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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

XXVI*. PREPARATION OF SOME SILYLATED ALLENES CONTAINING FUNCTIONAL GROUPS FROM HEXACHLOROPROPENE

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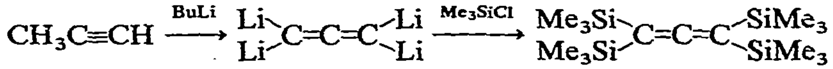
SUMMARY

The reaction of hexachloropropene with magnesium and some chlorosilanes containing Si–H groups is described, producing persilylated allenes containing Si–H groups intact.

As part of a general study on the preparation of unsaturated silicon compounds from polyhalogenated compounds, tetrakis(trimethylsilyl)allene has been prepared from a variety of polyhalogenated compounds (aliphatic, aromatic and heterocyclic), lithium (or magnesium) and chlorotrimethylsilane[1-5]. In another approach tetrakis(trichlorosilyl)allene[6] was treated with methyllithium[7]. This compound had been previously prepared by West and co-workers from the tetralithium derivative of propyne[8], a compound which may be tetralithioallene[9].



$$CH_3C{\equiv}CH \xrightarrow{BuLi} Li_2C{=}C{=}CLi_2 \xrightarrow{Me_3SiCl} (Me_3Si)_2C{=}C{=}C(SiMe_3)_2$$

Hexabromobenzene, similarly to hexachlorobenzene[1,2], gave rise to the tetrakis(trimethylsilyl)allene on treatment with lithium and chlorotrimethylsilane in THF[4]. In contrast hexafluorobenzene failed to give the "allene" under these conditions[1,2]. Treatment of hexabromobenzene with magnesium and chlorodimethylsilane under similar conditions failed to give the corresponding silylated allene, giving instead a 27% yield of hexakis(dimethylsilyl)benzene[4].

$$C_6Br_6 + 12\ HMe_2SiCl + 12\ Mg \rightarrow C_6(HMe_2Si)_6$$

In connection with the preparation of silicon compounds containing functional groups (such as Si–H, Si–Cl) which could lead to thermally stable polymeric species it was of interest to try and prepare silylated allenes containing functional groups. The formation of such compounds has not been observed in our experiments using lithium (or magnesium) and a polyhalo-aromatic compound together with the respective chlorosilane in THF.

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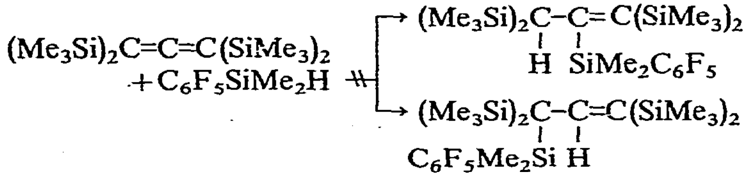
* For Part XXV see ref. 14.

Interaction of chlorodimethylsilane, chloromethylphenylsilane or chlorodiphenylsilane in an *in situ* reaction with magnesium and hexachloropropene gave yields of up to 56% of the corresponding persilylated allene. Using magnesium/chlorosilane/hexachloropropene ratio of 10:5:1 had little or no effect on the yield of product obtained.

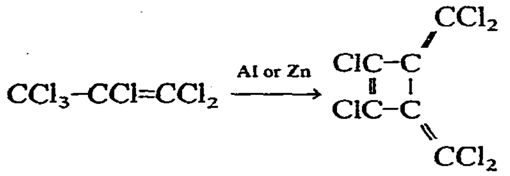
$$CCl_3{-}CCl{=}CCl_2 + 10\ PhMeSiHCl + 20\ Mg \xrightarrow[THF]{25°} (PhMeHSi)_2C{=}C{=}C(SiHMePh)_2\ (33\%)$$

Such compounds are of interest because of the presence of 4 reactive Si–H groups which, in the presence of a catalyst, are known to add across the unsaturated linkage in such compounds as olefins and acetylenes. A possibility could be addition of RR'SiH groups across the olefinic linkage of another molecule of the silylated allene thus giving rise to polymeric materials. However, tetrakis(trimethylsilyl)allene does not react with (pentafluorophenyl)dimethylsilane using hexachloroplatinic acid as catalyst, and this may be due primarily to steric factors[10].



$$(Me_3Si)_2C{=}C{=}C(SiMe_3)_2 + C_6F_5SiMe_2H \not\rightarrow \begin{cases} (Me_3Si)_2\underset{H}{C}{-}\underset{SiMe_2C_6F_5}{C}{=}C(SiMe_3)_2 \\ (Me_3Si)_2\underset{C_6F_5Me_2Si}{C}{-}\underset{H}{C}{=}C(SiMe_3)_2 \end{cases}$$

The formation of the persilylated allene can be attributed, in a simple manner, to one of two explanations. In the first case reduction of the hexachloropropene to tetrachloroallene could take place. The interaction of hexachloropropene with certain metals such as aluminum and zinc in THF or ether gave rise to perchloro(3,4-dimethylene)cyclobutene in good yields[5,11]. This compound has been described by



Roedig[12] as resulting from the interaction of tetrachloroallene dimer [perchloro-(1,2-dimethylene)cyclobutane], which is easily formed by dimerisation of tetrachloroallene at room temperature, and aluminum in the presence of aluminum trichloride.

It is possible therefore that tetrachloroallene monomer could react immediately with, for example, dimethylsilylmagnesium chloride formed as a transient intermediate from chlorodimethylsilane and magnesium:

$$4\ HMe_2SiMgBr + Cl_2C{=}C{=}CCl_2 \rightarrow (HMe_2Si)_2C{=}C{=}C(SiMe_2H)_2$$

Alternatively, reduction of the hexachloropropene could proceed to the unknown Grignard equivalent of tetralithioallene followed by coupling with chlorodimethylsilane. However, whether the reaction proceeds via an acetylene–allene rearrangement as envisaged by West[8] is not known. It is possible that the chlorine atoms of the CCl_3

$$(ClMg)_2C{=}C{=}C(MgCl)_2 + 4\ HMe_2SiCl \rightarrow (HMe_2Si)_2C{=}C{=}C(SiMe_2H)_2$$

are preferentially attacked as interaction of hexachloropropene with copper bronze gives, under suitable conditions, simple coupling producing decachloro-1,5-hexadiene[13].

Another possible reaction scheme could be by stepwise substitution of dimethylsilyl groups with reduction at some later stage of the reaction.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. THF was dried over sodium and freshly distilled from sodium benzophenone ketyl before use. Molecular weights were determined by mass spectrometry. Melting points are uncorrected. Hexachloropropene (technical grade) was used as purification had little effect on the yield of product obtained.

Tetrakis(dimethylsilyl)allene

Hexachloropropene (12.44 g, 0.05 mole) dissolved in THF (50 ml) was added during 12 h to a vigorously stirred mixture of chlorodimethylsilane (23.66 g, 0.25 mole) and magnesium (12.16 g, 0.5 g-atom) in THF (150 ml) at 0°. There was a prompt exothermic reaction with darkening of the solution and the precipitation of much magnesium chloride. After a further 6 h unreacted magnesium was removed and the product hydrolysed in 2 *N* hydrochloric acid and extracted with ether. Drying of the ethereal layer (magnesium sulfate) and removal of the volatiles using a rotary evaporator gave a yellow oil. Fractional distillation of this oil using a Nester–Faust spinning-band column gave tetrakis(dimethylsilyl)allene, b.p. 110–111°/17 mm, n_D^{20} 1.4750, 7.62 g, 56%. (Found: C, 48.2; H, 9.8, mol.wt. 272. $C_{11}H_{28}Si_4$ calcd.: C, 48.4; H, 10.3%, mol.wt. 272.) The IR spectrum showed the following characteristic absorptions: Si–H, 2127 cm^{-1} s; C=C=C, 1890 cm^{-1} s; Si–Me, 1250 cm^{-1} s.

Tetrakis(methylphenylsilyl)allene

Hexachloropropene (12.44 g, 0.05 mole) in THF (50 ml) was added during 12 h to a vigorously stirred mixture of chloromethylphenylsilane (78.35 g, 0.5 mole) and magnesium (24.32 g, 1 g-atom) in THF (150 ml) at 25°. An exothermic reaction promptly occurred with darkening of the solution and precipitation of a large quantity of magnesium chloride. After a further 12 h vigorous stirring the system was worked up as before to yield a brown oil. Fractional distillation afforded 1,3-dimethyl-1,3-diphenyldisiloxane, b.p. 90–98°/0.12 mm. Further distillation yielded tetrakis(methylphenylsilyl)allene, b.p. 142–144°/0.12 mm, n_D^{20} 1.5979, 8.60 g, 33%, as a syrupy very pale yellow oil. (Found: C, 71.3; H, 6.75, mol.wt. 520. $C_{31}H_{36}Si_4$ calcd.: C, 71.45; H, 6.92%, mol.wt. 520.) The IR spectrum showed the following characteristic absorptions: Si–H, 2116 cm^{-1} s; C=C=C, 1879 cm^{-1} s; Si–Ph, 1425 cm^{-1} s; Si–Me, 1245 cm^{-1} s.

Tetrakis(diphenylsilyl)allene

Hexachloropropene (24.88 g, 0.1 mole) dissolved in THF (60 ml) was added dropwise during 4 h to a vigorously stirred mixture of chlorodiphenylsilane (218.76 g, 1 mole) and magnesium (48.64 g, 2 g-atom) in THF (350 ml) at 25°. An exothermic reaction occurred with the usual darkening of the system and the separation of much magnesium chloride. After stirring vigorously for 13.5 h and allowing to stand for 32 h the usual work up gave a dark viscous oil. On distillation a fraction b.p. 138–177°/0.1 mm was isolated as a syrupy viscous liquid, containing by VPC mainly 1,1,3,3-tetraphenyldisiloxane; the IR spectrum of this fraction showed no allenic absorption. The still-pot residue crystallised as a dark sticky solid and, after attempts at recrystallisation from petroleum ether (60–70°) did not yield a pure product; chromatography using neutral alumina and petroleum ether (60–70°) as eluent gave tetrakis(diphenylsilyl)allene, m.p. 85–86°, 9.2 g, 12%, as fine white crystals. (Found: C, 79.62; H, 5.00. $C_{51}H_{44}Si_4$ calcd.: C, 79.65; H, 5.75%.) The IR spectrum showed the following absorptions: Si–H, 2127 cm^{-1} s; C=C=C, 1878 cm^{-1} vs; Si–Ph, 1425 cm^{-1} s.

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