protons was 6:13 (calcd 6:12). Several small impurity peaks at δ −0.05 to −0.55 were noted.

2,4,6′-Trimethyl-2′,4′,6-tris(2-thienyl)cyclotrisiloxane (2a).—Careful fractional distillation of the cyclotrisiloxane fraction from above afforded a pure sample of the higher boiling isomer: bp 145° (0.08 mm); n^{25}D 1.5544; mp 37–38° (from nitromethane). The nmr spectrum exhibited two methyl proton singlets at δ −0.52 and −0.50 in the ratio of 2:1; the ratio of thienyl to methyl protons was 1:1. Characteristic bands in the infrared spectrum were noted at 1260 (Si–CH_3),[3] 1220 and 1087 (thienyl),[18] 1020 (Si–O–Si, trimer),[3] and 784 cm^{-1} (*trans* trimer).[3]

2,4′,6,8′-Tetramethyl-2′,4,6′,8-tetrakis(2-thienyl)cyclotetrasiloxane (6a).—The cyclotetrasiloxane mixture was fractionally distilled. Upon standing, the higher boiling fractions deposited a crystalline isomer, mp 97.5–98.5° (from methanol). The nmr spectrum of this isomer consisted of a sharp methyl proton singlet at δ −0.37, in addition to two doublets at δ −7.09 (J = 3.4 and 4.6 cps), two doublets at δ −7.34 (J = 1.0 and 3.4 cps), and two doublets at δ −7.51 (J = 1.0 and 4.6 cps) corresponding to ring protons at the 4, 3, and 5 positions, respectively.[17] The ratio of methyl to thienyl protons was 1:1. Spiking experiments demonstated that the methyl proton peak was shifted to δ −0.38 in the tetramer mixture. The isomer was assigned the structure of **6a**, 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetrakis(2-thienyl)-cyclotetrasiloxane. No other crystalline isomers could be obtained from the tetramer mixture.

Hydrolysis of Methyl(2-furyl)dichlorisilane.—To a solution of 200.2 g (2.0 moles) of potassium bicarbonate in 500 ml of water was added over a 1-hr period a solution of 90.5 g (0.5 mole) of methyl(2-furyl)dichlorosilane in 150 ml of ether. The mixture was stirred vigorously at 5–10° while the ethereal solution of methyl(2-furyl)dichlorosilane was introduced below the surface of the aqueous solution by means of a filter tube extending to the bottom of the reaction flask. The mixture then was allowed to warm to room temperature and stand overnight. The organic layer was separated, treated with 5% acetic acid solution to acidify any silanolate salts present, and then washed with water until the washings had a constant pH of 6 (indicator paper). The ether was removed under reduced pressure and the residue distilled up to a pot temperature of 300° [19] to obtain 30.9 g (49%) of mixed methyl(2-furyl)cyclopolysiloxanes, bp 100–210° (0.35 mm). The pot residue consisted of a brittle resin. The crude product from two such runs was combined and fractionally distilled to obtain 2,4,6-trimethyl-2,4,6-tris(2-furyl)cyclotrisiloxane and 2,4,6,8-tetramethyl-2,4,6,8-tetrakis(2-furyl)cyclotetrasiloxane; vapor phase chromatography indicated purities of 98 and 99%, respectively. Analytical and physical property data are listed in Table I. A higher boiling fraction, bp 170–171° (0.15 mm), believed to be the cyclic pentamer, was not isolated in sufficient quantity or purity to permit accurate analysis. The infrared spectra of the trimer and tetramer fraction exhibited characteristic bands at 1270, 785 and 745 (Si–CH_3),[3] and 1205, 1125, and 1010 cm^{-1} (furyl);[18] Si–O–Si absorption at 1020 cm^{-1} in the trimer fraction was shifted to 1090 cm^{-1} in the tetramer fraction.

2,4,6′-Trimethyl-2′,4′,6-tris(2-furyl)cyclotrisiloxane (2b).—Upon standing, the cyclotrisiloxane mixture deposited crystals, mp 47–48° (from nitromethane). The nmr spectrum of this crystalline isomer showed methyl proton resonance at δ −0.48 and −0.45 in the ratio of 2:1 and the compound was assigned the structure of 2,4,6′-trimethyl-2′,4′,6-tris(2-thienyl)cyclotrisiloxane, isomer **2b**.

2,4′,6,8′-Tetramethyl-2′,4,6′,8-tetrakis(2-furyl)cyclotetrasiloxane (6b).—The cyclotetrasiloxane mixture, upon standing for several months, deposited a crystalline isomer, mp 94–98° (from methanol). Based on its nmr spectrum (sharp methyl proton singlet at δ −0.31), the crystalline isomer was identified as 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetrakis(2-furyl)cyclotetrasiloxane (**6b**).

(19) When the reaction was repeated on a 5-mole scale and distillation of the product attempted, a strongly exothermic reaction, accompanied by violent gas evolution and carbonization of the pot residue, occurred at 260–280°.

Reductions in the 7-Substituted Norbornadienyl System. A Synthesis of *syn*-7-Substituted Norbornenes[1]

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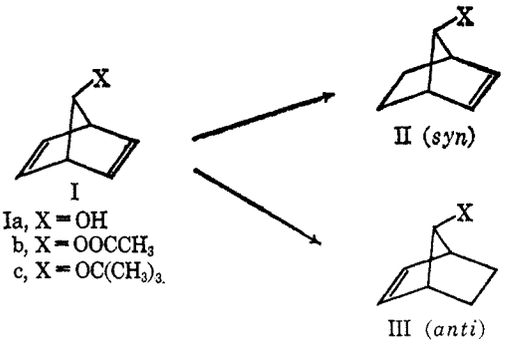
Catalytic reduction of 7-substituted norbornadienes yields primarily the *syn* product. The ratio of *syn*/*anti* product (with a fixed 7 substituent) is strongly dependent on the type of catalyst used for reduction. Thus, the *syn*/*anti* product ratio varies from a low of 1.2/1 with a Pd–C catalyst to essentially an infinite ratio (no detectable *anti* isomer) with the use of a platinum catalyst. Isolation of *syn*-7-acetoxynorbornene from both 7-acetoxynorbornane and a small amount of *anti*-7-acetoxynorbornene is readily accomplished by complexation of the *syn* isomer with Ag^+. This separation is aided by a high ratio of complexation constants of *syn*-acetate/*anti*-acetate, $\cong$ 11/1. This synthesis of the *syn*-acetate from 7-acetoxynorbornadiene, coupled with a previous synthesis of the *anti* isomer, leads to both *syn*- and *anti*-norbornenyl derivatives from a common precursor.

As part of a continuing study of the chemistry of 7-substituted norbornadienes and norbornenes, convenient syntheses for the *syn* and *anti* isomers of the latter compounds were desired. Potential routes to these structures appeared to be the specific reduction of either the *anti* or the *syn* double bond of the corresponding norbornadienes[2] (eq 1) by means of the properly selected chemical or catalytic reducing system. In a previous publication, the reduction of 7-substituted norbornadienes (Ia–c) by the chemical reducing agent, diimide (N_2H_2), to yield *anti*-7-substituted norbornenes (IIIa–c) as the exclusive norbornene product has been reported.[3] This paper describes the preparation of



(1)

the *syn*-7 isomers (IIa–c) by the hydrogenation of these dienes in the presence of transition metal catalysts.

(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p O-10.

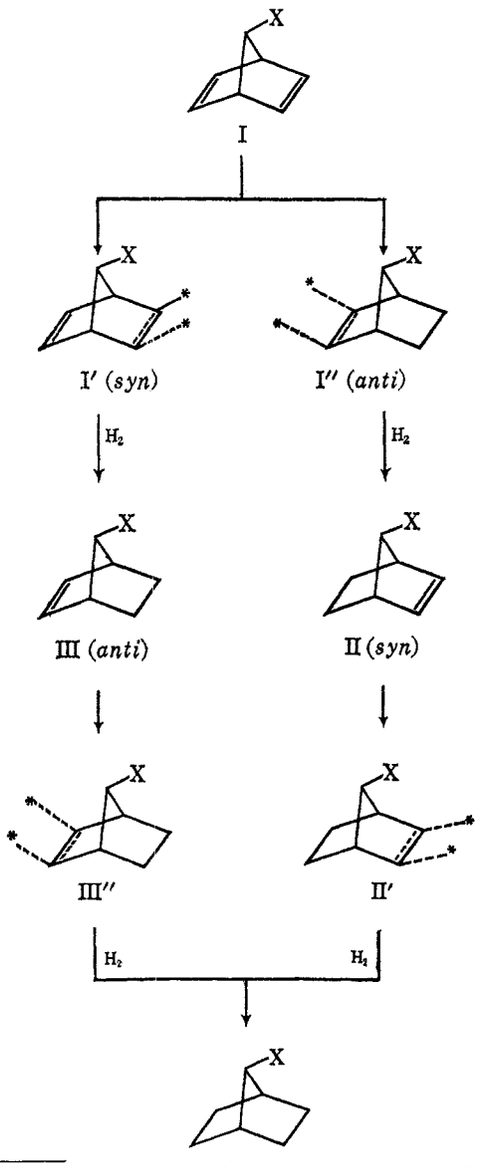
(2) These compounds may be readily prepared according to published synthetic procedures: P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(3) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Am. Chem. Soc.*, **89**, 410 (1967).

Theoretical and stereochemical considerations had initially predicted that the diimide reduction of 7-substituted norbornadienes (I) would involve only the *anti* double bond and lead to the exclusive formation of *syn* product (II).[3] The observed exclusive formation of *anti* isomer (III) through selective diimide reduction of the *syn* double bond was totally unanticipated. This anomalous result has been tentatively rationalized by the suppression of adverse steric factors by a potent electronic effect involving stabilization of the *syn* double bond–diimide transition state.[4]

In situations where this electronic factor is nonoperative, then arguments regarding the steric shielding of the *syn* double bond by the 7 substituent should remain valid. Consequently, catalytic hydrogenation of these dienes (I) should proceed primarily with the formation of *syn* product (II) since, on the basis of steric reasons, the formation of the *syn* transition state (I′, II′) should be less favorable than that of the corresponding *anti* transition state (I″, III″)[5] (Scheme I). It is obvious that this reasoning regarding the steric influence of the 7 substituent is acceptable only if the olefinic bonds of the diene system experience *exo* addition. In this respect, an abundant literature exists demonstrating conclusively the preferred tendency of the norbornadienyl and norbornenyl ring systems to undergo *exo* addition.[3,6] In marked contrast, only three instances of *endo* addition to these compounds have been noted.[7-9] Furthermore, catalytic reduction of 2,3-disubstituted norbornenes has been shown to proceed through *exo,cis*-hydrogen addition.[10] *exo,cis*-hydrogenation has also been observed by van Tamelen and Timmons,[11] who have shown that olefin reduction is definitely subject to steric control under the influence of bulky substituents. The parent olefin, norbornadiene, has been found to undergo catalytic reduction by deuterium to give *exo,cis* deuterated products exclusively.[12]

SCHEME I



On the basis of these considerations, it was concluded that catalytic hydrogenation of 7-substituted norbornadienes (I) should proceed preferentially to the formation of *syn*-7-substituted norbornenes (II).[13] Since synthetic routes to the corresponding *anti* isomers (III) from the same compounds have previously been described,[3,14] success in this endeavor would provide convenient syntheses of both *syn* and *anti* isomers from a common precursor.

In order to maximize the yield of desired *syn* isomer from these diene hydrogenations, it was necessary to determine the optimum level to which the reduction could be carried. It was apparent that underreduction would retain significant amounts of unreacted diene; overreduction would compromise the production of *syn* product by subsequent conversion to the norbornane derivative. The maximum concentration of *syn* isomer in the product mixture was achieved when the consumption of hydrogen approached 50–60% of theory based on diene. Consequently, all reductions were allowed to proceed to this level.

Inspection of the chemistry of these reduction reactions reveals that the relative amounts of *syn* and *anti* isomers present in the reaction mixture at any given time are actually dependent upon two distinct reactions (Table I). The first of these is the conversion of diene into *syn*- (k_1) and *anti*-norbornenes (k_2); the second is the subsequent reduction of these isomeric olefins (k_3 and k_4) to saturated product. From the data

(4) This stabilization is believed to arise from coordination of the partially positive diimide nitrogen–nitrogen bond with an electron-donating atom (oxygen) in the 7 position.[3]

(5) The asterisks represent single metal adsorption sites. For details concerning postulated mechanisms of olefin reductions, see G. C. Bond, "Catalysis By Metals," Academic Press Inc., New York, N. Y., 1962, Chapter 11.

(6) The number of *exo* additions to the norbornyl system are too many for us to enumerate in this paper. However, some of the more recent, interesting *exo* additions are as follows: epoxidation (a) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960), and (b) P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966); nitrosyl chloride (c) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964); diazomethane (d) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964) and (e) M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966); ethyl diazoacetate (f) R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964); methyl azidoformate (g) A. C. Oehlschlager, P. Tillman, and L. H. Zalkow, *Chem. Commun.*, 596 (1965); chloroalkylation (h) D. J. Trecker and J. P. Henry, *ibid.*, 258 (1966); thiophenol (i) S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, **30**, 207 (1965).

(7) H. G. Kuivila and C. R. Warner, *ibid.*, **29**, 2845 (1964).

(8) M. Green, *J. Chem. Soc.*, 541 (1965).

(9) F. Lauterschlaeger, *J. Org. Chem.*, **31**, 1679 (1966).

(10) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(11) E. E. van Tamelen and R. J. Timmons, *J. Am. Chem. Soc.*, **84**, 1867 (1962).

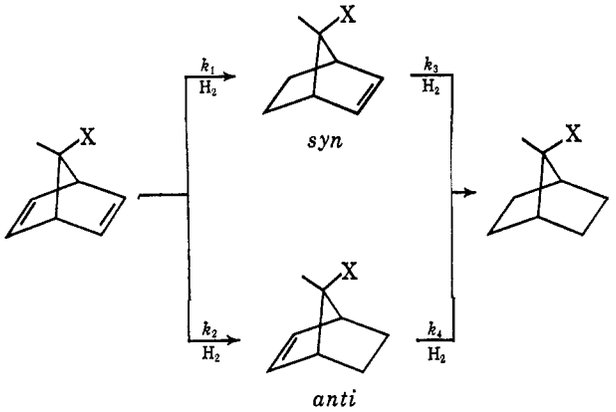
(12) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965).

(13) *syn*-7-Norbornenol (IIa) may also be synthesized by dehydrohalogenation and saponification of *exo*-2-chloro-*syn*-7-acetoxynorbornane; see W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).

(14) B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965).

TABLE I

VARIATION OF *syn/anti* RATIO WITH PER CENT REDUCTION



Run	H_2 absorbed, %	*syn*, %	*anti*, %	Satd, %	Diene, %	*syn/anti*
1[a]	23.7	22.6	1.5	10.8	65.0	15/1
	47.8	44.3	1.3	28.1	41.5	34/1
	73.1	41.5	0	58.5	0	∞
2[b]	46.7	46.3	1.1	25.0	27.4	42/1
	70.5	53.5	0	45.3	1.2	∞
3[c]	27.0	30.5	2.2	12.0	55.3	14/1
	51.8	59.3	1.6	26.9	12.2	37/1
	76.2	40.4	0	59.6	0	∞

[a] PtO_2 (0.13 mmoles) and 2.0 mmoles of 7-acetoxynorbornadiene (Ib). [b] PtO_2 (0.14 mmoles), 2.1 mmoles of Ib, and ~0.1 ml of pyridine. [c] PtO_2 (0.13 mmoles), 2.0 mmoles of Ib, and 1 ml of pyridine.

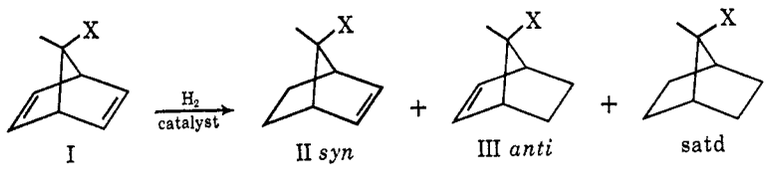
low conversions is rapidly transformed into saturated acetate at higher conversions. It also follows from Table I that this situation is not sensitive to catalyst poisons. Yet the net result of these competitive *anti* double bond reductions (k_1, k_4) is that the *syn/anti* ratios presented in Table II for ~50% reduction represent at best only a qualitative indication of catalyst selectivity.

The results of 7-hydroxy-, 7-*t*-butoxy-, and 7-acetoxynorbornadiene reductions with different catalyst systems are summarized in Table II. In runs 1–3 the catalyst (Pd–C) has been fixed and the 7 substituent varied from OH to OAc to O-*t*-Bu; in these runs the *syn/anti* product ratio varies from 2.9/1 to 5.2/1 to 1.2/1, respectively. From these results, it is quite clear that invocation of steric effects *per se* is meaningless since the O-*t*-Bu group is much larger than the OH group; nevertheless, the OH group "seems" to shield the double bond more efficiently than the *t*-butoxy group. Comparison of run 2 with runs 4 and 5 show that prereduction of a Pd–C catalyst results in a lower *syn/anti* ratio. Indeed, in the prereduced Pd–C catalyst, the amount of *anti* isomer is almost equal to the amount of *syn* isomer. This dramatic decrease of the *syn/anti* ratio from 5.2/1 observed for the nonprereduced catalyst to the 1.2/1 observed for the prereduced catalyst is at present not fully understood.

Although it has been shown that nickel boride is a highly specific hydrogenation catalyst,[15] the reduction

TABLE II

CATALYTIC REDUCTION OF 7-SUBSTITUTED NORBORNADIENES[a]



Run	X	Catalyst	*syn*, %	*anti*, %	Satd, %	*syn/anti*	Method
1	OH	Pd–C	45.9	16.0	14.3	2.9/1	*c*
2	OAc	Pd–C	41.0	7.9	30.5	5.2/1	*c*
3	O-*t*-Bu	Pd–C	30.6	26.0	20.6	1.2/1	*c*
4	OAc	Pd–C prereduced	26.5	20.5	22.7	1.3/1	*c*
5[b]	OAc	$PdCl_2$ + $NaBH_4$	39.5	27.5	20.4	1.4/1	*d*
6[b]	OAc	Ni_2B (from $Ni(OAc)_2 \cdot 4H_2O$ + $NaBH_4$)	59.0	17.6	14.3	3.4/1	*d*
7[b]	OAc	$Ni(OAc)_2$ + $NaBH_4$	52.6	15.3	13.4	3.4/1	*d*
8	OAc	PtO_2 + H_2 → Pt	44.3	1.3	28.1	34/1	*c*
9	OAc	PtO_2 + H_2 → Pt + pyridine (1 ml)	59.3	1.6	26.9	37/1	
10[b]	OAc	H_2PtCl_6 + $NaBH_4$	43.9	0	47.1	∞	*c*
11[b]	OAc	H_2PtCl_6 + $NaBH_4$ + $NH_2CH_2CH_2NH_2$ (0.1 ml)	48.3	0	35.0	∞	*d*
12[b]	OAc	H_2PtCl_6 + $NaBH_4$ + $NH_2CH_2CH_2NH_2$ (0.67 ml)	69.3	0	18.1	∞	*d*
13	OAc	Pt–C	35.8	3.0	29.3	11.9/1	*d*
14	OAc	Pt–C prereduced	44.2	4.0	21.3	11.1/1	*c*

[a] Hydrogen consumption was permitted to proceed to 50–60% of theory based on diene charged in all cases. [b] Norit was added in all these runs. [c] Gas buret. [d] Brown[2] hydrogenator.

of Table I, it is apparent that with PtO_2 as the catalyst not only is k_4 significantly larger than k_3, but k_1 must be greater than k_2 even assuming that all of the saturated product arises from the *anti*-acetate. These relationships truly indicate the preferential hydrogenation of the *anti* double bond in both diene and *anti* isomer (once formed) as opposed to the lack of reactivity on the part of the sterically hindered *syn* double bond. This fact is clearly evident from Table 1 where it is noted that the small amount of *anti*-acetate formed at low conversions is rapidly transformed into saturated acetate at higher conversions. It also follows from Table I that this situation is not sensitive to catalyst poisons. Yet the net result of these competitive *anti* double bond reductions (k_1, k_4) is that the *syn/anti* ratios presented in Table II for ~50% reduction represent at best only a qualitative indication of catalyst selectivity.

The results of 7-hydroxy-, 7-*t*-butoxy-, and 7-acetoxynorbornadiene reductions with different catalyst systems are summarized in Table II. In runs 1–3 the catalyst (Pd–C) has been fixed and the 7 substituent varied from OH to OAc to O-*t*-Bu; in these runs the *syn/anti* product ratio varies from 2.9/1 to 5.2/1 to 1.2/1, respectively. From these results, it is quite clear that invocation of steric effects *per se* is meaningless since the O-*t*-Bu group is much larger than the OH group; nevertheless, the OH group "seems" to shield the double bond more efficiently than the *t*-butoxy group. Comparison of run 2 with runs 4 and 5 show that prereduction of a Pd–C catalyst results in a lower *syn/anti* ratio. Indeed, in the prereduced Pd–C catalyst, the amount of *anti* isomer is almost equal to the amount of *syn* isomer. This dramatic decrease of the *syn/anti* ratio from 5.2/1 observed for the nonprereduced catalyst to the 1.2/1 observed for the prereduced catalyst is at present not fully understood.

Although it has been shown that nickel boride is a highly specific hydrogenation catalyst,[15] the reduction of Ib with this catalyst was not able dramatically to suppress formation of the *anti* isomer. This is shown in runs 6 and 7 with 7-acetoxynorbornadiene (Ib, X = OAc) where the *syn/anti* ratio is 3.4/1.

Large *syn/anti* ratios were obtained by employing platinum as a catalyst. This is demonstrated in runs 8–14 where *syn/anti* ratios cover a range from 11/1 to infinity. Runs 13 and 14 show that the platinum–car-

(15) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1005 (1963).

bon catalyst produced more of the *anti* isomer (*syn/anti* ratio ~11/1) compared with platinum on Norit formed by the sodium borohydride reduction of chloroplatinic acid (runs 10, 11, and 12; *syn/anti* = ∞). As can be seen from runs 8 and 9, PtO_2 lies somewhere between Pt–C and $NaBH_4$ reduced chloroplatinic acid toward formation of the *anti* isomer (*syn/anti* ≅ 34/1). The utilization of various organic amines as catalysts poisons or modifiers[16] had essentially no effect on the *syn/anti* ratio in the platinum-catalyzed reactions (runs 8–12). Similarly, lowering the reaction temperature to 0° [16] also had no influence on the reaction path. The structures of the reduction products from Ia and Ib (X = OH and OAc) were determined by comparative glpc and nmr with authentic compounds.[2,13,14,17] The identification of products from the catalytic reduction of 7-*t*-butoxynorbornadiene, Ic (X = 0-*t*-Bu), is described in the Experimental Section.

The isolation of the desired *syn* isomers from the reduction mixtures was accomplished by both mechanical and chemical techniques. The isolation of *syn*-7-acetoxynorbornene (IIb) from small-scale reductions of the dienyl acetate (Ib) could readily be achieved by preparative vapor phase chromatography. However, a chemical method of separation was desired for large-scale reductions. To this end the equilibrium constants for complexation of *anti*-7-acetoxynorbornene (IIIb) and *syn*-7-acetoxynorbornene (IIb) with silver nitrate were investigated. The technique used was essentially that of Traynham.[18,19] In order to check the reliability of our complexation constants, the complexation constant of cyclopentene with silver nitrate was determined using glpc to measure olefin concentration. A cyclopentene complexation constant (K_{eq}) of 0.111 compares favorably with 0.109 and 0.119 found by Traynham and Sehnert[18] using titrimetic techniques for ascertaining olefin concentration and a K_{eq} of 0.119 found by Traynham and Olechowski[19] using infrared spectra to determine olefin concentration. The complexation constants (K_{eq}) for the reactions of cyclopentene, *syn*-7-acetoxynorbornene (IIb), *anti*-7-acetoxynorbornene (IIIb), and norbornene with silver nitrate are shown in Table III. As anticipated, an electron-attracting acetoxy group caused K_{eq} for *anti*-7-acetoxynorbornene (IIIb) to be lower than that for norbornene. However, it was quite surprising to find that K_{eq} for *syn*-7-acetoxynorbornene was *greater* than that for norbornene. This enhanced complexation of the *syn*-7-acetate with silver ion relative to that of the *anti* isomer ($K_{eq(syn)}/K_{eq(anti)}$ = 0.400/0.036 = 11.1) and to that of the parent olefin is probably due to chelation of the silver ion by the acetoxy group and the double bond.

TABLE III

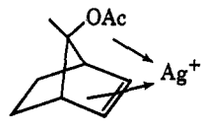
SILVER NITRATE COMPLEXATION CONSTANTS

$$\text{olefin}(CCl_4) + Ag^+(H_2O) \overset{K_{eq}}{\rightleftharpoons} \text{complex}^+(H_2O)$$

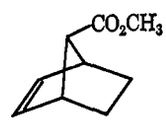
$$K_{eq} = \frac{[\text{complex}^+(H_2O)]}{[\text{olefin}\ (CCl_4)]\ [Ag^+(H_2O)]}$$

Olefin	K_{eq}	K_{eq} [(olefin)/(cyclopentene)]
Cyclopentene	0.111	1.00
anti-7-Acetoxynorbornene (IIIb)	0.036	0.32
syn-7-Acetoxynorbornene (IIb)	0.400	3.60
Norbornene[a]	0.268	2.41

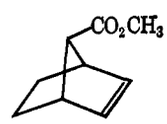
[a] See ref 19.



It is noteworthy that the order of complexation of the *syn*- and *anti*-acetates with silver ion in solution is not observed on glpc. While the *anti* isomer had a considerably longer retention time than the *syn* isomer on a diethylene glycol column, essentially no significant alteration or reversal of retention times occurred on a silver nitrate–diethylene glycol column. Sauers has previously attributed the longer retention time of *anti*-7-carbomethoxynorbornene (IV) relative to that of the corresponding *syn* compound (V) on a silver nitrate column to the availability of the unhindered *anti* double bond to complex with silver ion.[20,21] The contrasting results obtained in this work between silver ion complexation in solution and on a glpc column indicate that considerable caution must be exercised in relating silver–olefin complexation constants (K_{eq}) determined in solution to retention times observed on silver nitrate glpc substrates.



IV



V

The large complexation constant of *syn*-7-acetoxynorbornene (IIb) and the low complexation constant of the *anti*-acetate (IIIb) is of synthetic utility. Thus, after reduction of 7-acetoxynorbornadiene (Ib) with PtO_2 to *syn*-7-acetoxynorbornene (IIb), a trace of *anti*-7-acetoxynorbornene (IIIb) and 7-acetoxynorbornane, the *syn*-acetate could be selectively extracted with silver nitrate. The *syn*-acetate could then be isolated by decomposing the silver nitrate–*syn*-7-acetoxynorbornene complex with KCN. The synthesis of the *syn*-acetate (IIb) is shown in Scheme II along with the synthesis of the *anti*-alcohol (IIIa). As shown in Scheme II, a method for the synthesis of both *syn*- (IIb) and *anti*- (IIIc, IIIa) norbornenyl derivatives from a common precursor (Ib or Ic) is now provided.

Experimental Section

Vapor phase chromatographic analyses were carried out on a Perkin-Elmer Model 154-D fractometer, a Varian Aerograph Model 202, and a Perkin-Elmer Model 226 capillary fractometer. Preparative gas chromatography was performed using a Varian Aerograph Autoprep Model A-700. Nmr spectra were determined with a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard.

7-*t*-Butoxynorbornadiene and 7-acetoxynorbornadiene were prepared by the method of Story[2] and obtained by purchase from Frinton Labs, Vineland, N. J. In all cases, the purchased material (by glpc) was equal in purity to that material synthesized

(16) C. A. Brown (private communication) has made a detailed study of the effect of such modifiers which will shortly be reported.

(17) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

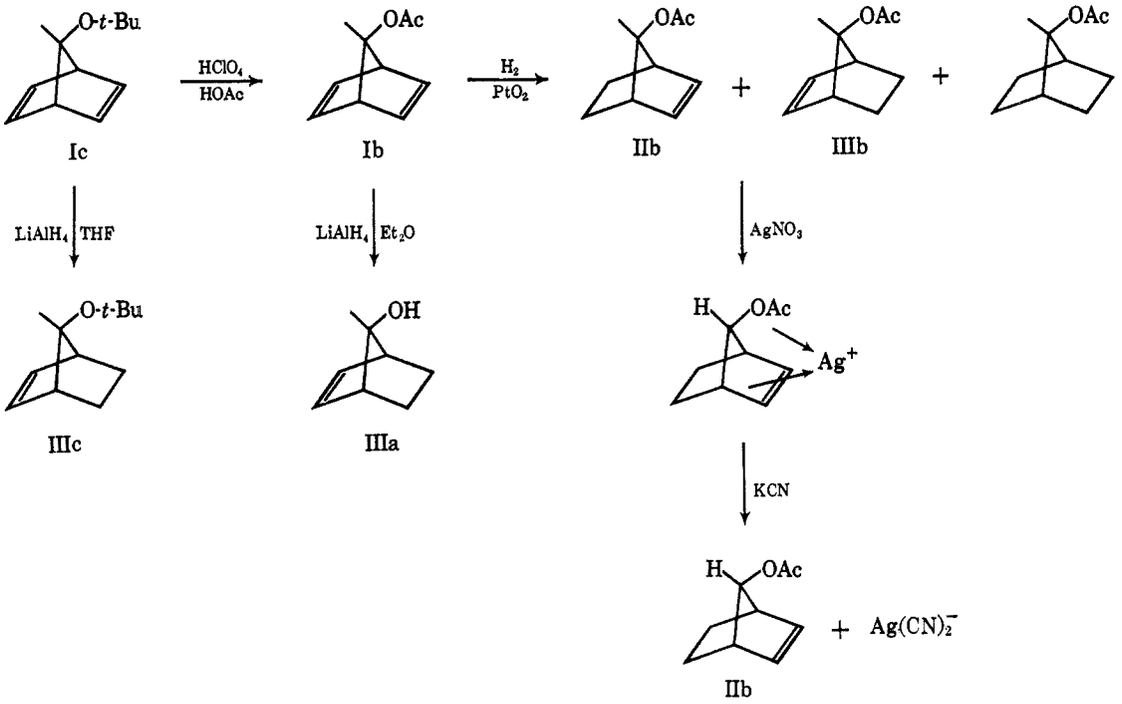
(18) J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956).

(19) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(20) R. R. Sauers, *Chem. Ind.* (London), 176 (1960).

(21) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).

SCHEME II
SYNTHESIS OF *syn*- AND *anti*-NORBORNENYL DERIVATIVES



by Story's method. 7-Norbornadienol and *anti*-7-norbornenol were prepared by Story's technique. *anti*-7-Acetoxynorbornene has been prepared as described previously[17] and *syn*-7-norbornenol was synthesized in these laboratories.[13] *syn*-7-Acetoxynorbornene has been synthesized and described in these laboratories.[13,17]

Analytical Glpc.—Analyses of the 7-acetoxynorbornyl compounds were accomplished with a 11.5 ft × 0.25 in. column packed with 20% FFAP (Varian Aerograph) at 135° using 85 ml/min helium flow. Retention times were as follows: *anti*-7-acetoxynorbornene (IIIb), 20 min; 7-acetoxynorbornane, 23 min; *syn*-7-acetoxynorbornene (IIb), 27 min; 7-acetoxynorbornadiene (Ib), 30 min.

The 7-hydroxynorbornyl compounds were analyzed with a 1 m × 0.25 in. column packed with 5% polypropylene glycol on Gas-Chrom P at 80° using 90 ml/min helium flow. Retention times were as follows: 7-norbornadienol (Ia), 2.9 min; *syn*-7-norbornenol (IIa), 4.0 min; *anti*-7-norbornenol (IIIa), 9.4 min; 7-norbornanol, 10.6 min. Glpc conditions and retention times for the 7-*t*-butoxynorbornyl compounds are given below.

Gas Buret Reductions.—In reductions employing a gas buret apparatus where the sole object was to determine product distribution, 0.1–0.5 g of the 7-norbornadienyl compound was dissolved in 7–10 ml 95% ethanol and was added to 0.02–0.20 g of catalyst. After the system was purged with hydrogen, the reductions were carried out at room temperature with vigorous stirring using a few centimeters of Hg pressure achieved by continually raising the buret leveling bulb. Periodically the reduction was interrupted by stopping the stirring. The catalyst was allowed to settle to the bottom of the flask and a 10–50-μl sample was removed through a septum with a syringe. The sample was immediately analyzed by glpc.

In cases where isolation of the reduction products was the experimental object, 0.5–4.0 g of 7-norbornadienyl compound was dissolved in 10–15 ml of methanol and added to 0.1–0.2 g of catalyst. When 50–60% reduction had taken place, *i.e.*, when there was sufficient H_2 uptake to reduce one double bond, the reaction mixture was filtered or decanted and then treated in a manner suitable for either preparative glpc or silver nitrate complexation (see below). In some instances (see Table II) the catalysts were prereduced by saturating them with H_2 in solvent before adding the olefin through a rubber septum.

Brown[2] Hydrogenator Reductions.—The procedure outlined by Brown[15] was utilized for the reductions carried out using the Brown[2] hydrogenator. H_2 was generated by dripping standard (0.1–1.0 *M*) sodium borohydride solution into glacial acetic acid. The catalysts were reduced before injecting the olefin into the ethanolic slurries. With 0.5 g (3.3 mmoles) of 7-norbornadienyl acetate the amounts of catalysts employed were as follows: 0.2 ml of 0.2 *M* H_2PtCl_6, 0.2 ml of 0.2 *M* $PdCl_2$, 0.4 ml of 0.13 *M* $Ni(OAc)_2$, 0.15 g of Pd on charcoal (for 0.3 g of acetate), and 0.03 g of PtO_2 (for 0.3 g of acetate). Analyses and work-ups of the partially reduced mixtures were performed in essentially the same manner as is described in the gas buret reductions.

Isolation of *syn*-7-Acetoxynorbornene (IIb). A. Silver Nitrate Complexation.—In a typical example, 4.45 g (27.5 mmoles) of 7-norbornadienyl acetate (Ib) was partially reduced *via* 0.183 g of PtO_2 in ethanol using the Brown[2] hydrogenator. After an uptake of 37.4 mmoles of H_2 (68% of theory), the reduction was stopped and analyzed by glpc. The composition of the mixture was 54% 7-acetoxynorbornane, 37.7% *syn*-7-acetoxynorbornene (IIb), and 8.3% 7-norbornadienyl acetate (Ib). The reduction mixture was filtered, diluted with 50 ml of H_2O, and extracted three times with ether. Extraction of the organic layer by shaking three times with 20-ml portions of 5 *M* $AgNO_3$ removed 90% of the *syn*-7-acetoxynorbornene (IIb). The complex was decomposed by adding the combined $AgNO_3$ extracts to 250 ml of cold 4 *M* KCN solution. Three 30-ml ether extractions of the aqueous solution were combined, washed with H_2O, and dried over anhydrous $MgSO_4$. After the ether was distilled at atmospheric pressure, the resultant residue was distilled to give 1.12 g, bp 62–63° (5.0 mm), which by glpc analysis was 84.3% *syn*-7-acetoxynorbornene (IIb), 8.7% 7-norbornadienyl acetate (Ib), and 7% other impurities.

B. Preparative Glpc.—In a typical experiment, 2.10 g (14.0 mmoles) of 7-norbornadienyl acetate (Ib) was partially reduced *via* 0.208 g of PtO_2 (prereduced) in 15 ml of methanol using the gas buret apparatus. When 55% of complete reduction had taken place, the reaction mixture was decanted and the catalyst was washed several times with methanol. The solution was concentrated to 4 ml by distillation at 200 mm pressure. Glpc analysis of the solution showed that, exclusive of methanol, it contained 48.4% *syn*-7-acetoxynorbornene (IIb), 28.4% 7-acetoxynorbornane, 14.4% 7-norbornadienyl acetate (Ib), 4.1% *anti*-7-acetoxynorbornene (IIIb), and 4.8% of a compound of unknown structure. Samples of 0.20 ml of the concentrated solution were injected into a 12 ft × 3/8 in. 20% FFAP column at 130° with 100 ml/min helium flow. Four fractions were collected in Dry Ice–isopropyl alcohol cooled traps. The third fraction which had a 50–58 min retention time contained 0.59 g and was 95% IIb and 5% Ib by glpc analysis. This represents a 56% recovery based on the analysis of the initial mixture of acetates and is a 27% yield of IIb based on the initial amount of 7-norbornadienyl acetate.

Equilibrium Constants for Silver Nitrate Complexation.—Traynham and Olechowski's method[19] was used with the exception that the olefinic ester concentration was determined by glpc analysis of the CCl_4 phase. A 5.00-ml solution containing 0.2906 g (0.382 *M*) of *anti*-7-acetoxynorbornene (IIIb) and 0.0918 g of dodecane was prepared with CCl_4 saturated with water. A 5.00-ml solution containing 0.2922 g (0.356 *M* based on 92.5% purity) of *syn*-7-acetoxynorbornene (IIb) and 0.0943 g of dodecane was similarly prepared. These solutions were analyzed by glpc to determine an initial acetate/dodecane peak area ratio. To 5.00 ml of a 0.999 *M* $AgNO_3$ solution in a glass bottle fitted with a rubber septum serum cap was added 2.00 ml of the above *anti*-acetate solution. The mixture was shaken at room temperature for 1 hr after which a sample of the CCl_4 layer was withdrawn and analyzed by glpc. In order to determine the amount of olefinic ester dissolved but not complexed in the H_2O layer, 2.00 ml of the ester solution was shaken as above with 5.00 ml of 0.994 *M* KNO_3 solution and then analyzed. Analyses were performed three times; the results are given in Table IV.

TABLE IV

PEAK AREA RATIO OF *anti*-7-ACETOXYNORBORNENE (IIIb)/DODECANE

	Initial	After $AgNO_3$	After KNO_3
	2.61	2.35	2.50
	2.67	2.39	2.60
	2.60	2.32	2.56
Av	2.63	2.35	2.56

The equilibrium constant was calculated as follows

$$K_{eq} = \frac{\text{complex}}{[(\text{olefin}) \text{ in } CCl_4][(Ag^+) \text{ in } H_2O]}$$

(complex) = 0.4 (initial concn of olefin − final concn of olefin − concn olefin dissolved in H_2O)

(Ag^+) in H_2O = initial concn of $AgNO_3$ − concn of complex

(olefin) in CCl_4 = $\frac{\text{area ratio after } AgNO_3}{\text{initial area ratio}} \times$ initial concn of olefin

thus

$$K_{eq} = \frac{0.012}{(0.342)(0.987)} = 0.036$$

The *syn*-acetate solution was treated and analyzed in an identical manner; the results are given in Table V which follows.

TABLE V

PEAK AREA RATIO OF *syn*-7-ACETOXYNORBORNENE (IIb)/DODECANE

	Initial	After $AgNO_3$	After KNO_3
	2.40	1.18	2.32
	2.42	1.23	2.46
	2.46	1.23	2.25
Av	2.43	1.21	2.34

The equilibrium constant was calculated as above.

$$K_{eq} = \frac{0.066}{(0.177)(0.933)} = 0.400$$

Partial Hydrogenation of 7-*t*-Butoxynorbornadiene *via* Pd–C.—7-*t*-Butoxynorbornadiene (1.6292 g, 9.95 mmoles), prepared according to Story's method,[2] was added to a flask containing Pd–C catalyst and absolute ethanol. The flask was attached to a gas buret reduction system and 243 cc (9.95 mmoles) of H_2 was added. Analysis of the mixture by glpc on a 2 m × 0.25 in. R column at 126° and 130 cc of He/min showed four peaks with the following retention times from air: 12.7 min (35.2%), 15.0 (22.5%), 17.5 (33.7%), and 20.0 (8.6%). After filtration of the catalyst and removal of solvent on a rotary evaporator, the first two peaks were separated from the last two peaks by preparative vapor phase chromatography. The first two peaks (12.7 and 15.0 min) were in the ratio of 58/42 compared with the initial ratio of 61/39. Similarly, the ratio of the last two peaks isolated (17.5 and 20.0 min) were in the ratio of 86/14 compared with an initial ratio of 80/20. Fraction 1 by nmr contained *anti*-7-*t*-butoxynorbornene (IIIc) and 7-*t*-butoxynorbornane. Glpc of an authentic sample of 7-*t*-butoxynorbornane (R column at 126°) had an 15.0-min retention time from air; therefore, the *anti* isomer (IIIc) had a 12.7-min retention time from air. The nmr analysis of fraction 2 showed three compounds, mostly *syn*-7-*t*-butoxynorbornene (IIc), some 7-*t*-butoxynorbornadiene (Ic), and an unidentified compound containing a *t*-butoxy group but no vinyl hydrogens. 7-*t*-Butoxynorbornadiene (Ic) had a retention time of 17.5 min from air (R column 126°); therefore, the peak at 17.5 min consisted of 7-*t*-butoxynorbornadiene (Ic) and *syn*-7-*t*-butoxynorbornene (IIc). The peak at 20.0 min is the unknown *t*-butoxy compound which we have labeled as compound "X". Analysis of the reduction mixture on a 300-ft capillary propylene glycol column at 125° which was capable of separating all the isomers gave the following analysis: diene (Ic), 12.0%; *syn* (IIc), 30.6%; *anti* (IIIc), 26.0%; saturated, 20.6%; and compound X, 9.4%. We were able to furnish samples of diene,[2] saturated *t*-butoxy ether, and the *anti* compound[17] so that we only had to decide between the *syn* compound and compound "X". Since the *syn* compound (IIc) was present in largest amount by nmr, it proved quite easy to assign retention times to both the *syn* compound (IIc) and compound "X". It is pertinent to note that the ratio of *syn*/*anti* by glpc (capillary) is 1.2/1, whereas the *syn*/*anti* calculated from nmr was 1.4/1. In view of the many different operations performed on these compounds, the agreement between the two methods is quite striking.

Structure proof for the *syn*- and *anti*-7-substituted norbornenes resides in our earlier observation that the *anti* bridge hydrogen (*syn* isomer) split the vinyl proton resonance into a doublet of triplets (doublet separation 0.70–0.96 cps), whereas the *syn* bridge hydrogen (*anti* isomer) exhibited only a triplet for the vinyl proton resonance.[17] Fraction 1 which contained the *anti* isomer (IIIc) (previously prepared[17]) showed only a vinyl proton triplet. Fraction 2 contained a compound (the major fraction) whose vinyl proton resonance exhibited a doublet of triplets (doublet separation 0.9 cps) typical of the *syn* isomer (IIc). Other nmr spectral parameters are as follows: vinyl H (2) 355 cps; bridge H (1) 215 cps; bridgehead H (2) 157 cps. The *t*-butoxy proton resonance for IIc at 65 cps could not be separated from *t*-butoxy resonance for Ic and the *endo*–*exo* proton resonance was contaminated slightly with the proton resonance from compound "X".

Registry No.—Ia, 822-80-0; Ib, 13426-49-8; Ic, 877-06-5; IIa, 13118-70-2; IIb, 13426-52-3; IIc, 13426-53-4; IIIa, 694-70-2; IIIb, 13426-55-6; IIIc, 3391-05-7.