771. *Addition of Silicon Hydrides to Cyclic Olefins. Part II.*[1] *Cyclo-octa-*1,3,5,7*-tetraene.*

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Addition of trichlorosilane, triethylsilane, or diethylsilane to cyclo-octa-1,3,5,7-tetraene under various conditions led to a variety of products. The mode of addition depends in part upon the nature of the silane. The ethylsilanes, in the formation of monosubstituted derivatives, react by 1,4-addition, but trichlorosilane gave predominantly the 1,2-addition product.

PART I of this series [1] dealt with the addition of silicon hydrides to cyclo-octene and cyclo-octa-1,5-diene. The present paper reports the addition of trichlorosilane, diethylsilane, and triethylsilane to cyclo-octa-1,3,5,7-tetraene. Platinum on γ-alumina [2] was used as the catalyst throughout. Since a multiolefinic reactant was employed, the products were mixtures in most cases. At present, the major emphasis has been directed toward the elucidation of the structures of the monosubstituted derivatives. The structures to be assigned to the disubstituted derivatives reported in this work are to be published later when confirmation has been obtained by alternative syntheses.

Addition of trichlorosilane to cyclo-octa-1,3,5,7-tetraene resulted in formation of a trichlorosilylcyclo-octatriene (I) (as determined by chlorine analysis) that with ethylmagnesium bromide gave 7-triethylsilylcyclo-octa-1,3,5-triene (II). The assignment of structure (II) was based on several observations. First, the ultraviolet spectrum of this material ($\lambda_{\text{max.}}$ 263, $\lambda_{\text{min.}}$ 233 mμ) was similar to that obtained by Cope and his co-workers [3] for cyclo-octa-1,3,5-triene ($\lambda_{\text{max.}}$ 265, $\lambda_{\text{min.}}$ 225 mμ), and also similar to that of what in all likelihood was 7-s-butylcyclo-octa-1,3,5-triene.[4] Secondly, the infrared absorption spectrum supported a conjugated-triene structure, by the fact that a triplet was observed in the 1600—1560 cm.$^{-1}$ range. Catalytic hydrogenation reduced 7-triethylsilylcyclo-octa-1,3,5-triene (II) to triethylsilylcyclo-octane (V), as shown by a comparison of the refractive index and infrared spectrum with those of an authentic sample.[1] This reduction supported the skeletal structure of the triene.

An independent synthesis further supported the structure of the triene. This route, described by Cope and Estes,[5] involved allylic bromination of 5-triethylsilylcyclo-octene[1] (IV) to yield an intermediate 3,8-dibromo-5-triethylsilylcyclo-octene that was dehydrohalogenated, without isolation, in the presence of potassium t-butoxide. The purified product was identical with our product (II) in physical properties and infrared and ultraviolet spectra.

Addition of triethylsilane to cyclo-octa-1,3,5,7-tetraene resulted in several products, the number and type of which depended upon the conditions. Reaction at 170° for three days under autogenous pressure, gave compounds (III) and (VI), along with other materials not investigated further. Analyses, in conjunction with infrared and ultraviolet absorption spectra, favoured 5-triethylsilylcyclo-octa-1,3,6-triene as the structure for (III). In particular, the ultraviolet spectrum was in close agreement with one obtained by Cope and Hochstein [6] for the unsubstituted cyclo-octa-1,3,6-triene. Supporting evidence was obtained by isomerisation of 5-triethylsilylcyclo-octa-1,3,6-triene (III) to 7-triethylsilylcyclo-octa-1,3,5-triene (II) by potassium t-butoxide—Cope and Hochstein [6] previously isomerised cyclo-octa-1,3,6-triene to the 1,3,5-isomer in this way.

Elemental analysis of compound (VI) supported none of the structures involving simple addition. Since trialkylsilanes may decompose thermally, it would not be unreasonable to consider that disproportionation of triethylsilane might have resulted in the formation

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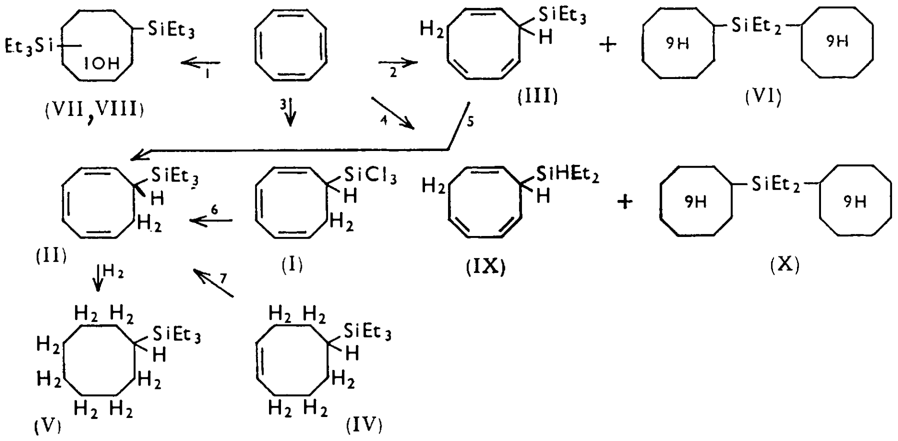
[1] Part I, Pike and McDonagh, *J.*, 1963, 2831.
[2] Wagner and Whitehead, U.S.P. 2,851,473/1958.
[4] Cope, Haven, jun., Ramp, and Trumbull, *J. Amer. Chem. Soc.*, 1952, **74**, 4867.
[5] Cope and Van Orden, *J. Amer. Chem. Soc.*, 1952, **74**, 168.
[6] Cope and Estes, jun., *J. Amer. Chem. Soc.*, 1950, **72**, 1129.

of diethylsilane.[7] This diethylsilane could have added to cyclo-octa-1,3,5,7-tetraene in a 1 : 2 molar ratio to give a di(cyclo-octatrienyl)diethylsilane (VI). Silicon analysis and a molecular-weight determination support this assignment. An attempt to prepare compound (VI) directly by addition of freshly prepared diethylsilane to cyclo-octa-1,3,5,7-tetraene gave several products. The lower-boiling fraction was assigned the structure 5-diethylsilylcyclo-octa-1,3,6-triene (IX) from its analysis and infrared and ultraviolet spectra. Attempts to hydrogenate it were complicated by what appeared to be destruction of the Si–H linkage (absence of the Si–H stretching vibration in the spectrum of the "reduced" material). The higher-boiling fraction from this run is a di(cyclo-octatrienyl)-diethylsilane (X). The infrared and ultraviolet absorption spectra of materials (VI) and (X) showed considerable similarity but were not identical. Further work must be carried out to establish the structures of these compounds, but from the present information they may be considered as isomeric di(cyclo-octatrienyl)diethylsilanes.



For compounds where the position of double bonds is unspecified, the number of hydrogen atoms attached to the ring is indicated inside the ring.

Reagents: 1, $SiHEt_3$ (2 mol.). 2, $SiHEt_3$ (1 mol.). 3, $SiHCl_3$. 4, SiH_2Et_2. 5. Bu^tOK. 6, MgEtBr. 7, $(CH_2 \cdot CO)_2NBr$, then Bu^tOK.

When a 2 : 1 molar ratio of triethylsilane to cyclo-octa-1,3,5,7-tetraene was employed, two liquid products, (VII) and (VIII), were obtained. Elemental analysis indicated each as a bistriethylsilylcyclo-octadiene. The infrared spectra indicated conjugated unsaturation for (VII) and an unconjugated system for (VIII). It is possible to form derivatives of this type by two 1,2-, two 1,4-, or a 1,2- and a 1,4-addition of the silane to the cyclo-octatetraene. The olefinic linkages in these compounds (VII) and (VIII) cannot be located with certainty on the present evidence.

EXPERIMENTAL

7-*Trichlorosilylcyclo-octa*-1,3,5-*triene* (I).—In a stainless-steel rocking autoclave were placed freshly distilled trichlorosilane (13·55 g., 0·1 mole), cyclo-octa-1,3,5,7-tetraene (11·0 g., 0·1 mole), and platinum–γ-alumina (0·1 g.). The autoclave was flushed with dry nitrogen, sealed, and heated with rocking at 200° for 3 hr. After cooling, the dark material was removed and distilled under reduced pressure. The main fraction, colourless 7-*trichlorosilylcyclo-octa*-1,3,5-*triene*, had b. p. 80—120°/0·2 mm. (8·0 g., 33%) (Found: Cl, 44·0. $C_8H_9Cl_3Si$ requires Cl, 44·45%).

7-*Triethylsilylcyclo-octa*-1,3,5-*triene* (II).—(*a*) To a solution of ethylmagnesium bromide [from ethyl bromide (8·9 g., 0·08 mole) and magnesium (1·9 g., 0·08 g.-atom)] in diethyl ether (40 ml.) was added, with stirring, 7-trichlorosilylcyclo-octa-1,3,5-triene (4·8 g., 0·02 mole) under

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[7] Cope and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2515.

nitrogen, at such a rate that the ether boiled. The mixture was then refluxed for 2 hr. After cooling, the precipitate was removed. Water (25 ml.) was added to the filtrate. The two-phase system was separated, toluene (25 ml.) was added to the organic layer, and the ether and toluene were removed by distillation, to leave a high-boiling liquid residue that was fractionated twice under reduced pressure, giving pale yellow liquid 7-*triethylsilylcyclo-octa*-1,3,5-*triene* (1·2 g.), b. p. 70·4°/0·05 mm., n_D^{25} 1·5019 (Found: C, 76·35; H, 11·0; Si, 12·7. $C_{14}H_{24}Si$ requires C, 76·4; H, 11·0; Si, 12·4%).

(*b*) In a 20 ml. flask attached to a reflux condenser and under nitrogen was placed 5-triethylsilylcyclo-octene [1] (IV) (2·0 g.) dissolved in carbon tetrachloride (5 ml.). To this, in four equal portions, was added *N*-bromosuccinimide (3·17 g., 0·178 mole), each addition being accompanied by carbon tetrachloride (6 ml.) and benzoyl peroxide (0·1 g.; as initiator). On the first addition, the reaction was refluxed for 2 hr. The colourless mixture became dark brown. After each addition the precipitated succinimide (total 1·5 g., 0·015 mole) was removed and washed with a little carbon tetrachloride which was then added to the filtrate. The final filtrate was added dropwise with stirring under nitrogen to a solution of potassium t-butoxide in t-butyl alcohol (prepared by refluxing 0·7 g. of finely divided potassium and 20 ml. of dry t-butyl alcohol). The mixture was refluxed for 24 hr., after which the precipitate of potassium bromide was filtered off and washed with carbon tetrachloride. The filtrate and washings were combined and concentrated by distillation to remove the carbon tetrachloride and t-butyl alcohol. The liquid residue (~1·0 ml.) was distilled under reduced pressure through a Sargent short-path sublimator several times until a very pale yellow liquid, b. p. 85° (bath-temp.)/0·08 mm., n_D^{25} 1·4995 (fleeting Beilstein test for halogen), was obtained.

(*c*) To a hot solution of freshly prepared potassium t-butoxide (from potassium 0·4 g. and t-butyl alcohol 10 ml.) were added 6 drops of 5-triethylsilylcyclo-octa-1,3,6-triene (III). The mixture became brown almost immediately. It was refluxed for 48 hr., after which several portions (each 2 ml.) of dry toluene were added to extract all the soluble material. The combined extracts were concentrated, leaving a dark liquid residue which on distillation through a Sargent short-path sublimator at 140°/0·08 mm. gave ~2 drops of a colourless liquid, n_D^{25} 1·5031.

Triethylsilylcyclo-octane (V).—Compound (II) (0·2 g.) was mixed with platinum oxide (0·1 g.) and shaken in hydrogen at 48·0 lb./in.^{2} for 72 hr. at 22°. After removal of the catalyst followed by short-path distillation, the liquid had n_D^{26} 1·4750. The infrared spectrum of this material and the triethylsilylcyclo-octane reported previously were similar.

5-*Triethylsilylcyclo-octa*-1,3,6-*triene* (III).—Freshly distilled triethylsilane (6·8 g., 0·06 mole) and cyclo-octa-1,3,5,7-tetraene (6·1 g., 0·06 mole) were heated in toluene (50 ml.) at 170° for 3 days in a rocking autoclave under autogenous pressure, with 0·1 g. of platinum–γ-alumina. After cooling, the dark red liquid was removed and fractionated under reduced pressure, to give several products. 5-Triethylsilylcyclo-octa-1,3,6-triene (III) (2·8 g.), b. p. 114—122°/0·55 mm., n_D^{25} 1·5050, was obtained (Found: Si, 12·4%; *M*, 229. $C_{14}H_{24}Si$ requires Si, 12·7%; *M*, 220). A second fraction (4·0 g.) had b. p. 137—155°/0·4 mm., n_D^{25} 1·5348. This product (VI) is probably a *di(cyclo-octatrienyl)diethylsilane* (Found: Si, 10·4%; *M*, 301. $C_{20}H_{28}Si$ requires Si, 9·5%; *M*, 296·3).

Bistriethylsilylcyclo-octadienes.—Reaction of triethylsilane (11·6 g., 0·1 mole), cyclo-octa-1,3,5,7-tetraene (5·2 g., 0·05 mole), and platinum–γ-alumina (0·1 g.) at 200° for 6 hr. gave two main fractions. The first, a pale yellow, mobile liquid (3·0 g.), b. p. 105—110°/0·35 mm., n_D^{25} 1·5080, was a *bis(triethylsilylcyclo-octadiene* (VII) (Found: C, 71·5; H, 11·7; Si, 16·3. $C_{20}H_{40}Si_2$ requires C, 71·4; H, 12·0; Si, 16·7%). Secondly, a pale yellow liquid (2·0 g.) had b. p. 120—125°/0·35 mm., n_D^{25} 1·5218, is also considered to be a *bistriethylsilylcyclo-octadiene* (VIII) (Found: C, 71·5; H, 12·1; Si, 16·1%).

5-*Diethylsilylcyclo-octa*-1,3,6-*triene* (IX).—Freshly prepared diethylsilane (17·62 g., 0·2 mole) and cyclo-octa-1,3,5,7-tetraene (20·8 g., 0·2 mole) in dry toluene (25 ml.) were heated in a rocking autoclave (300 ml.) with platinum–γ-alumina (0·5 g.) at 250° for 12 hr. Concentration of the resulting mixture, followed by fractionation of the high-boiling liquid residue, gave 5-*diethylsilylcyclo-octa*-1,3,6-*triene* (IX) (10·0 g.), b. p. 51—56°/0·15 mm., n_D^{25} 1·5104 (Found: C, 74·0; H, 9·7; Si, 14·6%; *M*, 189. $C_{12}H_{20}Si$ requires C, 74·9; H, 10·5; Si, 14·6%; *M*, 192). A higher-boiling fraction (3·5 g.), considered to be a *di(cyclo-octatrienyl)diethylsilane* (X), had b. p. 150—160°/0·15 mm., n_D^{25} 1·5396 (Found: C, 78·8; H, 9·6; Si, 9·9%; *M*, 295. $C_{20}H_{28}Si$ requires C, 81·05; H, 9·5; Si, 9·5%; *M*, 297).

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[8] Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, p. 199.