526. *Addition of Silicon Hydrides to Cyclic Olefins. Part I. Cyclo-octene and Cyclo-octa-1,5-diene.*

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A series of silicon-substituted cyclo-octanes and cyclo-octenes has been prepared by addition of trichloro-, diethyl-, and triethyl-silane to cyclo-octene and cyclo-octa-1,5-diene. Qualitative comparison showed the ease of addition to be $Cl_3SiH > Et_2SiH_2 > Et_3SiH$.

THE addition of a variety of substituted silicon hydrides to olefinic systems has previously been accomplished.[1] The olefins employed for the most part have been acyclic, one exception being cyclohexene. This paper reports the addition of trichloro-, diethyl-, and triethyl-silane to cyclo-octene and cyclo-octa-1,5-diene, platinum on γ-alumina[2] being used as catalyst. The object of this work was to prepare a series of silicon-substituted cyclo-octenes and cyclo-octanes. These compounds are to be used for comparative studies of derivatives obtained by addition of silicon hydrides to other unsaturated eight-membered cyclic compounds.

Trichlorosilylcyclo-octane was prepared by catalysed addition of trichlorosilane to cyclo-octene in toluene at 225° for 12 hr. under autogeneous pressure. Milder conditions gave no desirable product. Treatment of the product with ethylmagnesium bromide gave triethylsilylcyclo-octane, but attempts to prepare this by addition of triethylsilane to cyclo-octene were fruitless.

Diethylsilane and cyclo-octene in a 1 : 3 molar ratio were heated with catalyst at 250° under pressure for 24 hr. Several products were isolated, including diethylsilylcyclo-octane but not biscyclo-octyldiethylsilane.

Cyclo-octa-1,5-diene and trichlorosilane under similar conditions gave two products. Chlorine analysis indicated one to be 5-trichlorosilylcyclo-octene and the other, a bistrichlorosilylcyclo-octane. These with ethylmagnesium bromide gave 5-triethylsilylcyclo-octene and a bistriethylsilylcyclo-octane, respectively.

An alternative route to 5-triethylsilylcyclo-octene was addition of triethylsilane to cyclo-octa-1,5-diene in the absence of solvent, conditions being similar to those used for trichlorosilane. Catalytic hydrogenation of this cyclo-octene gave triethylsilylcyclo-octane, as indicated by similar infrared spectra and physical properties.

An attempt to prepare the bistriethylsilylcyclo-octane by addition of triethylsilane to cyclo-octa-1,5-diene in a 2 : 1 molar ratio was not successful, the main product being 5-triethylsilylcyclo-octene. This result was not surprising since under similar conditions cyclo-octene failed to react with triethylsilane. The disubstituted derivative must be either 1,4- or 1,5-bistriethylsilylcyclo-octane, and a distinction is being sought by another synthesis.

Qualitatively the ease of addition to the olefins was in the order $Cl_3SiH > Et_2SiH_2 > Et_3SiH$, in agreement with other workers.[3]

EXPERIMENTAL

Trichlorosilane and dichlorodiethylsilane were obtained from the Silicones Division of Union Carbide Corporation, Tonawanda, N.Y., and were distilled before use. Cyclo-octene and cyclo-octa-1,5-diene were obtained from Cities Service Research and Development Co., New York, N.Y. Diethylsilane[4] and triethylsilane[5] were prepared as previously described.

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[1] See, *e.g.*, George, Prober, and Elliott, *Chem. Rev.*, 1956, **56**, 1065; Eaborn, " Organosilicon Compounds," Butterworths Scientific Publns., London, 1960; Shuhara, Hoskyns, and Post, *J. Org. Chem.*, 1961, **26**, 4000.

[2] Wagner and Whitehead, U.S.P. 2,851,473/1958.

[3] Seyferth and Rochow, *J. Org. Chem.*, 1955, **20**, 250.

[4] Peake, Nebergall, and Chen, *J. Amer. Chem. Soc.*, 1952, **74**, 1526.

[5] Tannenbaum, Kaye, and Leweny, *J. Amer. Chem. Soc.*, 1953, **75**, 3753.

Trichlorosilylcyclo-octane.—In a 300-ml. stainless-steel rocking autoclave were placed freshly distilled trichlorosilane (27·2 g., 0·2 mole), cyclo-octene (22·0 g., 0·2 mole), dry toluene (25 ml.), and platinum on γ-alumina (0·5 g.). The autoclave was sealed after being flushed with dry nitrogen and heated with rocking at 225° for 12 hr. Toluene was removed by distillation under a nitrogen atmosphere. The high-boiling residue was distilled under reduced pressure. The main fraction, *trichlorosilylcyclo-octane*, had b. p. 85—89°/1·25 mm. (17·0 g., 35%) (Found: Cl, 43·4. $C_8H_{15}Cl_3Si$ requires Cl, 42·5%).

Triethylsilylcyclo-octane.—To a solution of ethylmagnesium bromide prepared from ethyl bromide (11·8 g., 0·11 mole) and magnesium (0·45 g., 0·11 g.-atom) in tetrahydrofuran (50 ml.) was added dropwise with stirring trichlorosilylcyclo-octane (8·9 g., 0·036 mole) under nitrogen. The mixture was then heated under reflux for 2·5 hr. The precipitate which had been formed was removed, and then the tetrahydrofuran by distillation. The liquid residue was fractionated under reduced pressure to give *triethylsilylcyclo-octane* (2·0 g., 26%), b. p. 82°/0·18 mm., n_D^{25} 1·4748 (Found: C, 74·9; H, 13·3%; *M*, 230. $C_{14}H_{30}Si$ requires C, 74·3; H, 13·4%; *M*, 226).

Triethylsilylcyclo-octane was also prepared by hydrogenation of 5-triethylsilylcyclo-octene (0·2 g.) at room temperature with platinum oxide (0·1 g.) at 47·5 lb./sq. in. for 60 hr. at 25° (pressure drop ~2 lb.). After removal of the catalyst the liquid was purified by sublimation and had n_D^{25} 1·4761 and an infrared spectrum similar to that of the preceding sample.

Diethylsilylcyclo-octane.—A mixture of diethylsilane (10·0 g., 0·13 mole), cyclo-octene (38·5 g., 0·35 mole), and 0·25 g. of platinum on γ-alumina was heated in the rocking autoclave at 250° for 24 hr. The resulting greenish-brown liquid was concentrated by distillation at atmospheric pressure. The amount of unchanged starting materials recovered indicated that the reaction occurred with difficulty. Increasing the reaction time to 35 hr. did not materially improve the yield. The liquid residue, after two distillations under reduced pressure through a semimicro-column, gave several fractions one of which was shown to be *diethylsilylcyclo-octane* (0·9 g., 3·6%), b. p. 80—81°/0·05 mm., n_D^{25} 1·4742 (Found: Si, 13·7%; *M*, 212. $C_{12}H_{26}Si$ requires Si, 14·2%; *M*, 198). The infrared spectrum exhibited bands for Si–H stretching at 2100 and Si–CH_2 deformation at 1230 cm.$^{-1}$.

5-*Trichlorosilylcyclo-octene.*—Freshly distilled trichlorosilane (28·0 g., 0·2 mole), cyclo-octa-1,5-diene (10·8 g., 0·1 mole), dry toluene (25 ml.), and platinum on γ-alumina (0·5 g.) were heated at 225° for 12 hr. in the apparatus described. The isolation procedure was also similar. Two colourless products were isolated on fractionation of the high-boiling liquid residue. The lower-boiling, 5-*trichlorosilylcyclo-octene* (22·2 g.), had b. p. 49—53°/0·2 mm. (Found: Cl, 42·5. $C_8H_{13}Cl_3Si$ requires Cl, 43·7%). Impure bistrichlorosilylcyclo-octane was isolated as a higher-boiling fraction (11·6 g.), b. p. 115—127°/0·35—0·45 mm. (Found: Cl, 48·4. Calc. for $C_8H_{14}Cl_6Si_2$: Cl, 56·1%). It is extremely reactive with atmospheric moisture. The identity of this product is also based on the fact that the bistriethylsilylcyclo-octane prepared from it by use of the Grignard reaction gave correct analyses.

5-*Triethylsilylcyclo-octene.*—(*a*) To a solution of ethylmagnesium bromide [from ethyl bromide (19·6 g., 0·18 mole) and magnesium (4·32 g., 0·18 mole)] in tetrahydrofuran (60 ml.) was added dropwise, with stirring, trichlorosilylcyclo-octene (10·0 g., 0·043 mole) under nitrogen. The time of reaction and the isolation procedure were similar to those described for the preparation of triethylsilylcyclo-octane. Fractionation of the colourless liquid residue gave 5-*triethylsilylcyclo-octene* (4·78 g., 50%), b. p. 80—85°/0·13 mm., n_D^{25} 1·4830 (Found: Si, 12·2%; *M*, 220. $C_{14}H_{28}Si$ requires Si, 12·6%; *M*, 224).

(*b*) 5-Triethylsilylcyclo-octene was also obtained by direct addition of triethylsilane (11·6 g., 0·1 mole) to cyclo-octa-1,5-diene (10·8 g., 0·1 mole) by the procedure described for the other additions, at 210° for 12 hr., but no solvent was employed. 5-Triethylsilylcyclo-octene (3·0 g., 13·4%) had b. p. 83—86°/0·18 mm., n_D^{25} 1·4886 (Found: C, 74·5; H, 12·1; Si, 12·2. $C_{14}H_{28}Si$ requires C, 75·0; H, 12·6; Si, 12·5%). This material and that obtained by method (*a*) had similar infrared spectra.

Bistriethylsilylcyclo-octane.—To a solution of ethylmagnesium bromide (from ethyl bromide, 30·0 g., 0·28 mole, and magnesium, 6·7 g., 0·28 mole) in tetrahydrofuran (50 ml.) was added dropwise, with stirring, bistrichlorosilylcyclo-octane (11·6 g., 0·031 mole) under nitrogen. Procedure was as in the preparation of triethylsilylcyclo-octane. Fractionation gave *bistriethylsilylcyclo-octane* (4·0 g., 38%), b. p. 125—130°/0·2 mm., n_D^{25} 1·4876 (Found: C, 69·9; H, 13·0; Si, 15·6%; *M*, 343. $C_{20}H_{44}Si_2$ requires C, 70·5; H, 13·0; Si, 16·5%; *M*, 341.

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