. G. L. Larson, D. Hernandez, and A. Hernandez, J. Organometal. Chem., 76 [1974] 9.
5. H. Kono and Y. Nagai, Orgn. Prep. Proced. Intl., 6 [1974] 19.

6. G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, Tetrahedron Lett. [1974] 4319.

7. A. G. Brook and D. M. Macrae, J. Organometal. Chem., 77 [1974] C19.

8. R. D. Clark and C. H. Heathcock, Tetrahedron Lett. [1974] 2027.

9. R. D. Clark and C. H. Heathcock, Tetrahedron Lett. [1974] 1713.

10. F. Duboudin, E. Frainnet, G. Vincon, and F. Dabescat, J. Organometal. Chem., 82 [1974] 41.

11. E. Duranti and C. Balsamini, Synthesis [1974] 815.

12. D. Brandes and A. Blaschette, J. Organometal. Chem., 78 [1974] 1.

13. D. Brandes and A. Blaschette, J. Organometal. Chem., 73 [1974] 217.

14. N. M. Loim, V. A. Baranova, L. V. Moiseeva, L. P. Zalukaev, Z. N. Parnes, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim. [1974] 843.

15. D. Seyferth, G. H. Williams, P. L. K. Hung, and J. E. Hallgren, J. Organometal. Chem., 71 [1974] 97.

16. D. Seyferth, J. E. Hallgren, and C. S. Eschbach, J. Amer. Chem. Soc., 96 [1974] 1730.

17. J. L. Levenson and L. Kaplan, J. C. S. Chem. Commun. [1974] 23.

18. J. L. Fry, J. C. S. Chem. Commun. [1974] 45.

19. T. Ando, H. Hosaka, and W. Funasaka, Bull. Chem. Soc. Japan, 46 [1973] 3513.

20. T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett. [1974] 4405.

21. T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett. [1974] 331.

22. I. Ojima and Y. Nagai, Chem. Lett. [1974] 233.

23. I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett. [1974] 1889.

24. M. Tanaka, Y. Watanabe, T. Mitsudo, Y. Yasunoro, and Y. Takegami, Chem. Lett. [1974] 137.

25. I. Ojima, S.-I. Inaba, and Y. Nagai, J. Organometal. Chem., 72 [1974] C11.

26. I. Ojima, S.-I. Inaba, and Y. Nagai, Tetrahedron Lett. [1974] 4363.

27. M. P. Doyle, D. J. DeBruyn, S. J. Donnelly, D. A. Kooistra, A. A. Odubela, C. T. West, and S. M. Zonnebelt, J. Org. Chem. 39 [1974] 2740.

28. S. W. Baldwin, R. J. Doll, and S. A. Haut, J. Org. Chem., 39 [1974] 2471.

29. G. S. Li, D. F. Ehler, and R. A. Benkeser, Org. Syn., 53 [1973] 159.

30. K. Hensen and U. Tröbs, Chem. Ber., 107 [1974] 3176.

31. A. G. Hortmann, R. L. Harris, and J. A. Miles, J. Amer. Chem. Soc., 96 [1974] 6119.

32. T. J. Katz and K. C. Nicolaou, J. Amer. Chem. Soc., 96 [1974] 1948.

33. R. Breslow, K. Ehrlich, T. Higgs, J. Pecoraro, and F. Zanker, Tetrahedron Lett: [1974] 1123.

34. E. Vedejš and E. S. C. Wu, J. Org. Chem., 39 [1974] 3641.

35. P. F. Hudrlik and D. Peterson, Tetrahedron Lett. [1974] 1133.

36. R. K. Boeckman, Jr. and S. M. Silver, Tetrahedron Lett. [1973] 3497.

37. T. E. Chan, M. P. Li, W. Mychajlowskij, and D. N. Harpp, Tetrahedron Lett. [1974] 3511.

38. T. H. Chan and W. Mychajlowskij, Tetrahedron Lett. [1974] 171.

39. W. H. Daly and H. J. Hölle, J. Org. Chem., 39 [1974] 1597.

40. C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, J. Organometal. Chem., 66 [1974] 29.

41. T. H. Chan and E. Chang, J. Org. Chem., 39 [1974] 3264.

42. H. Sakurai, K. Nishiwaki, and M. Kira, Tetrahedron Lett. [1973] 4193.

43. S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, Tetrahedron Lett. [1974] 1403.

44. K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, J. Amer. Chem. Soc., 96 [1974] 1620.

45. D. Seebach, M. Kolb, and B.-T. Gröbel, Chem. Ber., 106 [1973] 2277.

46. D. S. Watt, J. Org. Chem., 39 [1974] 2799.

47. S. J. Selikson and D. S. Watt, Tetrahedron Lett. [1974] 3029.

48. G. R. Malone and A. I. Meyers, J. Org. Chem., 39 [1974] 618.

49. D. J. Dagli and J. Wemple, J. Org. Chem., 39 [1974] 2938.

50. G. Kyriakakou and J. Seyden-Penne, Tetrahedron Lett. [1974] 1737.

51. E. J. Corey and C. R. Cyr, Tetrahedron Lett. [1974] 1761.

52. T. C. Clarke and R. G. Bergmann, J. Amer. Chem. Soc., 96 [1974] 7934.

53. J. W. Patterson, Jr. and J. H. Fried, J. Org. Chem., 39 [1974] 2506.

54. G. Stork and J. D'Angelo, J. Amer. Chem. Soc., 96 [1974] 7114.

55. R. K. Boeckman, Jr., J. Amer. Chem. Soc., 96 [1974] 6179.

56. G. Stork and J. Singh, J. Amer. Chem. Soc., 96 [1974] 6181.

57. T. Mukaiyama and M. Hayashi, Chem. Lett. [1974] 15.

58. T. Mukaiyama, K. Banno, and K. Narasaka, J. Amer. Chem. Soc., 96 [1974] 7503.

59. C. Girard and J. M. Conia, Tetrahedron Lett. [1974] 3327.

60. C. Girard, P. Amice, J. P. Barnier, and J. M. Conia, Tetrahedron Lett. [1974] 3329.

61. C. Girard and J. M. Conia, Tetrahedron Lett. [1974] 3333.

62. S. Murai, T. Aya, T. Renge, I. Ryu, and N. Sonoda, J. Org. Chem., 39 [1974] 858.

63. B.-T. Gröbel and D. Seebach, Angew. Chem. Int. Ed. Engl., 13 [1974] 83.

64. G. Stork and M. E. Jung, J. Amer. Chem. Soc., 96 [1974] 3682.

65. G. Stork, M. E. Jung, E. Colvin, and Y. Noel, J. Amer. Chem. Soc., 96 [1974] 3684.

66. R. K. Boeckman, Jr. and K. J. Bruza, Tetrahedron Lett. [1974] 3365.

67. R. K. Boeckman, Jr. and D. M. Blum, J. Org. Chem., 39[1974]3307

68. Y. Kiso, K. Tamao, and M. Kumada, J. Organometal. Chem., 76 [1974] 105.

69. R. Calas, J. Dunoguès, G. Deleris, and F. Pisciotti, J. Organo-Chem., 69 [1974] C15.

70. T. N. Mitchell, J. Organometal. Chem., 71 [1974] 39.

71. T. N. Mitchell, J. Organometal. Chem., 71 [1974] 27.

72. I. S. Akhrem, N. M. Chistovalova, E. I. Mysov, and M. E. Vol'-pin, J. Organometal. Chem., 72 [1974] 163.

73. I. Ojima and M. Kumagai, Tetrahedron Lett. [1974] 4005.

74. D. Seebach, M. Kolb, and B.-T. Gröbel, Tetrahedron Lett. [1974] 3171.

75. P. Bourgeois, J. Organometal. Chem., 76 [1974] C1.

76. D. A. Evans, G. L. Carroll, and L. K. Truesdale, J. Org. Chem. 39 [1974] 914.

77. W. C. Still and T. L. MacDonald, J. Amer. Chem. Soc., 96 [1974] 5561.

78. B. M. Trost and R. A. Kunz, J. Org. Chem., 39 [1974] 2648.

79. N. H. Nam, J. P. Beaucourt, H. Hoellinger, and L. Pichat, Bull. Soc. Chim. France [1974] 1367.

80. T. Wakamatsu, K. Akasaka, and Y. Ban, Tetrahedron Lett. [1974] 3879.

81. T. Wakamatsu, K. Akasaka, and Y. Ban, Tetrahedron Lett. [1974] 3883.

82. I. Ojima, S. Inaba, and Y. Nagai, Tetrahedron Lett. [1973] 4271.

83. I. Ojima, S. Inaba, and Y. Nagai, Chem. Lett. [1974] 1069.

84. P. Bourgeois, J. Dunoguès, N. Duffaut, and P. Lapouyade, J. Organometal. Chem., 80 [1974] C25.

85. J. P. Pillot, J. Dunoguès, and R. Calas, C. R. Acad. Sci., Ser. C, 278 [1974] 787.

86. R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, J. Chem. Soc. Perkin I [1974] 2391.

87. J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, J. Chem. Soc. Perkin I [1974] 2530.

88. R. N. Haszeldine, D. L. Scott, and A. E. Tipping, J. Chem. Soc. Perkin I [1974] 1440.

89. B. M. Trost and S. Kurozumi, Tetrahedron Lett. [1974] 1929.

90. J. Salaun, B. Garnier, and J. M. Conia, Tetrahedron Lett. [1974] 1413.

91. S. Danishefsky and T. Kitahara, J. Amer. Chem. Soc., 96 [1974] 7808.

92. S. C. Welch and R. L. Walters, Synth. Commun., 3 [1973] 419; J. Org. Chem., 39 [1974] 2667.

93. G. Stork and J. F. Cohen, J. Amer. Chem. Soc., 96 [1974] 5270.

94. I. Ojima, S.-I. Inaba, and Y. Nagai, J. C. S. Chem. Commun., [1974] 826.

95. H. R. Kricheldorf, Makromol. Chem., 175 [1974] 3343.

96. P. Dowd and K. Kang, Synth. Commun., 4 [1974] 151.

97. J. M. Denis, J. Champion, and J. M. Conia, Org. Syn., 53 [1973] 158.

98. J. P. Barnier, J. Champion, and J. M. Conia, Org. Syn., 53 [1973] 159.

99. M. E. Jung, J. C. S. Chem, Commun., [1974] 956.

100. C. U. L. Delbaere and G. H. Whitham, J. Chem. Soc. Perkin I [1974] 879.

101. P. Y. Johnson and M. A. Priest, J. Amer. Chem. Soc., 96 [1974] 5618.

102. G. A. Russell, D. F. Lawson, H. L. Malkus, R. D. Stephens, G. R. Underwood, T. Takano, and V. Malatesta, J. Amer. Chem. Soc., 96 [1974] 5830.

103. R. Calas, J. Dunoguès, A. Ekouya, G. Merault, and N. Duffaut, J. Organometal. Chem., 65 [1974] C4.

104. G. Merault, P. Bourgeois, J. Dunoguès, and N. Duffaut, J. Organometal. Chem., 76 [1974] 17.

105. J.-P. Picard, J. Dunoguès, and R. Calas, J. Organometal. Chem., 77 [1974] 167.

106. B. N. Ghose and D. R. M. Walton, Synthesis [1974] 890.

107. B. Ganem, Tetrahedron Lett. [1974] 4467.

108. H. R. Kricheldorf and M. Fehrle, Synthesis [1974] 420.

109. K. Itoh, M. Okamura, and Y. Ishii, J. Organometal. Chem., 65 [1974] 327.

110. J. Häusler and V. Schmidt, Chem. Ber., 107 [1974] 2804.

111. H. R. Kricheldorf and M. Fehrle, Chem. Ber., 107 [1974] 3533.

112. V. F. Mironov, V. P. Kozyukov, and V. P. Bulatov, J. Gen. Chem. USSR, 43 [1973] 2077; Zh. Obsh. Khim., 43 [1973] 2089.

113. M. Ott and W. Pfleiderer, Chem. Ber., 107 [1974] 339.

114. K. Harzer and W. Pfleiderer, Helv. Chim. Acta, 56 [1973] 1225.

115. M. Schmid, M. Schranner, and W. Pfleiderer, Chem. Ber., 107 [1973] 1952.

116. G. Ritzmann and W. Pfleiderer, Chem. Ber., 106 [1973] 1401.

117. W. Pfleiderer, G. Ritzmann, K. Harzer, and J. C. Joachims, Chem. Ber., 106 [1973] 2982.

118. T. L. Chwang and C. Heidelberger, Tetrahedron Lett. [1974] 95.

119. G. Ritzmann, R. S. Klein, B. Ohrui, and J. J. Fox, Tetrahedron Lett. [1974] 1519.

120. G. R. Revankar, R. K. Robins, and R. L. Tolman, J. Org. Chem. 39 [1974] 1256.

121. P. Dea, G. R. Revankar, R. L. Tolman, R. K. Robins, and M. P. Schweizer, J. Org. Chem., 39 [1974] 3226.

122. U. Niedballa and H. Vorbruggen, J. Org. Chem., 39 [1974] 3654.

123. U. Niedballa and H. Vorbruggen, J. Org. Chem., 39 [1974] 3660.

124. U. Niedballa and H. Vorbruggen, J. Org. Chem., 39 [1974] 3664.

125. U. Niedballa and H. Vorbruggen, J. Org. Chem., 39 [1974] 3668.

126. U. Niedballa and H. Vorbruggen, J. Org. Chem., 39 [1974] 3672.

127. H. Vorbruggen and P. Strehlke, Chem. Ber., 106 [1973] 3039.

128. F. W. Lichtenthaler, P. Voss, and A. Heerd, Tetrahedron Lett. [1974] 2141.

129. G. Rauschwalbe and H. Albrecht, Synthesis [1974] 663.

130. L. H. Hellberg and A. Juarez, Tetrahedron Lett. [1974] 3553.

131. H. Paulsen, Z. Györgydeak, and M. Friedmann, Chem. Ber., 107 [1974] 1568.

132. E. Maxa, G. Schulz, and E. Zbiral, Liebigs Ann. Chem. [1974] 933.

133. F. D. King and D. R. M. Walton, J. C. S. Chem. Commun. [1974] 256.

134. F. P. Tsui, T. M. Vogel, and G. Zon, J. Amer. Chem. Soc., 96 [1974] 7144.

135. J. H. Rasmussen and A. Hassner, J. Org. Chem., 39 [1974] 2558.

136. G. Siegemund, Chem. Ber., 106 [1973] 2960.

137. G. L. Larson and A. Hernandez, Synth. Commun., 4 [1974] 61.

138. P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, J. Amer. Chem. Soc., 96 [1974] 4562.

139. E. F. Fuchs and J. Lehmann, Chem. Ber., 107 [1974] 721.

140. H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, Tetrahedron Lett. [1974] 853.

141. M. Mukaiyama, T. Takeda, and K. Atsumi, Chem. Lett. [1974] 187.

142. D. Seebach and M. Teschner, Tetrahedron Lett. [1973] 5113.

143. R. H. Reuss and A. Hassner, J. Org. Chem., 39 [1974] 1785.

144. S. Murai, Y. Seki, and N. Sonoda, J. C. S. Chem. Commun., [1974] 1032.

145. R. B. Miller and T. Reichenbach, Tetrahedron Lett. [1974] 543.

146. J. Häusler and V. Schmidt, Chem. Ber., 107 [1974] 145.

147. H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, Tetrahedron Lett. [1974] 3391.

148. A. G. Brook and J. M. Duff, Can. J. Chem., 51 [1973] 2024.

149. A. Wright and R. West, J. Amer. Chem. Soc., 96 [1974] 3214.

150. A. Wright and R. West, J. Amer. Chem. Soc., 96 [1974] 3222.

151. G. A. Russell, G. W. Holland, K. Y. Chang, R. G. Keske, J. Mattoz, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, and Y. Kosugi, J. Amer. Chem. Soc., 96 [1974] 7237.

152. R. D. Miller and D. L. Dolce, Tetrahedron Lett., [1973] 5217.

153. R. W. Thies and J. E. Billigmeier, J. Amer. Chem. Soc., 96 [1974] 200.

154. J. A. Katznellenbogen and K. L. Christy, J. Org. Chem., 39 [1974] 3315.

155. R. C. De Selms, J. Amer. Chem. Soc., 96 [1974] 1967.

156. T. S. Chou, J. R. Burgtorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, J. Amer. Chem. Soc., 96 [1974] 1609.

157. T. S. Chou, Tetrahedron Lett., [1974] 725.

158. H. R. Kricheldorf, Synthesis [1974] 561.

159. H. R. Kricheldorf, Liebigs Ann. Chem. [1973] 1816.

160. Y. Sato, T. Aoyama, and H. Shirai, J. Organometal. Chem., 81 [1974] 21.

161. H. Sugiyama, S. Tsuchiya, and S. Seto, Tetrahedron Lett. [1974] 3291.

162. H. J. Schneider and R. Hornung, Liebigs Ann. Chem. [1974] 1864.

163. B. Ganem and V. R. Small, J. Org. Chem., 39 [1974] 3728.

164. G. D. Prestwich and J. N. Labowitz, J. Amer. Chem. Soc., 96 [1974] 7103.

165. H. Hosoda and J. Fishman, J. C. S. Chem. Commun. [1974] 546; J. Amer. Chem. Soc., 96 [1974] 7325.

166. H. Hofmeister, H. Laurent, G. A. Hoyer, and R. Wiechert, Chem. Ber., 107 [1974] 1235.

167. R. Wies and P. Pfaender, Liebigs Ann. Chem. [1973] 1269.

168. Y. Yamada, K. Hosaka, H. Nagaoka and K. Iguchi, J. C. S. Chem. Commun. [1974] 519.

169. B. Ragonnet, M. Santelli, and M. Bertrand, Bull. Soc. Chim. France [1973] 3119.

170. L. Pichat and J. P. Guilbert, C. R. Acad. Sci., Ser. C [1973] 1157.

171. L. Pichat, J. Godbillon, and M. Herbert, Bull. Soc. Chim. France [1973] 2709.

172. L. Pichat, J. Godbillon, and M. Herbert, Bull. Soc. Chim. France [1973] 2712.

173. L. Pichat, J. Godbillon, and M. Herbert, Bull. Soc. Chim. France [1973] 2715.

174. L. Pichat, J. Godbillon, and M. Herbert, Bull. Soc. Chim. France [1973] 2719.

175. L. Pichat, J. Godbillon, and M. Herbert, J. Labelled Compound, 9 [1973] 607.

176. M. J. Robins and E. M. Trip, Tetrahedron Lett. [1974] 3369.

177. E. Zbiral, Synthesis [1974] 775, ref. 76.

178. K. K. Ogilvie, Can. J. Chem., 51 [1973] 3799.

179. K. K. Ogilvie, E. A. Thompson, M. A. Quilliam, and J. B. Westmore, Tetrahedron Lett., [1974] 2865.

180. K. K. Ogilvie, K. L. Sadana, M. A. Quilliam, and J. B. Westmore, Tetrahedron Lett., [1974] 2861.

181. E. W. Yankee, U. Axen, and G. L. Bundy, J. Amer. Chem. Soc, 96 [1974] 5865.

182. E. L. Cooper and E. W. Yankee, J. Amer. Chem. Soc., 96 [1974] 5876.

183. E. J. Corey, K. C. Nicolaou, and D. J. Beames, Tetrahedron Lett. [1974] 2439.

184. E. J. Corey, G. W. J. Fleet, and M. Kato, Tetrahedron Lett. [1974] 3963.

185. J. D. Richardson, T. C. Bruice, S. M. Waraskiewicz, and G. A. Berchtold, J. Org. Chem., 39 [1974] 2088.

186. H. R. Kricheldorf and M. Fehrle, Synthesis [1974] 422.

187. Y. Sato, Y. Fukami, and H. Shirai, J. Organometal. Chem., 78 [1974] 75.

188. K. L. Marsi, J. Org. Chem., 39 [1974] 265.

189. C. R. Hall and D. J. H. Smith, Tetrahedron Lett. [1974] 1693.

190. L. D. Quin and R. C. Stocks, J. Org. Chem., 39 [1974] 686.

191. G. Märkl and D. Matthes, Tetrahedron Lett. [1974] 4381.

192. Y. Segall, I. Granoth, and A. Kalir, J. C. S. Chem. Commun. [1974] 501.

193. T. H. Chan and B. S. Ong, J. Org. Chem., 39 [1974] 1748.

194. J. Lörberth, J. Organometal. Chem., 71 [1974] 158.

195. R. Appel and R. Milker, Chem. Ber., 107 [1974] 2658.

196. T. Hata and M. Sekine, Tetrahedron Lett. [1974] 3943.

197. T. Hata and M. Sekine, J. Amer. Chem. Soc., 96 [1974] 7364.

198. O. J. Scherer, P. Klusmann, and N. Kuhn, Chem. Ber., 107 [1974] 552.

199. D. Fenske and H. J. Becher, Chem. Ber., 107 [1974] 117.

200. H. Schumann and L. Rösch, Chem. Ber., 107 [1974] 854.

201. K. Itoh, H. Hayashi, M. Fukui, and Y. Ishii, J. Organometal. Chem., 78 [1974] 339.

202. H. W. Roesky and S. Tutkunkardes, Chem. Ber., 107 [1974] 508.

203. I. Ruppert, V. Bastian, and R. Appel, Chem. Ber., 107 [1974] 3426.

204. J. A. Gibson and G.-V. Röschenthaler, J. C. S. Chem. Commun. [1974] 694.

205. R. Schmutzler, J. Chem. Soc. Dalton [1974] 2687.

206. R. Appel, I. Ruppert, R. Milker, and V. Bastian, Chem. Ber., 107 [1974] 380.

207. R. Keat, J. Chem. Soc. Dalton [1974] 876.

208. H. Nöth and R. Ullmann, Chem. Ber., 107 [1974] 1019.

209. H. Binder and R. Fischer, Chem. Ber., 107 [1974] 205.

210. W. Heider, U. Klingebiel, T.-P. Lin, and O. Glemser, Chem. Ber., 107 [1974] 592.

211. H. W. Roesky and B. Kuhtz, Chem. Ber., 107 [1974] 1.

212. V. Horn and R. Paetzold, Z. Anorg. Allg. Chem., 404 [1974] 213.

213. H. Nöth, W. Tinhof, and T. Taeger, Chem. Ber., 107 [1974] 3113.

214. P. Jutzi and M. Kuhn, Chem. Ber., 107 [1974] 1228.

215. P. Jutzi, H.-J. Hoffman, K. Beier, and K.-H. Wyes, J. Organometal. Chem., 82 [1974] 209.

216. P. Jutzi, H.-J. Hoffman, and K.-H. Wyes, J. Organometal. Chem. 81 [1974] 341.

217. P. Jutzi, H.-J. Hoffman, D. J. Brauer, and C. Krüger, Angew. Chem. Int. Ed. Engl., 12 [1973] 1002.

218. H. W. Roesky and W. Schaper, Chem. Ber., 107 [1974] 3451.

219. R. Höfer and O. Glemser, Angew. Chem. Int. Ed. Engl., 12 [1973] 1000.

220. H. Nöth and W. Storch, Chem. Ber., 107 [1974] 1028.

221. G. Srivastava, J. Organometal. Chem. 69 [1974] 179.

222. G. Srivastava, J. C. S. Perkin I [1974] 1916.

223. J. W. Anderson. G. R. Barker, J. E. Drake, and M. Rodger, J. C. S. Dalton [1973] 1716.

224. G. R. Barker, J. E. Drake, and R. T. Hemmings, J. C. S. Dalton [1974] 450.

225. G. Oates and J. M. Winfield, J. C. S. Dalton [1974] 119.

226. E. C. Ashby and J. Nakashi, J. Organometal. Chem., 72 [1974]11.

227. W. Malisch and M. Kuhn, Angew. Chem. Int. Ed. Engl., 13 [1974] 84.

228. W. Malisch and M. Kuhn, J. Organometal. Chem., 73 [1974] C1.

229. W. Malisch and M. Kuhn, Chem. Ber., 107 [1974] 979.

230. G. F. Bradley and S. R. Stobart, J. C. S. Dalton [1974] 265.

231. A. C. Szary, S. A. R. Knox, and F. G. A. Stone, J. C. S. Dalton [1974] 662.

232. E. W. Abel, C. A. Burton, M. R. Churchill, and K.-K. G. Lin, J. C. S. Chem. Commun. [1974] 268.

233. J. Chatt and J. R. Dilworth, J. C. S. Chem. Commun. [1974] 508.

234. J. Chatt and J. R. Dilworth, J. C. S. Chem. Commun. [1974] 517.

235. T. Kruck, G. Maueler, and G. Schmidgen, Chem. Ber., 107 [1974] 2421.

236. B. K. Nicholson, B. H. Robinson, and J. Simpson, J. Organometal. Chem., 66 [1974] C3.

237. M. F. Lappert and G. Speier, J. Organometal. Chem., 80 [1974] 329.

238. N. J. Archer, R. N. Haszeldine, and R. V. Parish, J. Organometal. Chem., 81 [1974] 335.

239. A. J. Hart, D. H. O'Brien, and C. R. Russell, J. Organometal. Chem., 72 [1974] C19.

240. R. D. Howells and H. Gilman, J. Organometal. Chem., 77 [1974] 177.

241. D. Sethi, R. D. Howells, and H. Gilman, J. Organometal. Chem. 69 [1974] 377.

242. G. A. Russell, P. R. Whittle, C. S. C. Chung, Y. Kosugi, K. Schmitt, and E. Goettert, J. Amer. Chem. Soc., 96 [1974] 7053.

243. G. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, J. Amer. Chem. Soc. 96 [1974] 2441.

244. L. R. C. Barclay, D. Griller, and K. U. Ingold, J. Amer. Chem. Soc., 96 [1974] 3012.

245. C. M. Camaggi, L. Lunazzi, and G. Placucci, J. Org. Chem., 39 [1974] 2425.

246. W. Parr, K. Grohmann, and K. Hägele, Liebigs Ann. Chem. [1974] 655.

247. D. Mansuy, J. F. Bartoli, and J. C. Chottard, J. Organometal. Chem., 77 [1974] C49.