TABLE II

STRAIN AT C–C–C BOND ANGLES IN HYPOTHETICAL FIVE-MEMBERED RINGS

Model	∠ α, deg.	∠ β, deg.	∠ γ, deg.	Angle strain Deg.[2]	Angle strain Kcal.
Cyclopentane	108	108	108	11	0.2
Cyclopentyl cation	108.32	104.93	113.5	85	1.5
Cyclopentene (III)	112.25	104.25	107	181	3.2
Δ^3-Cyclopentenyl cation, planar	112.48	101.52	112.0	304	5.3
Δ^3-Cyclopentenyl cation, bent IV	109.13	97.75	98.0	997	17.5

ice bath during 2 hr. The reaction mixture was stirred at room temperature overnight and then refluxed for 36 hr. It was filtered through glass wool and the filtrate poured over ice. The ether solution was separated, dried over calcium chloride, and the ether removed by distillation at atmospheric pressure. The residue was distilled at reduced pressure and yielded 37 g. (0.25 mole, 9.5%) of 4-bromocyclopentene boiling at 43° (35 mm.), $n^{25}\text{D}$ 1.4992.[21] The infrared spectrum of 4-bromocyclopentene in carbon tetrachloride shows peaks at 3.30 (m), 3.39, 3.48, 3.53 (s), 6.29 (m), 6.93, 7.34, 7.70 (s), 8.14 (vs), 8.64, 10.32 (w), 10.77 (m), 11.04 (s), 11.40 (w), and 14.74 μ (vs).

Δ^3-Cyclopentenol.—An 11-g. sample of 4-bromocyclopentene (0.075 mole) was refluxed for 12 hr. in a mixture of 75 ml. of water, 75 ml. of ethanol, and 8 g. of sodium carbonate (0.075 mole). Sodium bicarbonate precipitated and was filtered off. Most of the ethanol was removed by distillation. The residue was distilled at reduced pressure, and 2.1 g. of alcohol boiling at 83–85° (110 mm.) was obtained, $n^{25}\text{D}$ 1.4653 (lit.[22] b.p. 67–68° at 30 mm., $n^{25}\text{D}$ 1.4673).

p-Nitrobenzoate melted at 89° (from 95% ethanol).

Anal. Calcd. for $C_{12}H_{11}O_4N$: C, 61.79; H, 4.76; N, 6.01. Found: C, 61.73; H, 5.01; N, 6.12.

Measurement of Rate Constants.—The rates of solvolysis of bromocyclopentane and 4-bromocyclopentene were followed by titration of the acid produced. A solution of the bromide in 100 ml. of 50% aqueous acetone was prepared and this was evenly divided into 16 tubes which were sealed and placed in a constant temperature bath. A warm-up time of 2–3 min. was allowed and one tube was removed from the bath at this time to give an initial titer and a starting time. The tubes were cooled in Dry Ice–acetone baths for fast reactions and with running tap water for slower reactions. A 5-ml. aliquot was taken from each tube and diluted with 50 ml. of water. This mixture was then titrated with 0.01 *N* sodium hydroxide to pH 7.0 using a Beckman Autotitrator, Model K.

Product Recovery.—A 2.540-g. sample of 4-bromocyclopentene was added to 100 ml. of 50% aqueous ethanol and refluxed for 22 hr. The reflux temperature was 81°. The reaction mixture was kept neutral with1.5 *N* sodium hydroxide by keeping the brom thymol blue in the solution just green. When the hydrolysis was complete the ethanol was removed by distillation and the aqueous mixture was extracted with ether. The ethereal solution was dried over magnesium sulfate and the ether removed by distillation. The residue weighed 0.51 g., a yield of 37%. The infrared spectrum of this material was identical with that of a pure sample of 3-cyclopentenol.

When 0.592 g. of 3-cyclopentenol was dissolved in 50 ml. of 50% aqueous ethanol containing 0.6 g. of sodium bromide and refluxed for 22 hr., 0.205 g. of the alcohol was recovered using the same technique applied to the solvolysis reaction, a yield of 40.5%.

From 0.400 g. of material from the product study and 0.87 g. of *p*-nitrobenzoyl chloride, 0.495 g. of ester was obtained. From 0.400 g. of 3-cyclopentenol and 0.87 g. of *p*-nitrobenzoyl chloride, 0.50 g. of ester was obtained. Both samples melted at 89° after recrystallization from 95% ethanol and a mixture melting point showed no depression.

Acknowledgment.—This work was supported by the National Science Foundation.

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[21] In the course of work in this laboratory by Dr. Shelton Bank' this bromide has been converted into Δ^3-cyclopentylacetic acid, characterized and analyzed as its *p*-bromophenacyl ester, m.p. 66–67°, and into 2-(Δ^3-cyclopentenyl)ethanol, whose *p*-nitrobenzenesulfonate, prepared by Dr. George Schmid, melts at 65–66° [*cf.* R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961), m.p. 65–67°].

[22] S. Winstein, E. L. Allred, and V. Sonnenberg, *ibid.*, **81**, 5833 (1959).

Addition Reaction of Silanes to 1,5,9-Cyclododecatriene

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Monosilyl and bissilyl compounds were obtained by chloroplatinic acid-catalyzed addition of silanes, such as trichlorosilane and methyldichlorosilane, to *cis,trans,trans*-1,5,9-cyclododecatriene. These adducts were methylated, giving 1-trimethylsilyl-4,8-cyclododecadiene and bis(trimethylsilyl)cyclododecene, respectively. Catalytic hydrogenation of 1-trimethylsilyl-4,8-cyclododecadiene gave only trimethylsilylcyclododecene. The diene derivatives contained both *cis* and *trans* double bonds and the cyclododecene derivatives were mixtures of *cis* and *trans* isomers. Hydrolysis of 1-trichlorosilyl- and 1-(methyldichlorosilyl)-4,8-cyclododecadiene gave the corresponding hydroxyl derivatives.

Cyclododecatriene was prepared by trimerization of butadiene with various catalyst systems[1b] in good yields. We have found that an isomer of *cis,trans,trans*-1,5,9-cyclododecatriene also can be obtained in about 85% yield by using a catalyst of the titanium tetraalkoxide–dialkylaluminum halide system.[2] The reactions of the double bonds in the compound, *i.e.*, oxidation reactions with some organo peracids[3] and addition reactions of boranes,[4] halogen,[5] hydrogen chloride, and acetic acid,[6] have been reported by several workers. A *trans* double bond present in *cis,trans,trans*-1,5,9-cyclododecatriene is oxidized with organo per-

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[1] (a) Nishi-2-chome, Daini, Oyodoku, Osaka, Japan. (b) The catalyst systems are as follows: titanium tetrachloride–dialkylaluminum (or trialkylaluminum) chloride, chromium compounds, alkylaluminum compounds, and nickel compounds. See also G. Wilke, *Angew. Chem.*, **69**, 97 (1957); **73**, 33 (1961); **75**, 10 (1963); *J. Polymer Sci.*, **38**, 45 (1959); Studiengesellschaft Kohle m. b. H., Belgian Patents 555,180 (1957), 566,436 (1958); G. Wilke and H. Müller, German Patent 1,043,329 (1958).

[2] H. Takahasi and M. Yamaguchi, *J. Org. Chem.*, **28**, 1409 (1963).

[3] G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); L. I. Zakharkin and V. V Korneva, *Dokl. Akad. Nauk SSSR*, **132**, 1078 (1960).

[4] R. Köster, *Angew. Chem.*, **69**, 684 (1957); R. Köster and G. Griaznov, *ibid.*, **73**, 81 (1961).

[5] H. Takahasi and M. Yamaguchi, *J. Chem. Soc. Japan*, **83**, 1042 (1962).

[6] L. I. Zakharkin, V. V. Korneva, and A. V. Iogansen, *Dokl. Akad. Nauk SSSR*, **138**, 373 (1961).

TABLE I

ADDITION OF TRICHLOROSILANE TO *cis,trans,trans*-1,5,9-CYCLODODECATRIENE

$C_{12}H_{18}$,[a] g.	$HSiCl_3/C_{12}$,[b] mole ratio	Temp., °C.	Time, hr.	Recovered, $C_{12}H_{18}$, g.	Mono-Si[c] g.	Mono-Si[c] %[e]	Bis-Si[d] g.	Bis-Si[d] %[e]	Residue, g.
32.4[f]	1.25	180	18	16	16	53.7			9
43.2[f]	1.11	120	9	15	23	44.8			17
40[g]	1.0	140	72	3.5	50	75			8
40[g]	1.0	160	72	8	45	77			10
32[g]	2.0	150	72	20	8	35			16
24[g]	3.0	180	80	4	13	35	25	46	8

[a] *cis,trans,trans*-1,5,9-Cyclododecatriene. [b] Mole ratio of trichlorosilane to the cyclododecatriene. [c] 1-Trichlorosilyl-4,8-cyclododecadiene, b.p. 150–155° (6 mm.). [d] Bis(trichlorosilyl)cyclododecene, b.p. 205–210° (6 mm.). Yields of the fraction based on the reacted cyclododecatriene. [f] Trichlorosilane was dropped slowly in cyclododecatriene containing 0.33 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution at 180° (or 120°) under atmospheric pressure. [g] In a Carius tube of about 200-ml. capacity, a mixture of trichlorosilane, cyclododecatriene, and 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution was heated.

acids to give *cis,trans*-5,9-cyclododecadiene-1,2-diol.[7] Addition reactions of halogen and acetic acid to the double bonds show no selectivity in so far as the *cis* and *trans* configuration is concerned.

The competitive reactivities between the *cis* and *trans* double bonds in this compound excluding those mentioned previously seem not to be confirmed. As the Si–H bond in silanes can easily add to olefins, giving alkylsilanes, the addition reaction of silanes to *cis,trans,trans*-1,5,9-cyclododecatriene may offer a good scheme for explaining the relative reactivities of the double bonds in such a compound. The present paper deals with the results of chloroplatinic acid-catalyzed addition of hydrochlorosilanes to *cis,trans,trans*-1,5,9-cyclododecatriene.

When *cis,trans,trans*-1,5,9-cyclododecatriene was heated with one mole of trichlorosilane in the presence of chloroplatinic acid, the silane added to one of the three double bonds present in the cyclododecatriene. As shown in Table I, the best yield was 77%. When aluminum chloride was used as the addition catalyst nearly all of the trichlorosilane was recovered and the cyclododecatriene was converted into a viscous liquid. No reaction occurred when benzoyl peroxide was used as catalyst. The same was true in the absence of a catalyst. The adduct obtained from the chloroplatinic acid catalysis was assigned the 1-trichlorosilyl-4,8-cyclododecadiene structure (IIa, IIb) on the basis of its analyses of silicon and hydrolyzable chlorine. This compound was methylated with excess methylmagnesium chloride to yield 1-trimethylsilyl-4,8-cyclododecadiene (IIIa, IIIb). This compound (IIIa, IIIb) showed characteristic infrared absorption bands of the trimethylsilyl group and *trans* double bond, but not the absorption of a *cis* double bond near 700 cm.$^{-1}$.

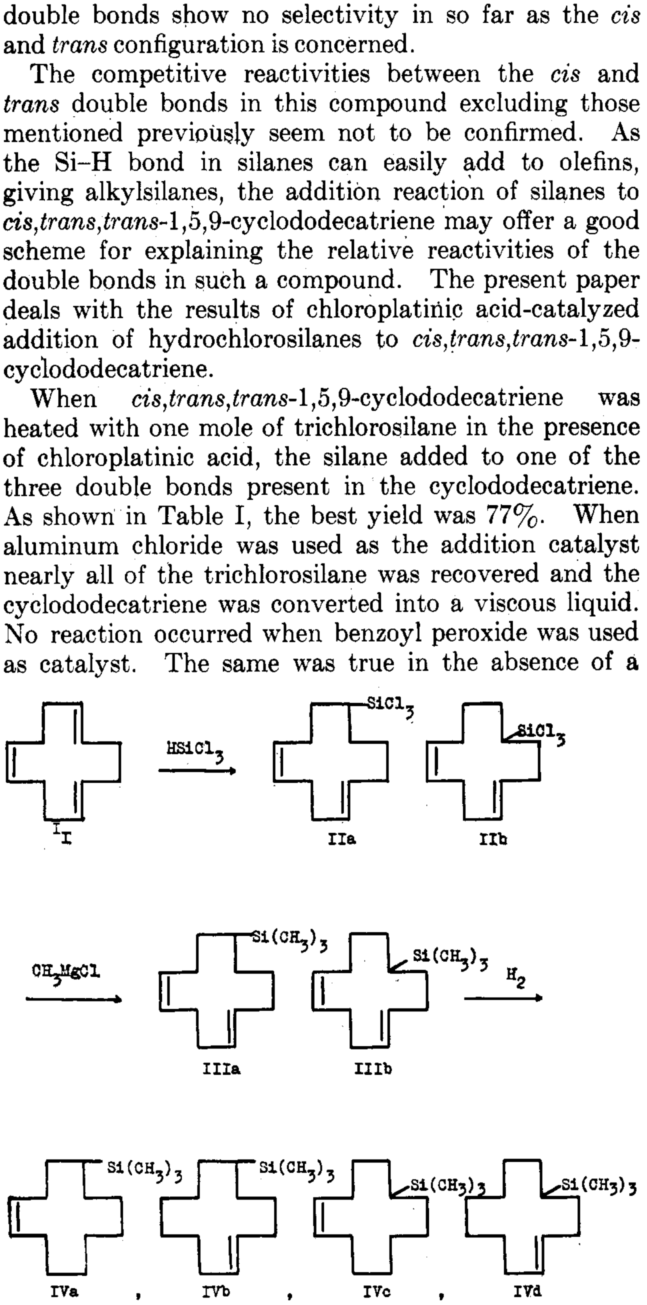

Figure 1.

For further investigation of the configuration of the two olefinic bonds present in this compound (IIIa, IIIb), the absorbance of the *trans* absorption band at about 970 cm.$^{-1}$ in carbon disulfide solution was compared with the *trans* absorption band of the original *cis,trans,trans*-1,5,9-cyclododecatriene (I) in carbon disulfide. A 6.0 mmole % solution of the 1-trimethylsilyl-4,8-cyclododecadiene (IIIa, IIb) gave an absorbance equal to that obtainable from a 3.0 mmole % solution of *cis,trans,trans*-1,5,9-cyclododecatriene. On the preceding basis it is concluded that the original reaction product possesses both *cis* and *trans* double bonds. From this it is logical to conclude that the silane adds to the *trans* double bond existing in the cyclododecatriene. Accordingly, 1-trichlorosilyl- and 1-trimethylsilyl-4,8-cyclododecadiene are most probably an isomeric mixture of IIa and IIb and an isomeric mixture of IIIa and IIIb in Fig. 1, respectively.

1-Trimethylsilyl-4,8-cyclododecadiene reacted with only one mole of hydrogen upon catalytic hydrogenation over palladium–charcoal to yield trimethylsilylcyclododecene, which seems to be a mixture of IVa, IVb, IVc, and IVd in Fig. 1 on the basis of infrared analysis of the *trans* double bond. Therefore, the catalytic hydrogenation of 1-trimethylsilyl-4,8-cyclododecadiene does not seem to operate in a selective manner so far as the *cis* or *trans* double bonds are concerned.

The addition reaction of two or more moles of trichlorosilane gave 1-trichlorosilyl-4,8-cyclododecadiene in 35% yields and bis(trichlorosilyl)cyclododecene in 46% yields as shown in Table I. The bissilyl compound was methylated with methylmagnesium chloride, giving bis(trimethylsilyl)cyclododecene. This compound seems to be a mixture of *cis*-VII and *trans*-VIII isomers on the basis of infrared analysis of the *trans* double bond and measurement of the double bond by Wijs' method (Fig. 2). Therefore, it seems that, even though one mole of the silane can add selectively to one *trans* double bond present in *cis,trans,trans*-1,5,9-cyclodo-

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[7] Benzoic peracid was used; see also L. I. Zakharkin and V. V. Korneva, *Dokl. Akad. Nauk SSSR*, **132**, 1078 (1960). We also obtained similar results with hydrogen peroxide.

TABLE II

ADDITION OF METHYLDICHLOROSILANE[a]

$C_{12}H_{18}$,[b] g.	Si/C_{12}[c]	H_2PtCl_6,[d] ml.	Recovered, $C_{12}H_{18}$,[b] g.	Mono-Si[e] g.	Mono-Si[e] %[g]	Bis-Si[f] g.	Bis-Si[f] %[g]	Residue, g.
96	1	1.2	16	91	66	16	8.5	22
88	2	0.8	10	63	47	26	14	46

[a] Reactions were operated in a Carius tube of about 200-ml. capacity at 185° for 60 hr. [b] *cis,trans,trans*-1,5,9-Cyclododecatriene. [c] Mole ratio of methyldichlorosilane to cyclododecatriene. [d] 0.1 *N* Chloroplatinic acid–propyl alcohol solution. [e] 1-(Methyldichlorosilyl)-4,8-cyclododecadiene, b.p. 165–175° (9 mm.). [f] Bissilyl compound of cyclododecene, b.p. 195–215° (9 mm.). [g] Yields of the fraction based on the reacted cyclododecatriene.

decatriene, the addition of the second mole of the silane to the cyclododecatriene is not selective to either the *cis* or *trans* double bond.

Addition of methyldichlorosilane yielded monosilyl and bissilyl compounds as shown in Table II. 1-(Methyldichlorosilyl)-4,8-cyclododecadiene (IXa, IXb) was methylated with methylmagnesium chloride, to give 1-trimethylsilyl-4,8-cyclododecadiene (Fig. 3). The infrared spectrum and refractive index were identical with that derived from 1-trichlorosilyl-4,8-cyclododecadiene (IIa, IIb). A fraction of the bissilyl compound had a chlorine content of 32.0% in contrast to pure bis(methyldichlorosilyl)cyclododecene with a chlorine content of 36.6%, which was not isolable. Nevertheless, this fraction yielded bis(trimethylsilyl)-cyclododecene in good yields, by methylation, which had the same physical constants as that derived from bis(trichlorosilyl)cyclododecene (V, VI).

Although trimethylsilane was treated with *cis,trans,-trans*-1,5,9-cyclododecatriene in the presence of chloroplatinic acid catalyst in an autoclave at 250° for 48 hr., no addition product was isolated and the starting cyclododecatriene was recovered in about 90% yields. As mentioned previously, trichlorosilane could add to the cyclododecatriene in 77% yields at 160° but methyldichlorosilane required a higher temperature of 185° for reaction. It is evident that for addition to proceed, the silane moiety should contain at least one negative group in the form of chlorine, etc.

By using one mole of trichlorosilane for each mole of the cyclododecatriene, only the monosilyl compound was obtained in 77% yields. When three moles of trichlorosilane was used, the yields of monosilyl and bissilyl compounds were 35% and 46%, respectively, and the residue was smaller than the monosilyl and bissilyl compounds. These facts show that the reactivity of the remaining double bond decreases considerably with the increased addition of silanes. The same result is obtained in the hydrogenation. Catalytic hydrogenation of cyclododecatrienes over palladium–charcoal yields cyclododecane, but reduction of 1-trimethylsilyl-4,8-cyclododecadiene, on the other hand, yields only trimethylsilylcyclododecene and no trimethylsilylcyclododecane.

1-Trichlorosilyl-4,8-cyclododecadiene upon hydrolysis yielded a white solid which contained one hydroxy group on one silicon atom, and its polymerization grade was approximately 6. Hydrolysis of 1-(methyldichlorosilyl)-4,8-cyclododecadiene gave a mixture of 1-(methyldihydroxysilyl)-4,8-cyclododecadiene and its dimer.

Experimental

1-Trichlorosilyl-4,8-cyclododecadiene.—A mixture of 40 g. (0.25 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene, 34 g. (0.25 mole) of trichlorosilane, and 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution was heated in a Carius tube of about 200-ml. capacity at 160° for 72 hr. After removing trichlorosilane, 8 g. of cyclododecatriene was recovered and there was obtained 45 g. of a fraction boiling at 150–155° (6 mm.), 77.0% based on the reacted cyclododecatriene, with 10 g. of residue. Redistillation gave a fraction boiling at 148–150° (4 mm.), $n^{20}D$ 1.5175.

Anal. Calcd. for $C_{12}H_{19}SiCl_3$: Cl, 36.01; Si, 9.43. Found: Cl, 35.65; Si, 9.61.

The recovered cyclododecatriene gave identical infrared absorption with that of the starting cyclododecatriene.

1-Trimethylsilyl-4,8-cyclododecadiene.—To an ether solution of methylmagnesium chloride prepared from 2 g. of magnesium, was added 10 g. of 1-trichlorosilyl-4,8-cyclododecadiene in 40 ml. of benzene and refluxed for 3 hr. under stirring. After cooling, the mixture was poured into ice–water to decompose the Grignard reagent. The organic layer was separated and the water layer extracted with ether. The ether extract and the organic layer were dried over anhydrous sodium sulfate. After the solvent was removed, the product was distilled in vacuo, to give 6.5 g. of a fraction boiling at 120–125° (5 mm.), 76.5%. Redistillation gave a fraction boiling at 122° (5 mm.), $n^{25}D$ 1.4960, d^{25}_4 0.8946.

Anal. Calcd. for $C_{15}H_{28}Si$: C, 76.19; H, 11.94; Si, 11.87. Found: C, 76.48; H, 11.96; Si, 12.00.

Infrared spectrum of the compound showed characteristic absorptions of the trimethylsilyl group at 1243, 828–863, 747, and 683 cm.$^{-1}$, and *trans* double bond at 965 cm.$^{-1}$. Absorbance

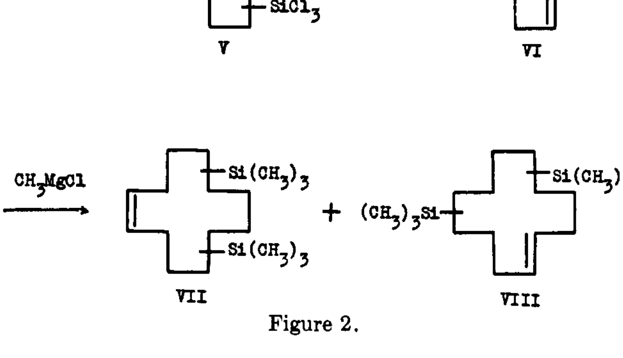

Figure 2.

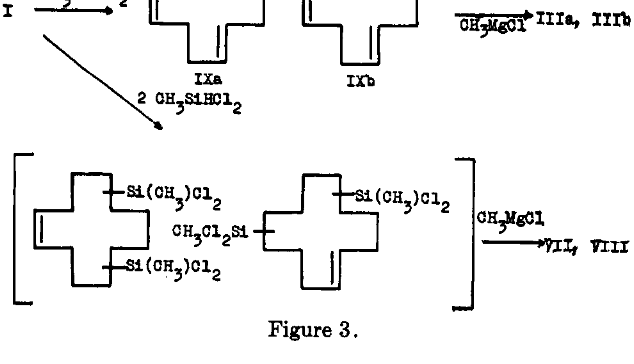

Figure 3.

of the *trans* absorption band at 965 cm.$^{-1}$ in 6.0 mmole % carbon disulfide solution of this compound was identical with that of 3.0 mmole % carbon disulfide solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

Trimethylsilylcyclododecene.—A solution of 7 g. (0.029 mole) of 1-trimethylsilyl-4,8-cyclododecadiene in alcohol was stirred with 3 g. of 10% palladium–charcoal at 40° under atmospheric pressure of hydrogen. After 650 ml. (0.029 mole) of hydrogen was absorbed in the course of 2 hr., the catalyst was filtered and the solvent was removed to give a fraction boiling at 98–100° (1 mm.), n^{25}_{D} 1.4921, d^{25}_{4} 0.8909. It was determined by Wijs' method that the compound had one double bond. Absorbance of the *trans* absorption band at 965 cm.$^{-1}$ in 7.9 mmole % carbon disulfide solution of this compound was identical with that of 2.5 mmole % solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

Anal. Calcd. for $C_{15}H_{30}Si$: C, 75.55; H, 12.68; Si, 11.77. Found: C, 75.75; H, 12.55; Si, 11.95.

Bis(trichlorosilyl)cyclododecene.—A mixture of 24 g. (0.15 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene and 60 g. (0.45 mole) of trichlorosilane was heated with 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution in a Carius tube at 180° for 80 hr. From the mixture, 30 g. of trichlorosilane and 4 g. of the cyclododecatriene were recovered. From reaction products, 13 g. (35%) of 1-trichlorosilyl-4,8-cyclododecadiene, 25 g. (46%) of a fraction boiling at 200–220° (6 mm.), and 8 g. of residue were obtained. The fraction was redistilled, giving a fraction boiling at 200–202° (5 mm.), d^{25}_{4} 1.322.

Anal. Calcd. for $C_{12}H_{20}Si_2Cl_6$: Cl, 49.2; Si, 12.96. Found: Cl, 49.0; Si, 12.69.

Bis(trimethylsilyl)cyclododecene.—With excess methylmagnesium chloride, 10 g. of bis(trichlorosilyl)cyclododecene was methylated, giving 5 g. (70%) of a fraction, b.p. 132–133° (1 mm.), n^{20}_{D} 1.4894, d^{25}_{3} 0.8818.

Anal. Calcd. for $C_{18}H_{38}Si_2$: C, 69.60; H, 12.33; Si, 18.07. Found: C, 69.32; H, 12.32; Si, 18.17.

It was determined by Wijs' method that the compound had one double bond. Absorbance of the *trans* absorption band at about 970 cm.$^{-1}$ in 6.6 mmole % carbon disulfide solution of this compound was identical with that of 2.2 mmole % carbon disulfide solution of *cis,trans,trans*-1,5,9-cyclododecatriene.

1-(Methyldichlorosilyl)-4,8-cyclododecadiene.—A mixture of 96 g. (0.57 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene, 65 g. (0.57 mole) of methyldichlorosilane, and 0.20 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution was heated in a Carius tube of about 200-ml. capacity at 185° for 60 hr. The mixture was distilled, giving 18 g. of methyldichlorosilane, 16 g. of cyclododecatriene, 91 g. of a fraction boiling at 165–175° (9 mm.), 66% based on the reacted cyclododecatriene, 16 g. of a fraction boiling at 195–215° (9 mm.), 8.5% based on the reacted cyclododecatriene, and 22 g. of residue. The fraction boiling at 165–175° (9 mm.) was redistilled, giving 1-(methyldichlorosilyl)-4,8-cyclododecadiene, b.p. 180–182° (15 mm.), n^{20}_{D} 1.511.

Anal. Calcd. for $C_{13}H_{22}SiCl_2$: Cl, 25.6; Si, 10.12. Found: Cl, 26.0; Si, 10.13.

Methylation of 9 g. of the compound gave 5 g. (63%) of 1-trimethylsilyl-4,8-cyclododecadiene, n^{25}_{D} 1.4957, which showed identical infrared absorption spectrum with that of the compound derived from 1-trichlorosilyl-4,8-cyclododecadiene.

The fraction boiling at 195–215° (9 mm.) was redistilled, giving a fraction boiling at 200–202° (5 mm.), chlorine content 32.0%. Methylation of the fraction gave bis(trimethylsilyl)-cyclododecene in 76% yields, n^{20}_{D} 1.4894. Its infrared spectrum was identical with that of the compound derived from bis(trichlorosilyl)cyclododecene.

Attempted Addition Reaction by Trimethylsilane.—A mixture of 49 g. (0.3 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene and 30 g. (0.4 mole) of trimethylsilane was heated with 0.8 ml. of 0.1 *N* chloroplatinic acid–propyl alcohol solution in an autoclave at 250° for 48 hr. The mixture was distilled, recovering the starting material, *cis,trans,trans*-1,5,9-cyclododecatriene (92%). No adduct of trimethylsilane was obtained.

Hydrolysis of 1-trichlorosilyl-4,8-cyclododecadiene.—An ether solution of 1-trichlorosilyl-4,8-cyclododecadiene was poured into a mixture of ice and ether. The mixture was neutralized with aqueous ammonia and the ether layer was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* at room temperature and the residue was dried at room temperature *in vacuo* for a day, leaving white solid; content of OH group, 7.8% [calcd. for $(C_{12}H_{19}SiO)OH$, 7.6%]; molecular weight, 1300 [calcd. for $(C_{12}H_{19}SiOOH)_6$, 1344].

Hydrolysis of 1-(Methyl dichlorosilyl)-4,8-cyclododecadiene.—White solid was obtained by the method mentioned previously; content of OH group, 11.6% [calcd. for $C_{13}H_{22}Si(OH)_2$, 14.2%]; molecular weight, 330 [calcd. for $C_{13}H_{22}Si(OH)_2$, 240].

Deamination of 7-Aminobicyclo[4.1.0]heptane

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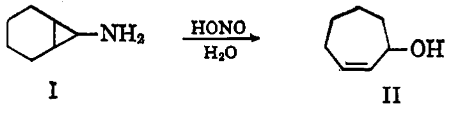
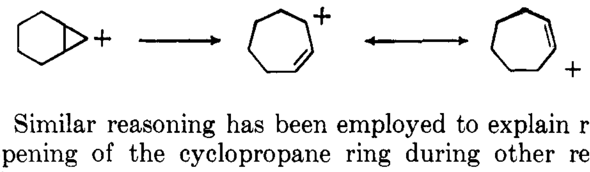
Nitrous acid deamination of 7-aminonorcarane leads, with ring expansion, to cyclohept-2-enol and not to 7-hydroxynorcarane as has been reported.

Deamination of small ring amines with nitrous acid usually leads to ring contraction or expansion or to ring opening. For example, cyclopropylamine yields allyl alcohol.[1] Deamination of either cyclobutylamine or cyclopropylcarbinylamine furnishes similar mixtures of cyclopropylcarbinol, cyclobutanol, along with some allylcarbinol.[2] Even in five- and six-membered ring systems the formation of some product, where possible, due to expansion of the ring during deamination is common.[3]



Considering these results one should expect the deamination of 7-aminonorcarane (7-aminobicyclo[4.1.0]-heptane, I) to lead to ring expansion and formation of cyclohept-2-enol (II). From a theoretical point of view, if an electron-deficient intermediate is involved in some stage of the reaction, then ring opening with formation of the symmetrical allylic ion should be energetically favored as shown.



Similar reasoning has been employed to explain ring opening of the cyclopropane ring during other reactions.[4,5]

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[5] K. L. Rinehart, Jr., S. I. Goldberg, C. L. Tarimu, and T. P. Culbertson, *ibid.*, **83**, 225 (1961).