679. *The Reaction of Diazoalkanes with Group IV Hydrides.*[1]

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Diazomethane reacts with alkyl-silanes, -germanes, and -stannanes in ether only in the presence of ultraviolet light or copper powder, which suggests that the reaction involves insertion of carbene. The yields of methyl derivatives depend on the steric hindrance due to the alkyl substituent.

Diazoethane reacts similarly with phenylsilane, to give ethylphenylsilane in 5% yield. Studies with radioactive tracers suggest that insertion of ethylidene takes place.

The reaction of diazoalkanes with metal and metalloid halides has been successfully applied to the preparation of 1-halogenoalkyl derivatives from a range of Group IV halides.[2] Yakubovich and Ginsburg[3] suggested that a free-radical mechanism was involved, a free alkylene biradical being formed which then attacked the metal–halogen bond. However, the decreasing readiness with which the chlorine atoms of silicon tetrachloride are successively replaced is the opposite of the behaviour of carbon tetrachloride, from which pentaerythrityl chloride, $C(CH_2Cl)_4$, is the only product.[4] This supports the idea of a polar mechanism such as that suggested by Seyferth,[2] which involves initial co-ordination of the diazoalkane to the silicon, followed by loss of nitrogen and intramolecular rearrangement to the halogenoalkylsilane. Such reactions occur with a wide range of chloro- and bromo-silanes, trichlorosilane, for instance, giving mainly dichlorochloromethylsilane[5] when treated with diazomethane. The latter reaction shows that chlorine migrates in preference to hydrogen. The present investigation was designed to find the conditions under which the silicon–hydrogen bond can be methylenated, and to compare its behaviour with that of the carbon–hydrogen bond, whose methylenation has been extensively studied.[6] The work was extended to include some germanes and stannanes.

Preliminary work showed that silane and arylsilanes do not react with diazomethane in ether in the temperature range $-70°$ to $+20°$ in the absence of catalysts. This is in sharp distinction to the rapid reaction of the corresponding chlorides, and is in keeping with the expected effect of the low polarity of the silicon–hydrogen bond in hindering a polar method of attack. Similarly Lesbre *et al.*[7] found that a catalyst such as copper powder was necessary in the alkylation of alkylstannanes with diazomethane and other diazoalkanes, and of alkylgermanes with diazoacetic ester.

However, methylenation of the silicon–hydrogen bond takes place readily in ethereal solution in the presence of ultraviolet radiation. Phenylsilane gives methylphenylsilane and dimethylphenylsilane in yields of 70% and 5%, respectively: $Ph{\cdot}SiH_3 \longrightarrow PhMeSiH_2 \longrightarrow PhMe_2SiH$. Although a three-molar excess of diazomethane was used, no trimethylphenylsilane could be detected in the products by vapour-phase chromatography or mass spectrometry, nor was there any evidence of attack on the phenyl group. In all the photolyses in diethyl ether, ethyl n-propyl and ethyl isopropyl ether were also formed by methylenation of the solvent, as would be expected for a reaction involving free methylene.

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[1] Preliminary communication: Kramer and Wright, *Angew. Chem.*, 1962, **74**, 468; *Tetrahedron Letters*, 1962, 1095.

[2] Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

[3] Yakubovich and Ginsburg, *Zhur. obshchei Khim.*, 1952, **22**, 1783; cf. Yakubovich, Makarov, Ginsburg, Gavrilov, and Merkulova, *Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 69.

[4] Urry and Eiszner, *J. Amer. Chem. Soc.*, 1952, **74**, 5822.

[5] Seyferth and Rochow, *J. Amer. Chem. Soc.*, 1955, **77**, 906.

[6] (*a*) Meerwein, Rathjen, and Werner, *Ber.*, 1942, **75**, 1610; (*b*) Doering, Buttery, Laughlin, and Chaudhuri, *J. Amer. Chem. Soc.*, 1956, **78**, 3224; (*c*) Kopecky, Hammond, and Leermakers, *ibid.*, 1962, **84**, 1015.

[7] (*a*) Lesbre and Buisson, *Bull. Soc. chim. France*, 1957, 1204; (*b*) Lesbre and Satge, *Compt. rend.*, 1958, **247**, 471.

The high yield of methylsilanes compared with the low yield of propyl ethers from a solution containing far fewer Si–H bonds than C–H bonds shows that attack by the methylene must be selective between them. An approximate calculation gives a minimum ratio of 100 : 1 for Si–H/C–H attack in ether. This is in apparent contrast with the " first collision " reaction which has been previously suggested for singlet methylene to explain its almost random methylenation of hydrocarbons.[6b] However, silane groups have been shown by us in other ways to be unusually reactive to carbenes. Thus, although the decomposition of diazomethane when catalysed by copper powder gives no methylenation of ether and only norcarane from cyclohexene (see also ref. 6*c*), phenylsilane in ether is converted into methylphenylsilane when a copper catalyst is used; the yield of methylphenylsilane (3%) is much lower than that obtained on photolysis.

Photochemical methylenations of phenylsilane were carried out in a number of solvents and it was found that diethyl ether gave the highest yield of insertion products. The yields of methylphenylsilane obtained under standardized conditions with various solvents were: diethyl ether, 70%; cyclohexane, 8%; benzene, 5%; tetrahydrofuran, 3%; n-hexane, 3%; benzonitrile, 0. The absence of methylenation of the silane in benzonitrile may be due to the polarity of this solvent. The yields of methylphenylsilane in the other solvents show little selectivity of the methylene towards the silane groups, approximate calculations giving 2 : 1 for tetrahydrofuran, benzene, and n-hexane, and 6 : 1 in cyclohexane. These values may not be significantly different from unity, but the divergence in diethyl ether is definite. A possible explanation would be that diazomethane forms a weak complex with phenylsilane in diethyl ether, thus giving an unusually high reactivity to the silane.

It might be expected that the amount of methylenation produced would be be very much affected by increased substitution of the silane, since the lifetime of methylene must be very short. It can be seen from the annexed results in the series phenylsilane, diphenylsilane, and triphenylsilane that the amount of methylenation is very sensitive to the degree of substitution of the silane. The decrease in yield, particularly between di- and tri-phenylsilane, is apparently not due to an electronic effect of the phenyl rings, since triethylsilane also gives a low yield.

Yields of methylenated products from silanes in diethyl ether.

	Monoinsertion	Di-insertion	Tri-insertion
Phenylsilane	70%	3%	Nil
Diphenylsilane	50%	Nil	—
Triphenylsilane	traces <0·1%	—	—
Triethylsilane	~1%	—	—

Phenylsilane reacts similarly with diazoethane. No insertion products are formed when a copper catalyst is used, but when the reaction mixture is photolysed ethylphenylsilane is formed. The reaction requires about ten hours for completion, the mixture being continuously purged with a slow stream of nitrogen. The yield of ethylphenylsilane (about 5%) is much lower than that of methylphenylsilane, and no diethylphenylsilane is formed even when a 2 : 1 molar excess of diazoethane is employed. The ethylphenylsilane was identified by comparing its residence time on a vapour-phase chromatogram with that of a reference sample, with silicone wax and dibutyl phthalate as stationary phases. The ethylphenylsilane was examined also by mass and infrared spectrometry, which confirmed its structure.

Two possible routes to the ethylphenylsilane must now be considered. The first, by insertion of ethylidene into an Si–H bond, is suggested by the reaction conditions and analogy with the methylene insertion reaction:

$$\mathrm{CH_3{\cdot}CHN_2 \longrightarrow CH_3{\cdot}CH\colon + N_2}$$
$$\mathrm{CH_3{\cdot}CH\colon + Ph{\cdot}SiH_3 \longrightarrow PhEtSiH_2}$$

The photolysis of diazoethane in the gas phase has been shown to give ethylidene initially, and thence ethylene and but-2-ene.[8] A recent investigation confirmed this [9] and showed that ethylidene can add to propene to give *cis*- and *trans*-1,2-dimethylcyclopropane. However, there was no evidence of insertion reactions with saturated hydrocarbons,[9] and we similarly obtained no products from reaction with the solvent.

A second suggested mechanism for the formation of ethylphenylsilane is the addition of phenylsilane to the ethylene formed from the diazoethane through rearrangement of ethylidene. Since ethylene is a major product ($>30\%$) of the diazoethane photolysis under these conditions, this mechanism was initially favoured. However, no ethylphenylsilane was formed when a similar experiment was carried out without diazoethane but under 30 cm. partial pressure of gaseous ethylene. Since this result could be due to the absence of a free-radical initiator, the experiment was repeated with ^{14}C-labelled ethylene at an initial partial pressure of 7 cm. and about one-tenth of the diazoethane used previously. Ethylphenylsilane was then formed, but in a yield ($\sim 0{\cdot}5\%$) decreased roughly in proportion to the decrease in diazoethane concentration. The total ^{14}C-activity of the silane fraction corresponded to $<0{\cdot}1\%$ yield (all the activity being assumed to be due to $PhEtSiH_2$). However, analysis of this fraction, on a vapour-phase chromatogram fitted with dual hot-wire katharometer and ^{14}C-activity detectors, showed that this activity was not associated with the ethylphenylsilane. This, therefore, appears to be the first well-established example of ethylidene insertion.

Extension of these insertion reactions to diazoacetic ester apparently gave insertion products from both phenylsilane and diphenylsilane (presumably $Ph{\cdot}SiH_2{\cdot}CH_2{\cdot}CO_2Et$ and $Ph_2SiH{\cdot}CH_2{\cdot}CO_2Et$, respectively), but the products were not isolated in high purity and their structures were not rigorously proved. No reaction occurred on mixing of the silanes with diazoacetic ester, but use of ultraviolet irradiation or a copper catalyst gave reactions with about 20% yield of the insertion product in each case. The absence of such silane products when phenylsilane was treated with diphenyldiazomethane and 9-diazofluorene is therefore significant; copper powder as catalyst gave only benzophenone azine and difluorenylidene, respectively, in high yields.

Under the same conditions, a series of trisubstituted germanes gave methyl derivatives in the following yields:

Hydride	Product	Yield (%)
Et_3GeH	Et_3GeMe	9
$Pr^n{}_3GeH$	$Pr^n{}_3GeMe$	5
$Bu^n{}_3GeH$	$Bu^n{}_3GeMe$	2
Ph_3GeH	No reaction	—

The decrease in the yields of methylenation product with the increased size of the substituent groups can be interpreted as being due to steric shielding of the GeH group. However, the yields also suggest that trisubstituted germanes react more readily than the corresponding silanes. Lesbre and Buisson [7a] showed that trialkylstannanes are methylenated by diazomethane in the presence of copper powder, but they did not state the yields. In our experience, triethylstannane is the most readily alkylated of the series of triethyl hydrides. The corresponding yields are: $SiEt_3Me$, 1%; $GeEt_3Me$, 9%; and $SnEt_3Me$, 75%. Methylenation of trimethylstannane with a copper catalyst appears to give lower yields of methylenated material. Thus trimethylstannane gave tetramethylstannane in only 30% yield. These variations also are likely to be of steric origin, since there are no large differences in the electronegativity or chemical behaviour among the central atoms in these compounds, but there is a progressive increase in the atomic radii.

EXPERIMENTAL

Diazomethane was prepared in ether from methylnitrosourea.[10] Solutions in other solvents were prepared by blowing diazomethane from a reaction mixture containing 50% aqueous

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[8] Brinton and Volman, *J. Chem. Phys.*, 1951, **19**, 1394.

[9] Frey, *J.*, 1962, 2293.

[10] Arndt, *Org. Synth.*, 1947, Coll. Vol. II, p. 165.

potassium hydroxide and some decalin through a 12″ Vigreux column into a cold trap containing the required solvent. The solutions were dried with potassium hydroxide before standardization.[5]

Diazoethane was prepared by the action of sodium cyclohexyl oxide on 4-(*N*-ethyl-*N*-nitrosoamino)-4-methylpentan-2-one,[11] and was standardized similarly.

Diazoacetic ester was prepared by diazotization of glycine ester hydrochloride [12] and redistilled before use.

Phenylsilane, diphenylsilane, triphenylsilane, and triethylsilane were prepared by published syntheses.[13] The trisubstituted germanes and stannanes were prepared by the reduction of the corresponding bromides with lithium aluminium hydride.

Attempted Reaction with Silane.—Silane, prepared by the reduction of silicon tetrachloride (0·05 mole) with lithium aluminium hydride in ether, was mixed with nitrogen and passed through a trap at $-80°$ to remove any halogenosilanes and then into a diazomethane solution (0·273 mole in 450 ml. of ether) stirred at $-75°$. There was no change in the normality of the diazomethane after 16 hours' stirring and vapour-phase chromatography did not show the formation of any new component.

Photolysis.—The photochemical reactions were carried out in a cylindrical Pyrex vessel. A Hanau mercury lamp cooled with water was placed centrally, in a silica tube. In a typical experiment, 10 g. (0·09 mole) of phenylsilane were dissolved in 460 ml. of 0·348M-diazomethane solution under nitrogen, and the whole placed in the outer jacket of the apparatus. A slow stream of nitrogen was passed through the mixture throughout the photolysis to remove traces of oxygen and photolysis products. The reaction was complete in about 10 hr. In order to analyse the products, the solvent in the reaction mixture was removed through a short distillation column, and the residue examined on a vapour-phase chromatograph, with 6 ft. × 0·25 in. glass columns, packed with E 301 Silicone wax or dibutyl phthalate supported on Celite and fitted with a hot-wire katharometer. It was assumed that the peak area on the recorder was proportional to the contents of starting material and products. These fractions were then analysed by mass spectrometry in a modified Metropolitan-Vickers MS2 mass spectrometer, which in all cases gave well-defined parent peaks due to the methyl compounds.

Owing to the small yields of methylenated materials obtained in many of the experiments, it was usually not possible to obtain pure samples for analysis. However, methylphenylsilane was obtained pure by fractional distillation and had b. p. 120°/730 mm. (lit.,[14] 53°/30 mm.), n_D^{25} 1·504 (lit., n_D^{25} 1·505) (Found: C, 68·5; H, 8·6. Calc. for $C_7H_{10}Si$: C, 68·8; H, 8·3%), as was methyldiphenylsilane, b. p. 88—90°/0·3 mm. (lit.,[15] 93·5°/1 mm.), n_D^{20} 1·5713 (lit., n_D^{20} 1·5717). Ethylphenylsilane was identified by comparing its residence times on a vapour-phase chromatograph with that of a reference sample, prepared from bromophenylsilane and ethylmagnesium bromide.[14]

The methyl compounds from the germane methylenations gave well-defined peaks in the mass spectrometer at the expected mass numbers. In addition, triethylmethylgermane was prepared independently from triethylgermanium bromide and methylmagnesium iodide, in 77% yield, with the same b. p. (135°) and refractive index (n_D^{20} 1·4332) as the sample prepared by Lesbre and Mazerolles.[16] This material had the same residence times as the sample prepared by methylenation.

Tetramethyltin, from trimethylstannane and diazomethane, had residence times identical with those of a reference sample prepared from tin tetrachloride and methylmagnesium iodide. Triethylmethyltin, from the methylenation of triethylstannane, had the expected b. p. (159°/745 mm.) and refractive index (n_D^{20} 1·4656),[17] and microanalysis was in approximate agreement (Found: C, 38·7; H, 8·6. Calc. for $C_7H_{18}Sn$: C, 38·1; H, 8·2%).

Diazoacetic ester reacted with phenylsilane in ether, on irradiation with ultraviolet light, to give an organosilicon ester, b. p. 116—118°/15 mm., in 27% yield (Found: C, 59·2; H, 7·6. Calc. for $C_{10}H_{14}O_2Si$: C, 61·8; H, 7·3%). With a copper powder catalyst an identical material was obtained. Diphenylsilane also reacted under both conditions, to give an organosilicon

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[11] Adamson and Kenner, *J.*, 1937, 1551.

[12] Gattermann–Wieland, " Die Praxis des organischen Chemikers," De Gruyter, Berlin, 1954, p. 241.

[13] Eaborn, " Organosilicon Compounds," Butterworths, London, 1960.

[14] Harvey, Nebergall, and Peake, *J. Amer. Chem. Soc.*, 1954, **76**, 4555.

[15] Mironov and Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1957, 383.

[16] Lesbre and Mazerolles, *Compt. rend.*, 1958, **246**, 1708.

[17] Luijten and van der Kerk, Tin Research Institute, Middlesex, England, 1952.

ester, b. p. 110—115°/0·03 mm., in 20% yield (Found: C, 74·5; H, 6·5; Si, 10·9. Calc. for $C_{16}H_{18}O_2Si$: C, 71·1; H, 6·7; Si, 10·4%). The results are summarized in the annexed Table.

Starting material	Amount of hydride (g.)	Amount of hydride (mole)	Amount of diazomethane (mole)	Product	Yield (%)
$Ph{\cdot}SiH_3$	5·0	0·046	0·16	$PhMeSiH_2$	70
				$PhMe_2SiH$	5
Ph_2SiH_2	8·0	0·043	0·23	Ph_2MeSiH	50
Ph_3SiH	4·0	0·015	0·11	Ph_3MeSi	<0·1
Et_3SiH	7·8	0·067	0·20	Et_3MeSi	1
Et_3GeH	7·5	0·047	0·10	Et_3MeGe	9
$Pr^n{}_3GeH$	6·6	0·033	0·12	$Pr^n{}_3MeGe$	5
$Bu^n{}_3GeH$	6·0	0·025	0·08	$Bu^n{}_3MeGe$	2
Me_3SnH	25·0	0·150	0·19	Me_4Sn	30
Et_3SnH	9·0	0·044	0·18	Et_3MeSn	75

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