The stereospecificity of the addition appears to involve the reacting groups entering from opposite sides of the molecule in which the two double bonds exist side by side in one conformation with which a concerted reaction could occur as indicated. In contrast, free-radical transannular cycloadditions to *cis,cis*-1,5-cyclooctadiene have been reported[6] to give yields up to 63% of *exo*-substituted *cis*-tricyclo[3.3.0]octanes which have configurations of the substituent groups relative to the *cis*-fused rings opposite from that of the presently reported novel ionic transannular cycloaddition to cyclodecadiene. X-Ray crystallographic studies are currently in progress on the substituted cyclodecadiene to determine the relative position of the two olefinic groups.

Other high-yield transannular cycloaddition reactions of this type of cyclodecadiene will be reported separately. The inactivity of the tetraethyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate toward conventional tests for olefinic groups including tetranitromethane is unusual and is exhibited by other similarly substituted 1,6-cyclodecadienes synthesized in this work. However, further investigation will be required to determine whether steric factors alone or in combination with interaction of the double bonds account for the inactivity.

This stereospecific transannular cycloaddition reaction also provides an experimental analogy to a hypothetical reaction scheme for sesquiterpene biogenesis involving proposed stereospecific double bond cyclizations.[7]

Acknowledgment. Two of the authors (H. W. G. and S. H. S.) are greatly indebted to the Robert A. Welch Foundation of Houston, Texas, for support of this investigation.

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The Formation of Tetrakis(trimethylsilyl)allene by an Unusual Reaction from Hexachlorobenzene and Some Derivatives

Sir:

Incidental to a study concerned with the preparation of monomers containing a polyhalophenyl group and other substituents such as silicon, we have noted[1] that polychlorobenzenes react with trimethylchlorosilane and lithium in tetrahydrofuran to give mono- and disilylated derivatives. With a view to the synthesis of compounds having a larger number of trimethylsilyl groups, hexachlorobenzene was treated with a liberal excess of trimethylchlorosilane and lithium. One of the products isolated contained no chlorine. Some of the physical constants were: bp 69–70° (0.2 mm), $n^{20}\text{D}$ 1.4770, $d^{20}{}_4$ 0.8322. The molecular weight by osmometry was 332 and 304, and by mass spectrography, 328. The compound appeared to be the highly unexpected tetrakis(trimethylsilyl)allene.

$$(\mathrm{Me_3Si})_2\mathrm{C{=}C{=}C(SiMe_3)_2}$$

This was supported by other analytical data: nmr, singlet at τ 9.78 (no other protons present); infrared, strong absorption at 1880 cm^{-1}. *Anal.* Calcd for $C_{15}H_{36}Si_4$; Si, 34.3; mol wt, 328; molar refraction, 111.4. Found: Si, 34.1, 34.4; mol wt, 328 (mass spectrum); molar refraction, 111.6.

The compound, which is colorless when freshly prepared but which turns light yellow on standing, reacted vigorously with bromine to give trimethylbromosilane.

Tetrakis(trimethylsilyl)allene was prepared previously in an elegant study by West, Carney, and Mineo[2] from the tetralithium derivative of propyne. Some arylated silicon allenes have been reported recently.[3] We have shown that our tetrakis(trimethylsilyl)allene has the same refractive index and retention time as a sample of the compound prepared previously.[4]

Some additional observations are made at this time relative to studies on mechanisms for the formation of the allene. Among mechanisms being considered are those involving precursory benzyne, dibenzyne, and to a lesser extent the carbenoid types,[5] as well as anion radicals. (1) As might have been expected, pentachlorophenyltrimethylsilane as well as 1,4-di(trimethylsilyl)-tetrachlorobenzene give on treatment with an excess of trimethylchlorosilane and lithium in THF the tetrakis(trimethylsilyl)allene. (2) The yield of allene starting with 1,4-di(trimethylsilyl)tetrachlorobenzene was in *excess* of 50%. (3) The formation of the allene is rapid, as evidenced by its detection (vpc) when a first aliquot was removed at the end of 5 min from the reaction starting with pentachlorophenyltrimethylsilane and also with 1,4-di(trimethylsilyl)tetrachlorobenzene.

The allene is not formed to any significant extent from hexafluorobenzene under the corresponding conditions used with hexachlorobenzene. Studies are being extended to a variety of polyhalogenated compounds, including homocyclic and heterocyclic types, and with trapping agents in addition to the organosilicon compounds.

Acknowledgments. This research, concerned with thermally stable compounds, was supported in part by the U. S. Air Force under Contact AF 33(615)-2368 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The authors are grateful to Dr. Thomas H. Kinstle and Robert L. Harrell, Jr., for assistance.

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Received August 31, 1966