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HYDROSILATION OF CYCLOOCTADIENES AND BICYCLO[3.3.0]OCTENE-2*

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SUMMARY

The addition of trimethylsilane to 1,5- and 1,3-cyclooctadiene in the presence of any platinum catalyst [chloroplatinic acid, *trans*-dichloro(ethylene)(pyridine)-platinum(II), and 5%-platinum on carbon] always gave 3-(trimethylsilyl)cyclooctene almost exclusively. On the other hand, the benzoyl peroxide initiated addition of trichlorosilane to 1,5-cyclooctadiene followed by methylation gave 2-(trimethylsilyl)bicyclo[3.3.0]octane. Both peroxide initiated and chloroplatinic acid catalyzed hydrosilations of bicyclo[3.3.0]octene-2 produced essentially the same mixture of 2- and 3-silyl-substituted bicyclo[3.3.0]octane.

INTRODUCTION

Several papers concerning the hydrosilation of 1,5-cyclooctadiene have been published recently. The products reported are all 5-silyl-substituted cyclooctenes. Thus, Pike and McDonagh[1] have obtained 5-(triethylsilyl)cyclooctene through the reaction of 1,5-cyclooctadiene with triethylsilane using platinum on alumina as catalyst. West *et al.*[2] have described the formation of 5-(phenylsilyl)cyclooctene from the reaction of the diene and phenylsilane in the presence of benzoyl peroxide in refluxing heptane. Krüger[3] has also reported the preparation of 5-(methyldichlorosilyl)cyclooctene with no experimental detail. We report here our results of addition of silicon hydrides to 1,5-cyclooctadiene in the presence of various types of platinum catalysts and of benzoyl peroxide, which are not in agreement with those reported by the previous workers. The hydrosilation of 1,3-cyclooctadiene and bicyclo[3.3.0]-octene-2 is also described.

RESULTS AND DISCUSSION

When a mixture of 1,5-cyclooctadiene and trimethylsilane was heated at 45° for 36 h in the presence of chloroplatinic acid as catalyst, almost pure 3-(trimethylsilyl)cyclooctene (I) was obtained in 35% yield. The use of *trans*-dichloro(ethylene)-(pyridine)platinum(II) as a homogeneous catalyst in benzene solution also gave (I)

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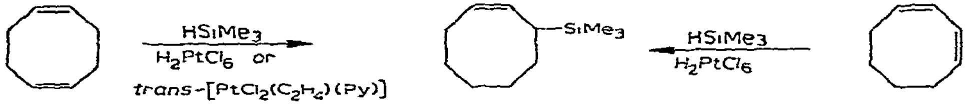
in 53% yield. In both cases a mixture of 1,3- and 1,5-cyclooctadiene in the ratio of *ca.* 95 : 5 (by GLC) was recovered. Hydrosilation of 1,3-cyclooctadiene with trimethylsilane in the presence of chloroplatinic acid gave the same product as above in 38 % yield. Yields of the adduct (I) from all these hydrosilations are almost quantitative if the amounts of unrecovered cyclooctadienes are based.



(I)

The same adduct (I) was also prepared in 32 % yield by heating a mixture of 1,5-cyclooctadiene and trimethylsilane over a catalyst of 5 %-platinum on carbon at 200° for 16 h. Here almost pure 1,3-cyclooctadiene was recovered.

The structure of compound (I) was verified by its proton NMR spectrum (Fig. 1). It shows a multiplet at τ 4.50 (due to vinylic protons), and two diffused multiplets centered at 7.90 (due to protons in the allylic position) and at 8.20 (due to protons on the ring carbon attached to the silicon atom), in addition to signals due to other ring protons (centered at 8.50) and methyl protons on silicon (singlet at 10.00), with relative integrated intensities of 2 : 2 : 1 : 8 : 9, respectively, as expected. Further evidence was afforded by degradation of (I) by trifluoroacetic acid and by bromine, leading to cyclooctene and 3-bromocyclooctene, respectively. The readiness of observed cleavage as well as formation of the 3-bromo derivative is consistent with the proposed structure bearing the *trimethylsilyl* group bonded to the allylic carbon.

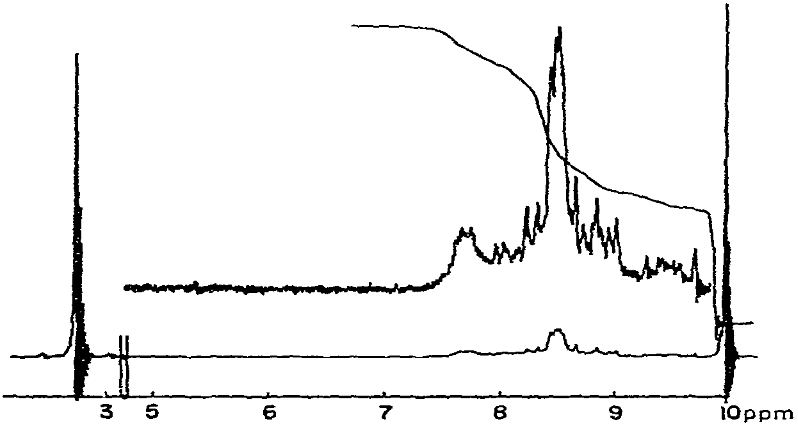
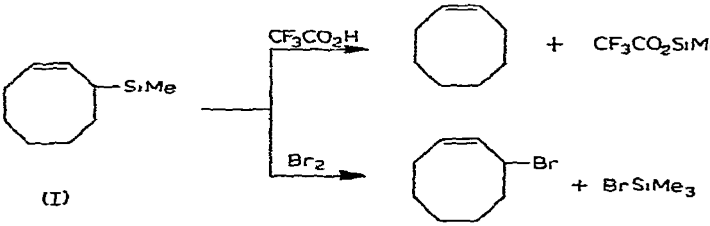


Fig. 1. NMR spectrum of 3-(trimethylsilyl)cyclooctene (I).



The results obtained in the present study thus differ from those reported by Pike and McDonagh[1] but have much analogy with the results of Fish and Kuivila[4] who have recently described that chloroplatinic acid-catalyzed addition of trimethylgermane to 1,3- and 1,5-cyclooctadiene gives rise to a single adduct, 3-(trimethylgermyl)cyclooctene.

It has been well known for some years that the addition of a silicon hydride to an inner olefin in the presence of a platinum catalyst is accompanied by an extensive isomerization of the olefin[5]. A mechanism for this type of hydrosilation reactions entangled by isomerization has recently been proposed by Chalk and Harrod[6]. More recently, Tayim and Bailar[7] have reported that hydrogenation of 1,5-cyclooctadiene catalyzed by some palladium complexes proceeds via stepwise migration of the double bonds to conjugation and the resulting conjugated diene is then hydrogenated to the monoolefin. In view of these facts as well as our results, it seems likely that, in the platinum-catalyzed hydrosilation of 1,5-cyclooctadiene, isomerization of 1,5-cyclooctadiene to conjugated 1,3-isomer takes place fast prior to the addition of trimethylsilane, which then may proceed mainly by the 1,4-mechanism as is generally observed with conjugated dienes. Any possibility of initial formation of 5-(trimethylsilyl)cyclooctene which then undergoes isomerization to the observed 3-trimethylsilyl derivative may be excluded, since addition-elimination reaction can hardly be observed even under more severe conditions[8].

By contrast, benzoyl peroxide initiated addition of trichlorosilane to 1,5-cyclooctadiene in refluxing heptane, followed by methylation of the adduct, gave 2-(trimethylsilyl)bicyclo[3.3.0]octane (II) in 60% yield but neither 3- nor 5-(trimethylsilyl)cyclooctene. The product was characterized by its IR and proton NMR spectra. The IR spectrum exhibits no bands characteristic of olefinic linkages. The NMR spectrum (Fig. 2) shows three groups of diffused multiplets at τ 7.70 (due to the angular protons), 8.50 (due to the ring methylene protons), and 9.40 (due to the proton on tertiary carbon atom attached to the silyl group), in addition to a singlet due to the methyl protons on silicon at 9.97, with relative integrated intensities of 2 : 10 : 1 : 9, respectively.

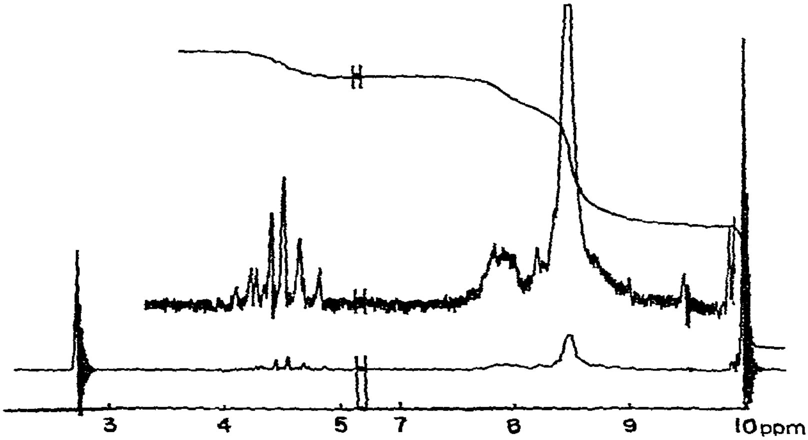
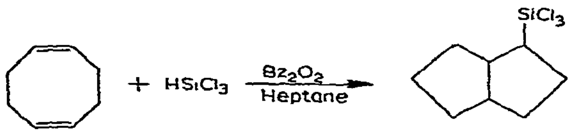
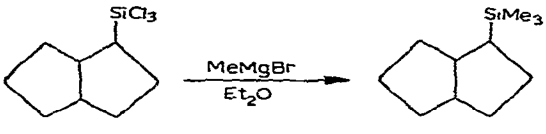


Fig 2. NMR spectrum of 2-(trimethylsilyl)bicyclo[3.3.0]octane (II).



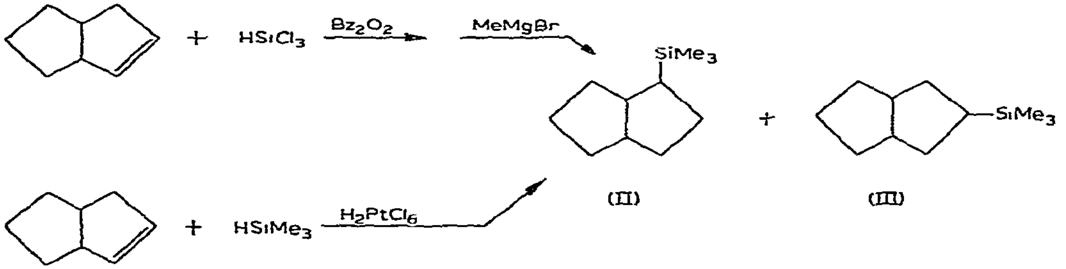


(II)

The reaction here must have proceeded by the widely accepted free radical chain mechanism[9]. It seems probable that the adduct (II) has a sterically favorable *exo-cis* configuration in analogy with the geometry of the addition products of carbon radicals to 1,5-cyclooctadiene[10].

After this study had been completed, a paper of Kuivila *et al.*[11] has appeared recently reporting that the free radical initiated addition of trimethyltin hydride to 1,5-cyclooctadiene gives rise to the formation of 2-(trimethylstannyl)bicyclo[3 3.0]-octane along with other products.

In this connection, hydrosilations of bicyclo[3.3.0]octene-2 with trichlorosilane in the presence of benzoyl peroxide, followed by methylation, and with trimethylsilane in the presence of chloroplatinic acid were carried out. In either case, a mixture of 2- and 3-(trimethylsilyl)bicyclo[3.3.0]octane, (II) and (III) respectively, in the ratio of approximately 1 : 2 was obtained. Although this mixture could not be separated into the components under any GLC conditions, analysis in terms of the chemical shifts for methyl protons on silicon [τ 9.97 for (II) and 9.99 for (III)] led to the above conclusion.



EXPERIMENTAL

1,5- and 1,3-cyclooctadiene were purchased and found to be gas chromatographically homogeneous. The analysis was carried out at 150–180°, a helium flow rate of 30–50 ml/min, with a 2.5 m (6 mm o.d.) column packed with 25% silicone DC-550 on celite. Bicyclo[3.3.0]octene-2 of 98% purity was prepared by isomerization of 1,3-cyclooctadiene, according to the procedure by Stapp and Kleinschmidt[12]. IR spectra were recorded in a liquid film using JASCO DS-402G spectrometer and NMR spectra in 15% carbon tetrachloride solution containing benzene as an internal standard using JEOL C-60H spectrometer. All boiling points reported were uncorrected.

(1) *Hydrosilation of* 1,5-*cyclooctadiene with trimethylsilane*

(*a*) *With chloroplatinic acid catalyst.* A mixture of 8.6 g of 1,5-cyclooctadiene, 8 ml of trimethylsilane, and 80 μl of 0.1 *M* chloroplatinic acid in isopropyl alcohol (10^{-4} mole/mole of olefin) was heated in a sealed glass tube at 45° for 36 h. At this point the reaction mixture was fractionally distilled to give two fractions: 4.9 g of 1,3-cyclooctadiene (97% pure) containing 1,5-isomer, b.p. 140.3–140.8°; and 5.0 g of 3-(trimethylsilyl)cyclooctene (I), b.p. 118.0–118.5°/50 mm, n_D^{20} 1.4749, d_4^{20} 0.8559, MR_D 59.98 (calcd. 59.99) (Found: C, 72.48; H, 12.36. $C_{11}H_{22}Si$ calcd.: C, 72.44; H, 12.16%.) Its proton NMR spectrum is reproduced in Fig. 1. The IR spectrum exhibited bands at 3014, 1637 and 710 cm^{-1}, characteristic of *cis*-olefins. GLC analysis revealed the formation of two other isomeric adducts, the peaks of which appeared very closely on either side of the main peak amounting to as much as 2.6% of the latter. Attempts to isolate them were, however, unsuccessful.

(*b*) *With trans-dichloro*(*ethylene*)(*pyridine*)*platinum*(*II*) *catalyst.* A mixture of 5.4 g of 1,5-cyclooctadiene, 5 ml of trimethylsilane, and 3.7 mg ($2 \cdot 10^{-4}$ mole/mole of olefin) of *trans*-$[PtCl_2(C_2H_4)(Py)]$ dissolved in 2.5 ml of benzene was heated in a glass tube at 45° for 46 h. The products were essentially the same as above. 1,3-Cyclooctadiene obtained (2.5 g) was about 93% pure with contamination by 1,5-isomer. 3-(Trimethylsilyl)cyclooctene (I), b.p. 117–118°/50 mm, n_D^{20} 1.4753, 4.8 g, contained as much as 4% of an isomeric adduct which had a slightly longer retention time in GLC than (I) and was believed to be 5-(trimethylsilyl)cyclooctene.

(*c*) *With* 5%-*platinum-on-carbon catalyst.* 1,5-Cyclooctadiene (2.17 g), trimethylsilane (2 ml), and 5%-Pt/C (40 mg, $5 \cdot 10^{-4}$ g-atom/mole of olefin) were placed in a thick-wall glass tube filled with argon and heated at about 200° for 16 h with shaking. After treatment of the reaction mixture in the usual way, the diene was recovered as almost pure 1,3-cyclooctadiene (1.0 g), and 1.1 g of 3-(trimethylsilyl)-cyclooctene (I) of 95% purity (contaminated with an isomeric adduct), b.p. 111–112°/39 mm, n_D^{20} 1.4753, was isolated.

(2) *Hydrosilation of* 1,3-*cyclooctadiene with trimethylsilane in the presence of chloroplatinic acid*

In the same manner as in Exp. (1a), 9.7 g of 1,3-cyclooctadiene was allowed to react with 9 ml of trimethylsilane in the presence of chloroplatinic acid solution (90 μl) to give 6.2 g of 3-(trimethylsilyl)cyclooctene (I), b.p. 110.5–110.7°/38 mm, n_D^{20} 1.4751, d_4^{20} 0.8560, MR_D 60.00 (calcd. 59.99). Its IR and NMR spectra were superimposable with those of the reaction product from 1,5-cyclooctadiene. In this case, (I) was very slightly contaminated with an isomeric product having shorter retention time in GLC than (I), which was possibly 4-(trimethylsilyl)cyclooctene having resulted from 1,2-addition of the silane to the diene.

(3) *Degradation of* (*I*) *by bromine and by trifluoroacetic acid*

In a test tube with a serum cap was placed 0.55 g of (I) dissolved in 1 ml of chloroform. To this was added bromine dropwise until a faint red color developed. The reaction was exothermic and quantitative. The mixture was analyzed by GLC.

Two products were formed, one being identified as trimethylbromosilane and the other as 3-bromocyclooctene[13]. Reaction of 0.55 g of (I) with an equivalent of trifluoroacetic acid (0.35 g) carried out in an analogous way gave rise to two products; one was identified as trimethylsilyl trifluoroacetate[14] and the other as cyclooctene by GLC.

(4) *Benzoyl peroxide-initiated addition of trichlorosilane to 1,5-cyclooctadiene*

In a flask equipped with a reflux condenser was placed a mixture of 10.8 g (0.1 mole) of 1,5-cyclooctadiene and 13.6 g (0.1 mole) of trichlorosilane in 100 ml of n-heptane. It was refluxed for 48 h, during which time a total of 1.7 g (0.007 mole) of benzoyl peroxide was added to it in four portions. The mixture was then cooled and added slowly to an excess of methylmagnesium bromide (1.7 *M* ether solution, 400 ml). After the addition was completed, the mixture was heated for a 20-h period and finally ether was removed by distillation. The residue was hydrolyzed, and the resulting organic layer was worked up in the usual way. Fractional distillation gave 1.3 g of unchanged 1,5-cyclooctadiene and 11 g of 2-(trimethylsilyl)bicyclo[3.3.0]octane (II), b.p. 108–109°/24 mm, n_D^{20} 1.4675, d_4^{20} 0.8697, MR_D 58.24 (calcd. 58.42) (Found: C, 72.38; H, 12.07. $C_{11}H_{22}Si$ calcd.: C, 72.44; H, 12.16%.) (II) did not react with bromine in carbon tetrachloride solution. Its IR and NMR spectra (see Fig. 2) are consistent with this structure.

(5) *Hydrosilation of bicyclo[3.3.0]octene-2*

(*a*) *With benzoyl peroxide initiator.* In essentially the same manner as in Exp. (4), a mixture of 4.3 g of bicyclo[3.3.0]octene-2, 5.4 g of trichlorosilane, and 0.68 g of benzoyl peroxide dissolved in 50 ml of n-heptane was refluxed for 64 h. Subsequent treatment of the reaction mixture with methylmagnesium bromide gave a product, b.p. 103°/22 mm, n_D^{20} 1.4684, in 34% yield. GLC analysis using several columns including Goley column (15 m×0.25 mm, SE-30 column, at 150°) revealed that this product was gas chromatographically homogeneous. However, its NMR spectrum exhibited, along with a number of diffused lines, two singlets at τ 9.97 and 9.99, with relative intensities of 1:2, which were assignable to two kinds of methyl protons on silicon in different environments. When a small amount of 2-(trimethylsilyl)bicyclo-[3.3.0]octane (II) was added to this sample, intensity for the signal at τ 9.97 distinctly increased. Therefore, another signal at τ 9.99 may be due to 3-(trimethylsilyl)bicyclo-[3.3.0]octane (III).

(*b*) *With chloroplatinic acid catalyst.* The adduct, n_D^{20} 1.4671, was obtained in 9% yield from the reaction of bicyclo[3.3.0]octene (4.3 g) with trimethylsilane (4 ml) in the presence of chloroplatinic acid (0.1 *M*, 8 μl) at 120° for 120 h. Its NMR spectrum also exhibited two kinds of methyl protons on silicon at τ 9.97 and 9.99 with the relative intensities of *ca.* 1:2.

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