

FORMATION OF SILYLATED ALLENES FROM SOME PERHALOGENATED HYDROCARBONS

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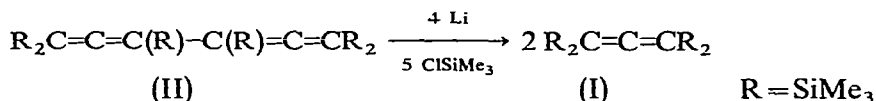
SUMMARY

The preparation of tetrakis(trimethylsilyl)allene and related compounds from cyclic halocarbons via *in situ* reactions with lithium or magnesium and chlorotrimethylsilane is described. Similar results are obtained using straight chain chloroalkenes. 1,1,3,4,6,6-Hexakis(trimethylsilyl)-1,2,4,5-hexatetraene is formed in many of these reactions, and can be converted by lithium and chlorotrimethylsilane to tetrakis(trimethylsilyl)allene. This conversion is of particular significance as it points to the novel tetraene as an important intermediate in some of the reactions.

A general study of the *in situ* coupling reactions of polyhalogenated hydrocarbons, metals and chlorotrimethylsilane has afforded tetrakis(trimethylsilyl)allene (I)^{1,2} from a number of different halocarbons³⁻⁷. Other silanes containing functional groups have given similar results⁸.

In a preliminary note⁵ we have described the formation of a "dimer" of (I), 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (II) from the *in situ* reaction of hexabromobenzene with a large excess of magnesium and chlorotrimethylsilane in tetrahydrofuran (THF). The yields of (II) in the above and related reactions using polychlorinated benzenes are low but extension of the work to aliphatic chlorocarbons afforded yields of up to 30% (Table 1).

The novel tetraene (II) is of particular interest in our reactions as it is easily cleaved by lithium (but not magnesium) and chlorotrimethylsilane in THF. This facile cleavage could account for the absence of (II) in reactions using lithium and points to the tetraene as an important intermediate in our systems.



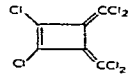
Decachloro-1,5-hexadiene afforded a 37% yield of the allene (I) in an *in situ*

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TABLE I

TRIMETHYLSILYLATION OF SOME ALIPHATIC AND ALCYCLIC CHLOROCARBONS AT 0° IN THF

Chlorocarbon	Metal	Yields (%)	
		(I) ^a	(II)
CCl ₂ =CCl-CCl ₂ -CCl ₂ -CCl=CCl ₂	Li	37	0
	Mg	0	28
CCl ₂ =CCl-CCl=CCl-CCl=CCl ₂	Li	61	0
	Li	32	0
	Mg	0	22

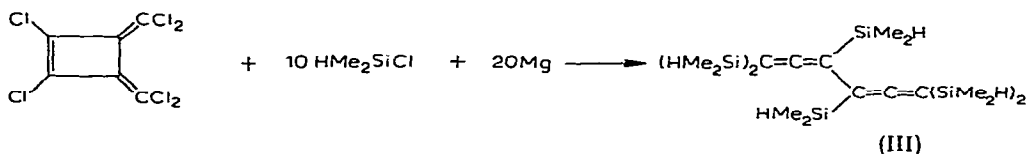
^a Yield of (I) calculated on basis of chlorocarbon (1 mole)→(I) (2 moles).

reaction with lithium; whereas the corresponding reaction using magnesium gave the tetraene (II) in 28% yield and none of (I). The reaction could be interpreted in a simple manner, by initial dechlorination to a 1,2,4,5-hexatetraene followed by Wurtz-Fittig coupling which would, in the case of magnesium, lead to the hexatetraene (II). In another route, dechlorination of decachloro-1,5-hexadiene to a 1,5-diyne could occur; such a scheme would involve an acetylene-allene rearrangement¹⁰ at some stage. The reaction using lithium may proceed by a similar scheme since (II) is easily cleaved to give (I).

Octachloro-1,3,5-hexatriene afforded (I) in 61% yield in a similar reaction with lithium and the chlorosilane. A rearrangement presumably occurs in this reaction as the production of (I) directly from the triene involves rupture of a double bond. Previous experiments^{6,7,11} have clearly demonstrated that rearrangements are a common feature of this type of system. The reaction may proceed by initial dechlorination and subsequent rearrangement to a 2,4-diyne, a structure more easily cleaved at the 3-position by lithium and chlorotrimethylsilane. The diyne could then undergo an acetylene-allene isomerisation. Such a scheme would allow for the production of (I) from octachloro-1,3,5-hexatriene via (II).

In an extension of the work to alicyclic systems 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene, produced by reaction of hexachloropropene with aluminum in THF, afforded (I) with lithium and chlorotrimethylsilane and (II) in the magnesium reaction. The simplest explanation for the production of (II) is via rupture of the ring between the 3- and 4-position *i.e.* between the exocyclic double bonds as ring rupture at other positions produces carbon atoms in a side chain. An extensive rearrangement must occur although we are not certain at which stage of the reaction this happens. Attempts to isolate any other reaction products, particularly cyclic species, have been unsuccessful.

In a similar manner 1,1,3,4,6,6-hexakis(dimethylsilyl)-1,2,4,5-hexatetraene (III) was produced by the reaction of 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene with an excess of magnesium and chlorodimethylsilane in THF. In contrast to the trimethylsilyl compound (II) the tetraene (III) did not undergo simple cleavage to tetrakis(dimethylsilyl)allene⁸ when reacted with lithium and chlorodimethylsilane. Instead, several types containing siloxane linkages (presumably



via attack at the Si-H bond and subsequent hydrolysis of a reactive species on work-up have been obtained.

Extensive carbon-carbon cleavage occurred when hexachlorocyclopentadiene and octachlorocyclopentene were tested under similar conditions with lithium and chlorotrimethylsilane. The former gave at least 20 components (by VPC). The infrared spectra of the products revealed no allenic absorption at $\sim 1880 \text{ cm}^{-1}$ characteristic of (I) and (II).

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. Lithium metal used contained 1% sodium.

Decachloro-1,5-hexadiene was prepared by the reaction of hexachloropropene with copper bronze¹². Octachloro-1,3,5-hexatriene was prepared by dechlorination of decachloro-1,5-hexadiene with alcoholic potassium hydroxide¹³. Hexachlorocyclopentadiene and octachlorocyclopentene were commercial products; 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene was synthesised from hexachloropropene and aluminum¹⁴ in THF⁷.

The general experimental procedure is illustrated by a few typical examples.

Hexabromobenzene, magnesium and chlorotrimethylsilane

A suspension of hexabromobenzene (27.6 g, 0.05 mole) in hexamethylphosphoric triamide (HMPT) (70 ml) was added with stirring to magnesium (24.3 g, 1 g-atom) and chlorotrimethylsilane (81.4 g, 0.75 mole) in HMPT (30 ml) at room temperature. A vigorous exothermic reaction occurred. After 12 h the mixture was filtered to remove magnesium. The filtrate was hydrolysed in dilute acid and extracted with ether. Drying (MgSO_4) of the ethereal layer and removal of the ether gave a dark semi-solid. Chromatography using an alumina column and petroleum ether (60–70°) as eluent afforded 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (II) as a colorless solid (2.6 g, 10%), m.p. 111–112° (from ethanol). The infrared spectrum of this product showed the characteristic allenic absorption at 1878 cm^{-1} . The ^1H NMR spectrum showed only SiCH_3 protons (two singlets; τ 9.84, 9.87, area ratio 2/1). The mass spectrum had a molecular ion 510, calcd. 510. (Found: C, 56.74; H, 10.28; Cl, 0; Si, 33.30. $\text{C}_{24}\text{H}_{54}\text{Si}_6$ calcd.: C, 56.46; H, 10.59; Cl, 0; Si, 32.94%.)

Cleavage of 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (II)

Lithium (0.084 g, 0.012 g-atom) was added to a solution of (II) (1.53 g, 0.003 mole) and chlorotrimethylsilane (1.6 g, 0.015 mole) in THF (25 ml). After stirring (15 min) at room temperature, VPC indicated the presence of the allene (I) in the mixture. After 6 h the normal work-up gave an oil which was distilled to afford (I) (1.3 g, 65%), b.p. 68–69°/0.15 mm (lit.¹ 69–70°/0.2 mm), n_D^{20} 1.4767 (lit.¹ 1.4770).

1,2-Dichloro-3,4-bis(dichloromethylene)cyclobutene, lithium and chlorotrimethylsilane

1,2-Dichloro-3,4-bis(dichloromethylene)cyclobutene (7.12 g, 0.025 mole) dissolved in THF (100 ml) was added dropwise (1½ h) to a vigorously stirred mixture of lithium (3.47 g, 0.5 g-atom) and chlorotrimethylsilane (27.15 g, 0.25 mole) in THF (150 ml) at 0°. A rapid exothermic reaction occurred with darkening and the precipitation of a solid. After 18 h the excess lithium was removed; the product was hydrolysed (2 N HCl) and extracted with ether. Drying of the ethereal layer (MgSO₄) and removal of volatiles gave a dark oil which on distillation afforded tetrakis(trimethylsilyl)-allene (I) (5.16 g, 31.5%), b.p. 66–68°/0.12 mm, n_D^{20} 1.4770.

1,2-Dichloro-3,4-bis(dichloromethylene)cyclobutene, magnesium and chlorodimethylsilane

1,2-Dichloro-3,4-bis(dichloromethylene)cyclobutene (14.24 g, 0.05 mole) dissolved in THF (100 ml) was added dropwise to a vigorously stirred mixture of magnesium (24.32 g, 1 g-atom) and chlorodimethylsilane (47.32 g, 0.5 mole) in THF (150 ml) at 0°. After initiation with a few drops of 1,2-dibromoethane, an exothermic reaction occurred, the system became dark in color and magnesium chloride was precipitated. The system was vigorously stirred at 0° for 18 h. Excess magnesium was removed and the products hydrolysed (2 N HCl). The organic products were extracted with ether, dried (MgSO₄) and volatile materials removed at 18 mm. The product, a dark oil, contained by VPC two main components and a number of minor components. A preliminary distillation afforded a number of fractions in the boiling range 95–145°/0.05 mm [containing 51–88% of the tetraene (III)]. Fractions in the boiling range 95–127°/0.05 mm [containing 83–88% of (III)] were combined and redistilled to give 1,1,3,4,6,6-hexakis(dimethylsilyl)-1,2,4,5-hexatetraene (III) (1.0 g, pure yield 4.7%), b.p. 114–116°/0.05 mm, n_D^{20} 1.5179, as a colorless viscous oil. The overall yield of (III) from VPC analysis of the preliminary distillation fractions was 33% (7.1 g). On standing at room temperature in the light, (III) became yellow and slowly decomposed; after 21 days a sample of (III) contained only 90% of the pure material; in the dark, decomposition was less pronounced. The infrared spectrum of (III) showed characteristic bands (cm⁻¹) for Si–H (2117), C=C=C (1896) and Si–Me (1245). The ¹H NMR spectrum of (III) (in CCl₄) showed SiMe (two superimposed doublets, τ 9.79–9.88) and SiH (multiplet, τ 5.65–5.95) protons in the integrated ratio 6/1 (calcd. ratio 6/1). (Found: C, 50.0, 50.2; H, 9.3, 9.4; mol. wt. by mass spectrum, 426. C₁₈H₄₂Si₆ calcd: C, 50.6; H, 9.9; mol. wt. 426.)

The other products of the reaction have not been separated but contain no characteristic allenic absorptions in the infrared spectrum.

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