3-Methyl-5-norbornen-2-one (X) had the following spectral data: ir, carbonyl at 1745 cm^{-1}; nmr, vinyl hydrogens at δ 6.1 and 6.5 (m, 2.0 hydrogen), methyl group at δ 1.1 (d, 2.8 hydrogens), all other hydrogens from δ 1.4 to 3.0 (m, 5.3 hydrogens).

Reaction of Mixtures of Norcamphor and 5-Norbornene-2-one with Sodium Hydride and Methyl Iodide.—The following reactions were run with 0.31 g (0.0076 mol) of a sodium hydride dispersion: a mixture of 1.65 g (0.015 mol) each of norcamphor and 5-norbornene-2-one with 2.1 g (0.015 mol) of methyl iodide; a mixture of 1.65 g (0.015 mol) of 5-norbornene-2-one and 6.6 g (0.060 mol) of norcamphor with 10.5 g (0.07 mol) of methyl iodide; and a mixture of 1.65 g (0.015 mol) of 5-norbornene-2-one and 0.83 g (0.0075 mol) of norcamphor with 2.1 g (0.015 mol) of methyl iodide. The main products were 2-methoxy-5-norbornene (VIII), 2-methoxynorbornane (II), and 3-methylnorcamphor (IV). The ratio of products indicated that both ketones reacted with sodium hydride at the same rate. The reason that no 3-methyl-5-norbornen-2-one (X) was formed is probably due to rapid proton transfer from norcamphor to the enolate of 5-norbornen-2-one. This transfer, much faster than methylation with methyl iodide, would give a product derived from the more stable enolate of norcamphor.

Preparation of 2-Methoxy-2-norbornene (XI).—2-Methoxy-2-norbornene (XI) was prepared in two steps by a procedure similar to that of Johannissian and Akunian.[13]

In a 50-ml flask under nitrogen was placed 4.4 g (0.09 mol) of norcamphor, 16 ml of methanol, a little *p*-toluenesulfonic acid, and 13 ml of trimethyl orthoformate. After refluxing 1 hr, the solution was cooled, a little potassium *t*-butoxide was added to neutralize the acid, and the solvent was boiled off. The product was distilled at 76–77° (20 mm); the yield of 2,2-dimethoxynorbornane was 5.5 g (88%).

A mixture of 5.3 g of this material and a little *p*-toluenesulfonic acid in a distillation apparatus was heated in an oil bath around 220°. The solution boiled vigorously and material slowly distilled over under nitrogen. The distillate was redistilled through a Nester/Faust Teflon spinning-band annular still, and the enol ether collected at 77–79° (75 mm). The yield of 2-methoxy-2-norbornene was 0.90 g: ir showed a strong $C{=}C$ band at 1610 cm^{-1}; nmr, vinyl hydrogens at δ 4.62 (d, 0.8 hydrogen), methoxy hydrogens at δ 3.52 (s, 3.1 hydrogens), bridgehead hydrogens at δ 2.75 and 2.90 (b, 1.7 hydrogens), all other hydrogens at δ 1.0–2.0 (m, 6.0 hydrogens). The material was very sensitive to moisture and could be stored only under a dry atmosphere.

Reaction of 2-Methoxy-2-norbornene (XI) with Sodium Hydride and Methyl Iodide.—2-Methoxy-2-norbornene (100 μl) was treated with 0.30 g (0.0074 mol) of a sodium hydride dispersion and 2.0 g (0.014 mol) of methyl iodide in 25 ml of glyme. Analyses of the reaction mixture after work-up showed the chief product to be norcamphor (formed by hydrolysis of the enol ether during work-up). Also present in small amounts were the products from the sodium hydride reduction of norcamphor in their normal proportion, probably owing to some hydrolysis of the enol ether before work-up because of traces of water in the reaction mixture. The yield of 2-methoxynorbornene was not unusually high; therefore the enol ether was not being reduced directly to the saturated ether.

Reaction of 2-Methoxy-2-norbornene (XI) and Norcamphor with Sodium Hydride and Methyl Iodide.—Norcamphor (1.53 g, 0.0139 mol) was treated with sodium hydride and methyl iodide in glyme as before, but in the presence of 0.51 g (0.0041 mol) of 2-methoxy-2-norbornene (XI). Analysis of the reaction mixture after work-up showed that the ratio of products formed was identical with that obtained in the absence of 2-methoxy-2-norbornene. Also present was some norcamphor, formed by hydrolysis of the enol ether during work-up. Since the yield of 2-methoxynorbornene was the same as in the absence of 2-methoxy-2-norbornene, the latter was not reduced by sodium hydride.

Reaction of Cyclopentanone with Sodium Hydride and Methyl Iodide.—Cyclopentanone (1.68 g, 0.02 mol) was treated with 4.1 g (0.10 mol) of a sodium hydride dispersion and 18 g (0.13 mol) of methyl iodide in 50 ml of glyme under the usual conditions. After work-up the products were analyzed by vpc. The only major product was 2,2,5,5-tetramethylcyclopentanone,[14] formed in 93% yield. Several small peaks indicated trace amounts of other products—one of these had a retention time identical with that of methoxycyclopentane,[15] and its size corresponded to a yield of 0.5% of this compound.

Registry No.—Sodium hydride, 7646-69-7; I, 17190-61-3; II, 10395-55-8; III (*exo*-OMe), 17206-77-8; III (*endo*-OMe), 17190-62-4; IV, 3915-75-1; V, 17190-85-1; VI, 13211-15-9; VII, 694-98-4; VIIIa, 17190-92-0; VIIIb, 17190-87-3; IX, 17190-88-4; X, 17190-89-5; XI, 17190-90-8; methyl iodide, 74-88-4.

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[13] A. Johannissian and E. Akunian, *Bull. Univ. État RSS Armenie*, **5**, 235, 245 (1930); *Chem. Abstr.*, **25**, 921 (1931).

[14] J. M. Conia, *Ann. Chim.* (Paris), **8**, 709 (1953).

[15] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

Addition Reactions of Benzonorbornadiene[1]

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Only products derived from initial *exo* attack by the reagent have been detected in the following reactions of benzonorbornadiene: the polar addition of *p*-toluenesulfenyl chloride, the radical additions of bromotrichloromethane and carbon tetrachloride, the catalytic additions of trichlorosilane, deuteriotrichlorosilane, and deuterium gas, and the reactions with dideuteriodiimide, *p*-tosyl azide, and picryl azide. From the radical addition of trichlorosilane and the chloroplatinic acid catalyzed additions of methyldichlorosilane and trimethylsilane, small amounts of the products of *endo* attack were obtained along with the predominant product of *exo* attack. The extent of *endo* addition is significantly greater than that observed in comparable addition reactions of norbornene, and considerably less than that observed with norbornadiene. From these results it is concluded that coordination control plays a much less important role in the chemistry of benzonorbornadiene than it does in the chemistry of norbornadiene. The value of pmr spectroscopy in elucidating the structures of substituted benzonorbornenes is discussed and illustrated.

A vast literature has accumulated which conclusively establishes that addition reactions of norbornene (I) proceed predominantly by way of initial attack from the *exo* side, regardless of the mechanistic category into which the reaction falls.[4] Only two accounts have appeared which report high yields of products derived from *endo* attack.[5] The overwhelming preference for *exo* attack is a consequence of the greater accessibility

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[1] This work is taken from the Ph.D. Thesis of R. A. Koster, University of Michigan, 1968.

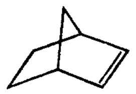
[2] Alfred P. Sloan Foundation Fellow, 1966–1968.

[3] Minnesota Mining and Manufacturing Fellow, 1965–1966; Petroleum Research Fund Fellow, 1966; NASA, Trainee, 1967.

[4] See footnotes 4, 5, and 6 of M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965), for an extensive bibliography of representative addition reactions of I.

[5] (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965); (b) A. C. Oehlschlager and L. H. Zalkow, *Chem. Commun.*, 5 (1966).

of the *exo* face; *endo* approach is blocked sterically by the ethano bridge to a greater extent than is *exo* approach by the methano bridge. In the norbornadiene system (II) there is also a distinct preference for *exo* attack.[6] However, there are several noteworthy examples of reactions which occur preferentially on the *endo* face of the norbornadiene structure. For example a number of metal carbonyl derivatives of norbornadiene have been prepared in which the norbornadiene serves as a bidentate ligand (structure III), a role it can play only if coordination with the metal occurs on the *endo* side of the molecule.[7] Norbornadiene reacts with several reactive dienophiles to produce tetracyclo-[3.2.1.1^{3,8}.0^{2,4}]nonane derivatives (structure IV),[6] in cycloaddition processes involving both of the double bonds of norbornadiene. Several dimerization reactions of norbornadiene give structures analogous to IV.[8] Some of the most intriguing examples of *endo* attack are provided by the chloroplatinic acid and platinum on carbon catalyzed additions of trichlorosilane,[6] methyldichlorosilane,[6] trimethylsilane,[6] and trimethylgermanium hydride[9] to norbornadiene, in which products of *endo* attack predominate.[10] Kuivila suggests that the unusual steric course of these addition reactions, the only ones which have been found to give predominantly products having the general structure V, is a consequence of a phenomenon he designates as coordination control. He suggests that a complex is formed between the silane or germanium hydride, the catalyst, and the olefin, in which the norbornadiene acts as a bidentate ligand. The product is then formed by an intramolecular ligand transfer process on the *endo* side of the molecule. In summary then, it appears that, although *exo* addition to norbornadiene is, for steric reasons, the preferred course of most of its addition reactions, attack from the less accessible *endo* side becomes the favored process when norbornadiene reacts as a homoconjugated diene or when it functions as a bidentate ligand.



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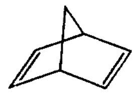

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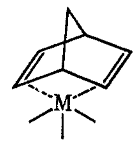

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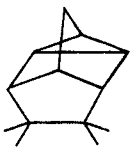

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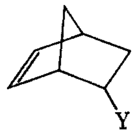
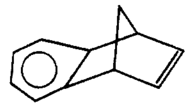


V



VI

It is of interest to establish the extent to which coordination control influences the addition reactions of benzonorbornadiene (VI). Since simple benzene derivatives are generally weaker π bases than olefins, benzonorbornadiene would be expected to be a poorer bidentate ligand than norbornadiene. However, since aromatic compounds are known to form complexes with a variety of types of reagents,[11] including halogens, certain Lewis acids, polyhalomethanes, certain free radicals, polynitroaromatics, metals, metal ions, maleic anhydride, and tetracyanoethylene, the operation of coordination control in benzonorbornadiene chemistry seemed a possibility worthy of study. The importance of such an effect would, of course, be revealed by the extent to which addition occurs from the usually less accessible *endo* side.

It was the general purpose of this work to characterize the products of a variety of addition reactions of benzonorbornadiene,[12] in order to assess the effect of the *o*-phenylene bridge on the reactions of the double bond, and to establish the similarities and differences in the chemistry of norbornene, norbornadiene, and benzonorbornadiene. In particular, it was undertaken in order to establish the importance of coordination control in the chemistry of benzonorbornadiene.

Results

The products of the following addition reactions of benzonorbornadiene (VI) have been characterized: electrophilic addition of *p*-toluenesulfenyl chloride; radical addition of bromotrichloromethane, carbon tetrachloride, and trichlorosilane; catalytic addition of deuterium, deuteriotrichlorosilane, trichlorosilane, methyldichlorosilane, and trimethylsilane; reduction by dideuteriodiimide; and reaction with *p*-tosyl azide and picryl azide. Unsuccessful attempts were also made to obtain adducts from VI and tetracyanoethylene and maleic anhydride under thermal and photolytic conditions. The results of these studies will be discussed in this section. Physical properties and procedural details may be found in the Experimental Section.

Proton magnetic resonance spectroscopy is a powerful tool in elucidating the structure of substituted norbornenes[13-15] and benzonorbornenes,[16] and the structures of the adducts prepared in this work were all established

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(6) For an extensive bibliography of representative addition reactions of II, see footnote 12 of H. G. Kuivila and C. R. Warren, *J. Org. Chem.*, **29**, 2845 (1964).

(7) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. I, Elsevier Publishing Co., New York, 1966, pp 81-87.

(8) (a) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012, 5941 (1966); (b) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967); (c) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967); (d) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966).

(9) R. H. Fish and H. G. Kuivila, *J. Org. Chem.*, **31**, 2445 (1966).

(10) Two other reports of *endo* addition to norbornadiene have appeared recently: (a) sulfur dichloride, F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966); (b) methylphosphonous dichloride, M. Green, *J. Chem. Soc.*, 541 (1965).

(11) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(12) The following is a bibliography of published studies of addition reactions to benzonorbornadiene and its derivatives: (a) Br_2, PhN_3, CH_2N_2, G. Wittig, and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) Br_2, CF_3CO_2H/H_2O_2, $KMnO_4/OH^-$, $Pb(OAc)_4$, J. Meinwald and G. A. Wiley, *J. Amer. Chem. Soc.*, **80**, 3667 (1958); (c) $Hg(OAc)_2$, T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); (d) H_2SO_4/H_2O, perphthalic acid, P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (e) $HOAc/H_2SO_4$, B_2H_6, P. Bruck, *Tetrahedron Lett.*, 449 (1962); (f) HBr, HCl, $HOAc/H_2SO_4$, G. A. Wiley and L. E. Barstow, 151st National Meeting of the American Chemical Society, Pittsburg, Pa., March 1966, p K5; (g) DCl, $DOAc/D_2SO_4$, S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966); (h) Br_2, Cl_2, S. J. Cristol and G. W. Nachtigall, *ibid.*, **32**, 3727 (1967); (i) Br_2, Cl_2, J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967); (j) N_3CO_2Et, K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 869 (1965); (k) 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene, K. MacKenzie, *J. Chem. Soc.*, 473 (1960); (l) TCNE, R. C. Cookson, J. Dance, and J. Hudec, *ibid.*, 5416 (1964); (m) H_2, K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966); (n) Rh/C dimerization, ref 8d.

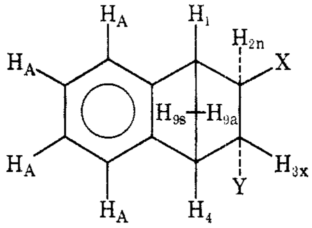
(13) J. C. Davis and T. V. VanAuken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

(14) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963).

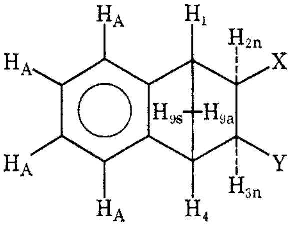
(15) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(16) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

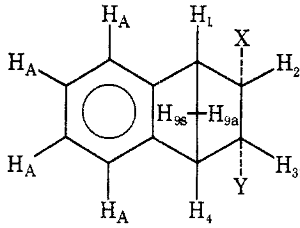
by interpretation of their pmr spectra. In disubstituted adducts (structures VII and VIII), it is usually possible to identify the signal due to each of the six different aliphatic protons present. If the signals due to the two nonequivalent bridgehead benzylic protons, H-1 and H-4, are of different complexity, it implies that one is adjacent to an *endo* proton and one is adjacent to an *exo* proton (since $J_{1,2n} = J_{4,3n} = 0$ cps and $J_{1,2x} = J_{4,3x} = 3.5$–$4.0$ cps), and consequently that the adduct has the *trans* structure (VII) rather than a *cis* structure, (VIII or IX). Likewise, if the signals due to H-9a and H-9s are of different complexities, it implies that there is at least one *endo* proton on the ethano bridge (since $J_{2x,9a} = J_{3x,9a} = 0$ cps, $J_{2x,9s} = J_{3x,9s} = 0$ cps, $J_{2n,9a} = J_{3n,9a} = 0$ cps, whereas $J_{2n,9s} = J_{3n,9s} = 1.5$–$2.5$ cps). From double resonance experiments it is possible to establish which protons are coupled, and from this information an unambiguous assignment of structure is possible. Examples to be discussed below will serve to illustrate the approach. In monosubstituted structures, such as XI and XII, it is not always possible to assign unambiguously a signal to each proton. However, H-1 and H-4 can always be identified, and, if the signals due to these protons differ in complexity, then only one can be adjacent to an *exo* proton, which would imply that X is *exo*, and that H-4 is adjacent to H-3n and H-3x, while H-1 is adjacent to H-2n. Chemical shifts for the protons of compounds prepared in this work are listed in Table I. Observed coupling constants for all cases in which simple visual examination of decoupled spectra permitted their calculation are listed in Table II.



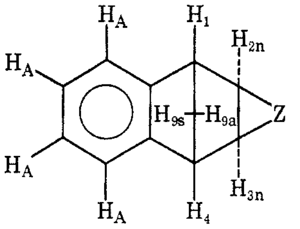
VIIa, $X = SC_6H_4CH_3$; $Y = Cl$
b, $X = CCl_3$; $Y = Br$
c, $X = CCl_3$; $Y = Cl$



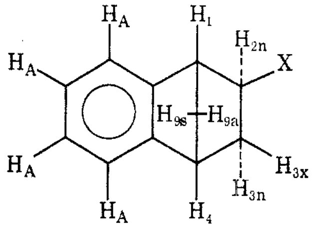
VIIIa, $X = SiCl_3$; $Y = D$
b, $X = Y = D$



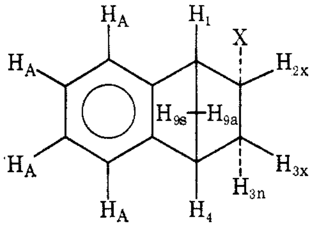
IX



Xa, $Z = NSO_2C_6H_4CH_3$
b, $Z = NC_6H_2(NO_2)_3$



XIa, $X = SiCl_3$
b, $X = SiCl_2CH_3$
c, $X = Si(CH_3)_3$



XIIa, $X = SiCl_3$
b, $X = SiCl_2CH_3$
c, $X = Si(CH_3)_3$

p-Toluenesulfenyl Chloride.—Upon treatment of VI with p-toluenesulfenyl chloride, a 96% yield of adduct was obtained. This product was identified as *endo*-3-chloro-*exo*-2-thiocresylbenzonorbornene (VIIa), the product of *trans* addition and initial *exo* attack. No other products were detected. The proof of structure of this compound will be discussed to illustrate the utility of pmr spectra in assigning structures to this type of compound. H-1 and H-4 appear as signals of different complexity at τ 6.77 (narrow multiplet) and 6.58 (broad complex multiplet), thereby implying a *trans* relationship between the protons on C-2 and C-3. The signal due to the proton on C-3, the carbon bearing the chlorine, appears at τ 5.75 (three-line multiplet), and the signal due to the proton on C-2, the carbon bearing the thiocresyl group, appears at 7.04 (three-line multiplet). Irradiation of the signal at τ 5.75 has no effect upon the signal at 6.77 but causes the signal at 6.58 to collapse to a narrow multiplet, resembling the signal at 6.77. Thus the proton of C-3 is coupled to H-4 and is, therefore, *exo*. This is affirmed by noting that irradiation of the signal at τ 5.75 has no effect upon the signals at 7.80 (two three-line mulitiplets) and 8.07 (two complex multiplets) assigned to H-9a and H-9s, respectively. The signal at τ 7.04, assigned to the proton on C-2, is reduced to a doublet by irradiation of H-3x, strongly implying that it is *endo*, since it would still be coupled to H-9s. Simultaneous irradiation of H-1 and H-4 reduces the three-line signal at τ 5.75 due to H-3x to a doublet, from which the coupling constant between H-3x and H-2n can be determined ($J = 3.5$ cps). This confirms the *trans* orientation of H-2 and H-3 since coupling constants between *cis* protons are larger than 3.5 cps. Irradiation of H-1 and H-4 has no effect on the three-line multiplet at τ 7.04 due to H-2n, confirming its *endo* orientation. Irradiating the signal at τ 7.04, due to H-2n, has no effect on the H-1 and H-4 signals, collapses the H-3x signal to a doublet, has no effect on the signal at τ 7.80, due to H-9a, and reduces the complexity of the signal at 8.07 due to H-9s. Simultaneous irradiation of H-9a and H-9s collapses the H-2n signal at τ 7.04 to a doublet and has no effect upon the H-3x signal at 5.75. There can be no doubt that the product of polar addition of p-toluenesulfenyl chloride to benzonorbornadiene is *endo*-3-chloro-*exo*-2-thiocresylbenzonorbornene (VIIa).

Bromotrichloromethane and Carbon Tetrachloride.—The free-radical additions of bromotrichloromethane and carbon tetrachloride to VI gave *endo*-3-bromo-*exo*-2-trichloromethylbenzonorbornene (VIIb) and *endo*-3-chloro-*exo*-2-trichloromethylbenzonorbornene (VIIc) in yields of 92 and 100%, respectively. Structures were established by interpretation of coupled and decoupled pmr spectra, as discussed above for the p-toluenesulfenyl chloride adduct. Both compounds are products of *trans* addition, with initial *exo* attack by the trichloromethyl radical, followed by chain transfer on the *endo* side. No products derived from initial *endo* attack were detected.

Trichlorosilane (AIBN Initiated).—The free-radical addition of trichlorosilane to VI gave an adduct in 55% yield. In the pmr spectrum of this adduct, there were signals at τ 6.50 (two narrow doublets) and 6.59 (broad complex multiplet) of quite different complexities,

TABLE I

CHEMICAL SHIFTS FOR PROTONS IN SUBSTITUTED BENZONORBORNENES[a]

Compd	Proton (τ units, TMS reference[b])									
	H-1	H-4	H-2n	H-3n	H-2x	H-3x	H-9a	H-9s	H_A	Other
VIIa	6.77 nm[c]	6.58 bcm	7.04 3lm	...	...	5.75 3lm	7.80 2 3lm	8.07 2 cm	2.6–3.1	7.72 $Ar-CH_3$
VIIb	6.38 nm	6.44 bcm	7.19 2 D	...	...	5.52 2 D	7.37 2 3lm	8.05 2 4lm	2.6–3.0	...
VIIc	6.32 nm	6.49 nm	7.30 2 D	...	...	5.52 3lm	7.43 2 m	8.09 2 4lm	2.5–3.1	...
VIIIa	6.55 nm	6.69 nm	8.61 2 D	8.84 2 D	...	...	8.24 2 3lm	8.45 2 5lm	2.8–3.2	...
XIa	6.50 2D	6.59 bcm	8.61 cm	8.84 cm	...	7.80 8lm	8.22 2 3lm	8.44 2 cm	2.7–3.2	...
XIb	6.60 nm	6.68 bcm	8.5 ↔ 9.2 cm		...	8.05 cm	8.41 ↔ 8.65 cm		2.8–3.2	9.34 $Si-CH_3$
XIc	6.90 nm	6.77 bcm	8.86 ↔ 9.7 cm		...	8.30 cm	8.41 ↔ 8.86 cm		2.8–3.3	9.97 $Si-CH_3$
Benzonorbornene	6.72 cm	6.72 cm	8.86 cm	8.86 cm	8.15 cm	8.15 cm	8.52 2 3lm	8.27 2 cm	2.8–3.2	...
VIIIb	6.72 3lm	6.72 3lm	8.86 D	8.86 D	...	...	8.57 2 3lm	8.26 2 cm	2.8–3.2	...
Xa	6.64 nm	6.64 nm	6.94 nm	6.94 nm	...	...	7.99 ↔ 2 nm	8.63 2 nm	2.0–3.1	7.60 $ArCH_3$
Xb	6.38 nm	6.38 nm	7.02 nm	7.02 nm	...	...	8.09 ↔ 2 nm	8.45 2 nm	2.93 A_2B_2	1.16 Picryl H_a

[a] The numbering system for the ring is as illustrated in structures VII–XII; see Chemical Abstracts Ring Index, entry 2557, p 329. [b] All spectra were obtained in CCl_4, except Xa ($CDCl_3$) and Xb (d_6-DMSO). [c] Abbreviations: nm, narrow multiplet; bcm, broad complex multiplet; 3lm, three-line multiplet; 2 3lm, two three-line multiplets; 2 D, two doublets; ↔, relative assignments uncertain.

TABLE II

COUPLING CONSTANTS[a] IN SOME SUBSTITUTED BENZONORBORNENES

Coupled protons[b]	Compound				
	VIIa	VIIb	VIIc	VIIIa	VIIIb
1–9a	2.0	1.5	1.5	1.5	2.0
1–9s	2.0	1.5	1.5	1.5	2.0
4–9a	2.0	1.5	1.5	1.5	2.0
4–9s	2.0	1.5	1.5	1.5	2.0
2n–9s	2.5	1.5	1.6	1.5	2.0
3n–9s	...	...	...	1.5	2.0
9a–9s	10.0	10.0	10.0	9.0	8.5
4–3x	4.0	3.5	4.0	...	...
2n–3x	3.5	5.0	5.0	...	...
2n–3n	...	...	...	9.0	6.8

[a] Coupling constants are given in cycles per second (cps). [b] The numbering system for the ring is as illustrated in structures VII–XII (See Chemical Abstracts Ring Index, entry 2557, p 329).

due to H-1 and H-4. This requires that H-2 is *endo*, and that the trichlorosilyl group is *exo*, suggesting that the product is *exo*-2-trichlorosilylbenzonorbornene (XIa). Authentic XIa, prepared by the catalytic addition of trichlorosilane to VI (*vide infra*) has a characteristic eight-line multiplet centered at τ 7.80, due to H-3x. In the radical adduct, this signal although similar, is somewhat different. The relative peak intensities differ, the peaks are wider, resolution is not so good, and there appear to be extra peaks. This is evidence for contamination by small amounts of the *endo* isomer (XIIa). H-3n of XIIa would give rise to a signal in the same region of the spectrum as H-3x of XIa, and it is doubtless owing to this signal that there are small differences in the appearance of the pmr spectra of the radical and catalytic trichlorosilane adducts. Unfortunately, no reliable method of obtaining a quantitative analysis of this product mixture was evident. Conversion into the trimethylsilyl derivative[6] did not proceed in sufficiently high yield to engender any confidence that the ratio of *exo*- to *endo*-trimethylsilyl derivatives (XIc to XIIc) produced was an accurate reflection of the ratio of XIa to XIIa in the initial mixture. The signals due to H-1 and H-4 in the radical addition product are very similar to, but not identical with, the corresponding signals in authentic XIa. This means that the radical adduct is predominantly XIa, since large amounts of XIIa in the mixture would have resulted in a marked difference in the appearance of the region of the pmr spectrum due to H-1 and H-4. We can only estimate that the radical adduct contains less than 10% *endo* isomer XIIa. At any rate, the addition has proceeded largely, but not exclusively, by way of initial *exo* attack.

Deuteriotrichlorosilane[17] (Chloroplatinic Acid Catalyzed).—The chloroplatinic acid catalyzed addition of deuteriotrichlorosilane to benzonorbornadiene gave a 79% yield of an adduct, which was shown to be *exo*-2-trichlorosilyl-*exo*-3-deuteriobenzonorbornene (VIIIa), the product of *exo,cis* addition. No other products

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[17] We wish to thank Dr. J. W. Ryan of the Dow Corning Corp. for his generous gift of a sample of deuteriotrichlorosilane.

could be detected, indicating that the reaction is 100% stereospecific. The signals due to H-1 and H-4 appear as similar narrow multiplets at τ 6.55 and 6.69, indicating that the protons on C-2 and C-3 must be *cis* and most likely are *cis,endo*. The signal due to H-9a appears at τ 8.24 (two three-line multiplets) and the signal due to H-9s appears at 8.45 (two five-line multiplets). The difference in multiplicity of the H-9a and H-9s signals requires that there be *endo* protons on C-2 and C-3. H-2 appears as two doublets centered at τ 8.61, and H-3 appears as two doublets at 8.84. Simultaneous irradiation of H-1 and H-4 causes the signal at τ 8.24, due to H-9a, to collapse to a doublet and the signal at 8.45, due to H-9s, to collapse to a pair of triplets, further confirming the presence of two *endo* protons. Irradiation of H-1 and H-4 has no effect upon the signals due to H-2 and H-3. Irradiation of the signal at τ 8.24, due to H-9a, had no effect upon the signals at 8.61 and 8.84 due to H-2n and H-3n, whereas irradiation of the H-9s proton at 8.45 caused the H-3n pair of doublets to collapse to a single doublet. The effects of irradiation of H-9s on the signal at τ 8.61, due to H-2n, was difficult to assess owing to saturation. There is no doubt that the product of the chloroplatinic acid catalyzed addition of deuteriotrichlorosilane to benzonorbornadiene is *exo*-2-trichlorosilyl-*exo*-3-deuteriobenzonorbornene (VIIIa).

Trichlorosilane, Methyldichlorosilane, and Trimethylsilane (Chloroplatinic Acid Catalyzed).—The chloroplatinic acid catalyzed addition of trichlorosilane to VI gave a 77% yield of *exo*-2-trichlorosilylbenzonorbornene (XIa). The assignment of structure is based on analogy to the deuteriotrichlorosilane addition which was shown to proceed exclusively by a *cis,exo* addition pathway. This is confirmed by the lack of identity of the signals due to H-1 (τ 6.50, two narrow doublets) and H-4 (τ 6.59, broad complex multiplet), indicating that only one bridgehead proton was adjacent to an *exo* proton. Since H-4 must be adjacent to both an *endo* and an *exo* proton, H-3n and H-3x, then the proton of C-2 must be *endo* and the trichlorosilyl group must be *exo*.

The chloroplatinic acid catalyzed addition of methyldichlorosilane gave a 77% yield of an adduct mixture. In the pmr spectrum, H-1 and H-4 were present as signals of differing complexity at τ 6.60 (narrow multiplet) and 6.68 (broad complex multiplet), indicating that the *exo* adduct, XIb, predominates. The ratio of *exo*-2-methyldichlorosilylbenzonorbornene (XIb) to *endo*-2-methyldichlorosilylbenzonorbornene (XIIb) was found to be 83:17. This ratio was established by measuring the relative areas of signals at τ 9.34 and 9.60, which were assigned to the methyl group of the dichloromethylsilyl group of the *exo* and *endo* adducts, respectively. The methyl group of the *endo* isomer will experience shielding from the phenylene group, and will appear at higher field.[6] Addition has thus occurred by predominant, but not exclusive, *exo* ligand transfer.

Trimethylsilane gave an 86% yield of an adduct mixture containing *exo*-2-trimethylsilylbenzonorbornene (XIc) and *endo*-2-trimethylsilylbenzonorbornene (XIIc) in a ratio of 96:4. Addition has thus occurred by predominant but not exclusive *exo* ligand transfer. The H-1 and H-4 protons appeared as signals of different complexity at τ 6.90 (narrow multiplet) and 6.77 (broad complex multiplet). The methyl groups of the trimethylsilyl groups appeared at τ 9.97 for the *exo* isomer and 10.38 for the *endo* isomer. Relative areas of these two peaks gave the ratio of XIc to XIIc.

Deuterium (Dideuteriodiimide Reduction and Catalytic Deuteration).—Reduction of benzonorbornadiene with dideuteriodiimide gave exclusively the *cis,exo* addition product (VIIIb). In benzonorbornene, H-2n and H-3n appear at τ 8.86, whereas H-2x and H-3x appear at 8.15.[12m] In the dideuteriodiimide reduction product, there is a signal at τ 8.86, but none at 8.15, indicating the absence of *exo* protons. Irradiation of the H-1 and H-4 protons at τ 6.72 has no effect on the signal at 8.86 due to the protons on C-2 and C-3, confirming that they are *endo*. Irradiation of H-1 and H-4 causes the signal at τ 8.57 (two three-line multiplets) to collapse to a doublet, and the signal at 8.26 (two five-line multiplets) to collapse to a pair of triplets. This confirms the assignment of the τ 8.57 signal to H-9a and the 8.26 signal to H-9s and further confirms the presence of two *endo* protons. There is no doubt that the product of reduction of VI with dideuteriodiimide is *cis,exo*-2,3-dideuteriobenzonorbornene (VIIIb).

Catalytic reduction of VI with deuterium gas using platinum on carbon, palladium on carbon, palladium on alumina, and rhodium on carbon as catalysts gave exclusively the product (VIIIb) derived from *cis,exo* addition.

Tosyl Azide.—A 45% yield of the *exo*-aziridine (Xa) was obtained from the reaction of VI with tosyl azide. No *endo* adduct was detected. The assignment of structure to this adduct was not so rigorous or full of cross checks as for the other adducts. The bridgehead protons, H-1 and H-4, appear as a rather narrow signal at τ 6.64, much narrower and less complex than any of the signals due to bridgehead protons adjacent to *exo* protons on C-2 or C-3 which have been observed in other adducts. It is thus concluded that H-1 and H-4 are not coupled to the protons on C-2 and C-3, which must, therefore, be *endo*. A similar argument has been advanced to differentiate between the *exo* and *endo* isomers of tricyclo[3.2.1.0^{2,4}]octene-6.[18] H-2 and H-3 appear as a narrow signal at τ 6.94. This is consistent with an *endo* orientation for H-2 and H-3, since, were they *exo*, they would be coupled to H-1 and H-4 to an extent readily observable in the spectrum ($J_{1,2x}$ = $J_{4,3x}$ = 3.5–4.0 cps). Coupling between *endo* protons on C-2 and C-3 with H-9s is generally around 1.5 cps, and so might not be so evident in the spectrum as coupling between an *exo* proton and a bridgehead proton. Coupling between H-2n or H-3n and H-9s might also be less in this compound than is usually the case as a consequence of changes in the angular relationship between these protons resulting from geometric modifications attendant to the introduction of the aziridine moiety.

Picryl Azide.—A 70% yield of the *exo* aziridine (Xb) was obtained from the reaction of VI with picryl azide. No *endo* adduct was detected. The structure was assigned on the basis of the narrow signals at τ 6.38, due to H-1 and H-4 and at 7.02 due to H-2n and H-3n.

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(18) K. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

Unsuccessful Additions.—Attempts to obtain a cycloadduct of benzonorbornadiene and tetracyanoethylene under thermal (100°, 20 hr) or photolytic conditions (Hanovia 450-W mercury lamp, Pyrex filter, 20 hr, with acetophenone) failed. Similarly, no benzonorbornadiene–maleic anhydride adduct could be isolated from sensitized (acetophenone, benzophenone) or unsensitized photochemical reactions

Discussion

Coordination Control.—In Table III the extents of *endo* attack by a variety of reagents on the three compounds norbornene (I), norbornadiene (II), and benzonorbornadiene (VI) have been tabulated. It is apparent that in no case is initial *endo* attack the predominant mode of attack on benzonorbornadiene (VI). Even picryl azide, a reagent which should complex readily with the aromatic ring, reacts exclusively on the *exo* side of the double bond. The two reactions which gave the greatest amount of *endo* product from VI, the radical additions of chlorine[12h] and deuterium bromide,[12f] give comparable results with norbornene (I),[19] in which no such effect as coordination control is possible. Indeed, from the processes summarized in Table I, it is clear that benzonorbornadiene (VI) resembles norbornene (I) in its behavior in addition reactions more closely than it does norbornadiene (II). The results of the catalytic hydrosilation reactions are most informative. The amount of *endo* product derived from benzonorbornadiene is significantly greater than from norbornene, but far less than from norbornadiene, from which it is the main product. Thus, it may be concluded that coordination control plays a minor role in benzonorbornadiene chemistry. This is probably a consequence of the reduced capacity of a benzene ring relative to a double bond to serve as a coordination site. Perhaps the ability of benzonorbornadiene to serve as a bidentate ligand could be enhanced by substituting the aromatic moiety with a group which would increase its π basicity, but it is clear that coordination control is a much less significant factor in determining the stereochemical course of addition reactions to benzonorbornadiene than to norbornadienes.

Pmr Spectra.—Examples discussed in the results serve to illustrate the great utility of pmr spectroscopy in assigning structures to substituted benzonorbornenes. Recently Cristol and Nachtigall[16] have published several generalizations concerning the pmr spectra of benzonorbornene compounds, based upon studies of the products of addition of bromine and chlorine to benzonorbornadiene. The data derived from adducts prepared in this work, summarized in Tables I and II, provides further documentation of their generalizations. (1) In benzonorbornene, H-9a appears at higher field than H-9s, but for all benzonorbornenes with an *exo* substituent at C-2, H-9s is at higher field then H-9a. (2) An *exo* substituent on C-2 causes H-3x to appear at lower field than H-3n. (3) $J_{1,9s}$ is smaller in the benzonorbornene system than in the norbornene system (1.5–2.0 cps *vs.* 2.1–3.1 cps). (4) $J_{2n,3x}$ is larger in the benzonorbornene system than in the norbornene system (3.5–5.0 cps *vs.* 2.6–2.9 cps). (5) There appears to be very weak coupling between H-1 and H-2n and between H-4 and H-3n in the benzonorbornene system, which is manifested by slightly broadened signals in appropriately decoupled spectra.

TABLE III
PERCENTAGES OF *endo* ATTACK ON NORBORNENE, NORBORNADIENE, AND BENZONORBORNADIENE

	Process	% *endo* attack I	II	VI
1.	Polar addition of Br_2	0[a]	0[b]	0[c–e]
2.	Polar addition of Cl_2	0[f]	. . .	0[d,e]
3.	Polar addition of DCl	0[g]	. . .	0[h]
4.	Polar addition of $Hg(OAc)_2$	0[i]	0[j]	0[k]
5.	Polar addition of $CH_3C_6H_4SCl$	0[l]	0[l]	0[m]
6.	Radical addition of Cl_2	. . .	. . .	20[d]
7.	Radical addition of DBr	20[n]	. . .	28[o]
8.	Radical addition of $BrCCl_3$	0[p]	0[q]	0[m]
9.	Radical addition of CCl_4	0[p]	0[r]	0[m]
10.	Radical addition of $HSiCl_3$	0[s]	8[s]	≤10[m]
11.	Catalytic addition of $HSiCl_3$	. . .	100[s]	0[m]
12.	Catalytic addition of $HSiCl_2CH_3$	3[s]	94[s]	17[m]
13.	Catalytic addition of $HSi(CH_3)_3$	. . .	77[s]	4[m]
14.	Catalytic addition of D_2	0[t]	0[t]	0[m]
15.	Reaction with N_2D_2	0[u]	0[u]	0[m]
16.	Reaction with arylsulfonyl azides	0[v]	0[w]	0[m]
17.	Reaction with picryl azide	. . .	. . .	0[m]

[a] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3116 (1950); H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954). [b] L. Schmerling, J. P. Luivisi, and R. W. Welch, *ibid.*, **78**, 2818 (1956); G. T. Youngblood, E. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958); S. Winstein, *J. Amer. Chem. Soc.*, **83**, 1516 (1961). [c] See ref 12b. [d] See ref 12h. [e] See ref 12i. [f] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954); M. L. Poutsma, *ibid.*, **87**, 4293 (1965). [g] H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3900 (1967). [h] See ref 12g. [i] T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 14 (1959); T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963). [j] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964); R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Amer. Chem. Soc.*, **82**, 535 (1960). [k] See ref 12c. [l] S. J. Cristol, R. P. Arganbright, G. P. Brindell, and R. M. Heitz, *J. Amer. Chem. Soc.*, **79**, 6035 (1957). [m] This work. [n] H. Kwart and J. T. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964). [o] See ref 12f. [p] E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964). [q] N. O. Brace, *ibid.*, **27**, 3027 (1962). [r] D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963). [s] See ref 6. [t] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965). [u] W. C. Baird, B. Franzus, and J. H. Surridge, *ibid.*, **89**, 400 (1967). [v] J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); L. H. Zalkow and A. C. Oehlschlager, *ibid.*, **28**, 3303 (1963); L. H. Zalkow, A. C. Oehlschlager, G. A. Cabot, and R. C. Hale, *Chem. Ind.* (London), 1556 (1964). [w] J. E. Franz and C. Osuch, *ibid.*, 2058 (1964); A. C. Oehlschlager and L. H. Zalkow, *ibid.*, 70 (1965).

Experimental Section

Benzonorbornadiene (VI) was prepared by the method of Witting and Knauss[12a] from cyclopentadiene and benzyne.[20]

Addition of *p*-Toluenesulfenyl Chloride to VI.—*p*-Toluenesulfenyl chloride[21] (0.91 g, 0.0057 mol) was added dropwise to 1.0 g (0.007 mol) of benzonorbornadiene at 0°. As soon as the red color of the *p*-toluenesulfenyl chloride had been discharged, excess olefin was removed by distillation at reduced pressure. The liquid residue (1.76 g) was chromatographed over 50 g of silica gel. A total of 1.64 g (96% yield) of product was eluted with 10–15% benzene in petroleum ether (30–60°). Recrystallization from absolute alcohol gave 1.50 g (88%) of *endo*-3-chloro-*exo*-2-thiocresylbenzonorbornene (VIIa), mp 63.5–64.5°.

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(19) See Table III, footnote *n*.

(20) L. Friedman, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

(21) H. Leckes, F. Holschneider, K. Koberle, W. Speer, and P. Stocklin, *Chem. Ber.*, **58**, 409 (1925).

Anal. Calcd for $C_{18}H_{17}ClS$: C, 71.86; H, 5.69; Cl, 11.78; S, 10.66. Found: C, 71.81; H, 5.75; Cl, 11.82; S, 10.60.

Addition of Bromotrichloromethane.—Benzonorbornadiene (1.80 g, 0.0127 mol), bromotrichloromethane (5.1 ml, 9.9 g, 0.050 mol), and benzoyl peroxide (0.05 g) were allowed to react for 24 hr at 75–80°. Excess bromotrichloromethane was removed by distillation at aspirator pressure. The residue was dissolved in a limited amount of hot absolute ethanol, and upon cooling a total of 3.97 g (92% yield) of product could be isolated. Further purification by recrystallization from ethanol gave a white solid, melting from 65–66°, identified as *endo*-3-bromo-*exo*-2-trichloromethylbenzonorbornene (VIIb).

Anal. Calcd for $C_{12}H_{10}Cl_3Br$: C, 42.33; H, 2.96; Cl, 31.24; Br, 23.57. Found: C, 42.48; H, 3.09; Cl, 31.08; Br, 23.60.

Addition of Carbon Tetrachloride.—A mixture of benzonorbornadiene (4.26 g, 0.030 mol), carbon tetrachloride (60 g, 0.39 mol), and benzoyl peroxide (0.03 g) was refluxed for 70 hr. Excess carbon tetrachloride was removed by distillation at reduced pressure, leaving a residue (8.89 g, 100%) which crystallized on standing. This unpurified product had an infrared and pmr spectrum indistinguishable from an analytical sample obtained by recrystallization from ethanol, mp 58.5–59.5°, identified as *endo*-3-chloro-*exo*-2-trichloromethylbenzonorbornene (VIIc).

Anal. Calcd for $C_{12}H_{10}Cl_4$: C, 48.69; H, 3.41; Cl, 47.91. Found: C, 48.62; H, 3.39; Cl, 47.74.

Radical Addition of Trichlorosilane.—A mixture of benzonorbornadiene (1.42 g, 0.01 mol), trichlorosilane (1.35 g, 0.01 mol), and azobisisobutyronitrile (0.25 g) was heated at 100° for 15 hr in a sealed tube. Volatile materials were removed on a rotary concentrator, and the residue was further purified by short-path distillation, giving 1.52 g (55%) of adduct largely *exo*-2-trichlorosilylbenzonorbornene (XIa), along with small amounts of the *endo* isomer (XIIa). A satisfactory elemental analysis of this material was not obtained as a consequence of its high hydrolytic reactivity.

The addition of deuteriotrichlorosilane to benzonorbornene was carried out using the same procedure described above. The pmr spectrum indicated a complex mixture of isomeric adducts resulting from predominant but not exclusive *exo* attack by the trichloromethyl radical, followed by chain transfer from both the *exo* and *endo* sides. A quantitative analysis of the mixture was not obtained. The results are reminiscent of those obtained when deuterium bromide is added to norbornene.[19]

Catalytic Addition of Trichlorosilane and Deuteriotrichlorosilane.[17]—A mixture of benzonorbornadiene (1.42 g, 0.01 mol), trichlorosilane (1.35 g, 0.01 mol), and 1 drop of a 0.1 *N* isopropyl alcohol solution of chloroplatinic acid was heated at 100° for 18 hr in a sealed tube. Volatile components were removed on a rotary concentrator, and the residue was purified by a short-path distillation, giving 2.2 g (77%) of adduct which was identified as *exo*-2-trichlorosilylbenzonorbornene (XIa) by its pmr spectrum. No *endo* isomer (XIIa) was present.

Deuteriotrichlorosilane, under identical reaction conditions, gave a 79% yield of *cis,exo*-3-deuterio-2-trichlorosilylbenzonorbornene (VIIIa).

Catalytic Addition of Methyldichlorosilane.—Over a 20-min period, 4.5 g (0.018 mol) of methyldichlorosilane was added to a mixture of 4.27 g (0.030 mol) of benzonorbornadiene and 0.1 ml of a 0.1 *N* ethanolic chloroplatinic acid solution. The reaction mixture was maintained at 50° for 4 hr, after which volatile material was removed on a rotary concentrator, and then the residue was distilled at 74° (0.1 mm) in a short-path apparatus, giving 5.9 g (77%) of adduct, identified as a mixture of *exo*- and *endo*-2-methyldichlorosilylbenzonorbornene (XIb and XIIb) in a ratio of 83:17.

Catalytic Addition of Trimethylsilane.—A mixture of 1.8 g (0.024 mol) of trimethylsilane, 2.84 g (0.02 mol) of benzonorbornadiene, and 0.1 ml of a 0.1 *N* isopropyl alcohol solution of chloroplatinic acid was heated at 180° for 6 hr in a sealed tube. After volatile components were removed on a rotary concentrator, the residue was distilled through a short-path apparatus giving 3.7 g (86%) of an adduct, identified as a mixture of *exo*- and *endo*-2-trimethylsilylbenzonorbornene (XIc and XIIc) in a ratio of 96:4.

Anal. Calcd for $C_{14}H_{20}Si$: C, 77.87; H, 9.17; Si, 12.71. Found: C, 77.70; H, 9.27; Si, 12.98.

Catalytic Addition of Deuterium.—An ethanol solution of benzonorbornadiene was allowed to react with deuterium gas at 1 atm at room temperature in the presence of 5% palladium on carbon, 5% palladium on alumina, 5% platinum on carbon, and 5% rhodium on carbon. In each case it was established that the product of reduction was *cis,exo*-2,3-dideuteriobenzonorbornene (VIIIb).

Reaction with Dideuteriodiimide.—Benzonorbornadiene was reduced to *cis,exo*-2,3-dideuteriobenzonorbornene (VIIIb) with dideuteriodiimide utilizing the procedure of Baird, Franzus, and Surridge.[22]

Reaction with Tosyl Azide.—A mixture of 0.71 g (0.005 mol) of benzonorbornadiene, 0.98 g (0.005 mol) of tosyl azide, and 3 ml of petroleum ether was allowed to stand at room temperature for 12 hr. The pasty reaction mixture was recrystallized three times from 95% ethanol. The purified yield of N-tosyl-3-azabenzotricyclo[3.2.1.0^{2,4}]octane (Xa), mp 155–156°, was 0.7 g (45%).

Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.24; H, 5.50; N, 4.50; S, 10.30. Found: C, 69.42; H, 5.47; N, 4.51; S, 10.32.

Reaction with Picryl Azide.—A mixture of 0.60 g (0.0042 mol) of benzonorbornadiene, 1.07 g (0.0042 mol) of picryl azide,[23] and 4 ml of chloroform was allowed to stand at room temperature for 12 hr. The pasty reaction mixture was recrystallized from ethanol. The purified yield of N-picryl-3-azabenzotricyclo-[3.2.1.0^{2,4}]octane (Xb), mp 223–224.5 dec, was 1.32 g (70%).

Anal. Calcd for $C_{17}H_{12}N_4O_6$: C, 55.41; H, 3.28; N, 15.21. Found: C, 55.51; H, 3.36; N, 15.19.

Registry No.—VI, 4453-90-1; VIIa, 17191-01-4; VIIb, 17191-02-5; VIIc, 17191-03-6; VIIIa, 17191-04-7; VIIIb, 13999-04-7; Xa, 17190-82-8; Xb, 17190-83-9; XIa, 17182-44-4; XIb, 17182-45-5; XIc, 17188-74-8; benzonorbornene, 4486-29-7.

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[22] See Table III, footnote *u*.

[23] E. Schrader, *Ber.*, **50**, 777 (1917)