

NOTE

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

XVII*. FORMATION OF TETRAKIS(TRIMETHYLSILYL)ALLENE FROM SOME ALIPHATIC POLYCHLORO COMPOUNDS

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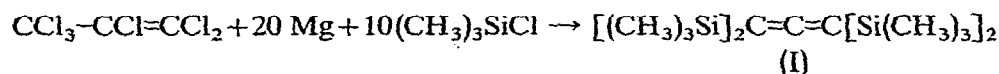
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(Received October 12th, 1967)

As part of our studies on thermally stable organosilicon compounds we have recently reported the production of tetrakis(trimethylsilyl)allene (I) in 30–52 % yields from the interaction of hexachlorobenzene, (trimethylsilyl)pentachlorobenzene or 1,4-bis(trimethylsilyl)tetrachlorobenzene with a liberal excess of chlorotrimethylsilane and lithium in tetrahydrofuran¹. This compound was prepared previously by West, Carney, and Mineo² from the tetralithium derivative of propyne. Tetrakis(trimethylsilyl)allene was also prepared from bromopentafluorobenzene, chloropentafluorobenzene, (trimethylsilyl)pentafluorobenzene and 1,4-bis(trimethylsilyl)-tetrafluorobenzene when treated under the above conditions, but in low yields³. In marked contrast, hexafluorobenzene did not react under similar conditions.

(I) has also been prepared by the interaction of tetrakis(trichlorosilyl)allene⁴ and methyllithium⁵.

In an extension of the studies on highly halogenated types we have found that hexachloropropene reacts with a liberal excess of chlorotrimethylsilane and lithium or magnesium at room temperature to give 37–42 % and 41–52 % yields of (I), respectively; at 0° a 65 % yield of (I) was obtained from hexachloropropene, chlorotrimethylsilane and magnesium.



Experiments under similar conditions with different metals with a view to effecting selective reactions have been less rewarding. Sodium and barium only form a trace of (I) whereas aluminum, zinc and beryllium do not react to give (I). In addition interaction of hexachloro-1,3-butadiene with chlorotrimethylsilane and lithium under similar conditions gives a large quantity of a hitherto unidentified solid (II) m.p. 276–277° which infrared spectroscopy shows to contain Si–Me groups but no allenic group; however, a small, but significant, amount of (I) is isolated as a byproduct.



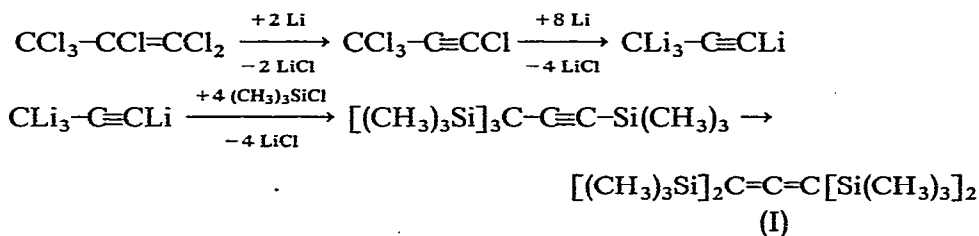
* For Part XVI see ref. 6.

Extension of the work from unsaturated to saturated aliphatic compounds gives an interesting result. Interaction of octachloropropane, chlorotrimethylsilane and magnesium under similar conditions at room temperature resulted in the formation of (I) in 56 % yield.

In an attempt to gain information about the course of reaction, hexachloropropene and magnesium were reacted at room temperature to give a dark brown liquid which contained no unreacted hexachloropropene. On addition of chlorotrimethylsilane, in this two-stage reaction, and subsequent work-up, none of (I) was detected.

In a typical reaction hexachloropropene (0.025 mole) dissolved in THF (25 ml) was added dropwise during two hours to a vigorously stirring mixture of magnesium (0.5 g-atom) and chlorotrimethylsilane (0.25 mole) dissolved in THF (140 ml). An exothermic reaction occurred. Stirring was continued for 19 hours and the product then filtered from unreacted magnesium and the filtrate hydrolysed in dilute hydrochloric acid and extracted with diethyl ether. Removal of the volatiles gave a residue of a brown oil which was fractionally distilled to give tetrakis(trimethylsilyl)allene (4.25 g) b.p. 69–70°/0.2 mm, n_D^{20} 1.4770. Yield (based on the hexachloropropene) 52%.

Possible reaction schemes being considered include initial reduction of the hexachloropropene by the metal to a chloro-alkyne or chloro-allene which in the presence of more metal could form a monometallic intermediate. This then might react stepwise with chlorotrimethylsilane with subsequent metalation, or the initial production of a polymetallic² species which could immediately react with the chlorotrimethylsilane, to give (I).



ACKNOWLEDGEMENT

This research was supported by the United States Air Force under Contract AF 33(615)2368 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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