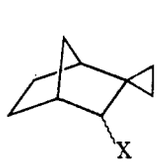
The Preparation of Some Spirocyclopropylnorbornyl Compounds[1a]

CHARLES F. WILCOX, JR.,[1b] AND RAYMOND G. JESAITIS[1c]

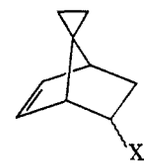
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14850

Received October 16, 1967

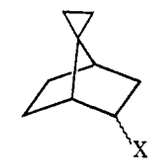
As part of a study of the steric contribution to the large *exo/endo* solvolytic rate ratio of norbornyl compounds, derivatives of norbornyl esters with a spirocyclopropane ring at C_3, I, were desired.[2] This paper describes two independent routes to this system. Also presented are aluminum isopropoxide equilibration data on the corresponding alcohol Ib and the related isomeric alcohols IIb and IIIb.



Ia, X = OAc
b, X = OH
c, X = OTs



IIa, X = OAc
b, X = OH
c, X = OTs



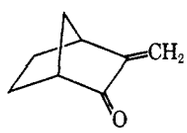
IIIa, X = OAc
b, X = OH
c, X = OTs

One route to I was by a Wagner–Meerwein rearrangement of the C_7-substituted alcohols, IIIb. Alder, Ache, and Flock[3] had synthesized mixtures of *exo*- and *endo*-spiro[cyclopropane-1,7′-[5]norbornenol], and spiro[cyclopropane-1,7′-norbornanol-2′], IIIb, but had not separated the isomers or specified their composition. Condensation of spiro[2.4]hepta-1,3-diene with vinyl acetate at 185° yielded the acetates IIa in a 9:1 *endo/exo* ratio. Saponification and hydrogenation over Pd on charcoal gave largely *endo*-alcohol that could be purified by fractional crystallization from pentane at low temperatures followed by fractional sublimation. This alcohol was converted into the *p*-toluenesulfonate derivative, which on acetolysis gave a high yield of the *exo*-3-spiro acetate, Ia. Lithium aluminum hydride reduction of the acetate gave the desired *exo*-alcohol, Ib.

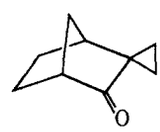
It was found that acetolysis of the *exo*-7-spiro tosylate, IIIc, gave a somewhat cleaner *exo*-3-spiro acetate.[4] Equilibration of the saturated alcohols gave a mixture containing 59% of the *exo*-alcohol (see Table I). Unfortunately, separation of these alcohols proved to be tedious on all glpc preparative columns tried so that equilibration was not a practical route to *endo* IIIb. An unpromising alternate possibility, the equilibration of the *exo*- and *endo*-alcohols of II with aluminum isopropoxide (to be followed by hydrogenation), gave a mixture containing only 41% *exo*-alcohol. It was judged preferable to prepare *exo* Ib by solvolysis of *endo* IIIc.

A quite different approach was taken for the preparation of the *endo*-alcohol of I. For it 3-methylene norcamphor IV was converted by the Simmons–Smith addition[5] of methylene to the 3-spirocyclopropane ketone V. This was converted into the desired *endo*-alcohol Ia by reduction with lithium aluminum hydride followed by low-temperature crystallization.

Equilibration of *endo* Ia gave a mixture containing 66% *exo* Ia but the very difficult separation of this mixture by preparative glpc did not make this a practical route to *exo* Ia.



IV



V

Since norcamphene was readily obtainable from the selective reduction of commercial methylene norbornylene, attempts were made to enter the 3-spirocyclopropane series from this precursor by reaction at the allylic position. Bromination of this alkene with NBS/CCl_4 followed by treatment with Ag_2O in water yielded a complex mixture of products. Similarly $Hg(OAc)_2$/HOAc oxidation[6] of norcamphene produced a mixture of three products, of which the desired one was in smallest proportion.

Experimental Section[7]

***endo*-Spiro[cyclopropane-1,7′-[5]norbornenyl] 2′-Acetate (*endo* IIa).**—Vinyl acetate (40 g), 28.6 g of spiro[2.4]hepta-1,3-diene, and a crystal of hydroquinone were placed in a screw cap Carius tube (Fischer & Porter, stock no. 320-002). The tube was heated at 185° for 18 hr. The resulting solution was distilled through a 3-ft Podbelniak column to yield 40 g (72%) of ester, bp 95° (9.3 mm) (lit.[2] bp 94° (11 mm)).

***endo*-Spiro[cyclopropane-1,7′-norboranyl] 2′-Acetate (*endo* IIIa).**—Acetate IIa (24 g), 110 ml of 95% ethanol, and 0.24 g of 5% palladium on charcoal catalyst were placed into a Parr hydrogenation apparatus. Hydrogen was added at 3 atm and the reaction was finished in 10 min. The solution was then distilled to yield 23.0 g (95%) of the acetate, bp 99° (13 mm) (lit.[3] bp 99° (13 mm).

***endo*-Spiro[cyclopropane-1,7′-norbornanol-2′] (*endo* IIIb).**—Aqueous KOH (20%, 50 ml) was added to 13.0 g of the acetate, IIIa, dissolved in 100 ml of ethanol. The solution was allowed to stand for 1 day, extracted with ether, and the ether solution then clarified with Norit. The ether solution was washed once with water, dried (magnesium sulfate), and evaporated to low volume. The compound was crystallized from pentane at low temperature to yield (crude) 10 g (98%) of *endo* IIIb. Further purification was obtained by fractional sublimation, mp 114° (lit.[3] mp 112°). The tosylate of this compound was made by the standard method (see below).

(1) (a) Abstracted in part from the Ph.D. dissertation of R. Jesaitis, Cornell University, Sept 1967; (b) Guggenheim Fellow, 1967; (c) National Science Foundation Graduate Fellow, 1963–1967.

(2) C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967).

(3) K. Alder, H. J. Ache, and F. H. Flock, *Ber.*, **93**, 1888 (1960).

(4) Acetolysis of the *endo*-tosylate yields 89.8% *exo*-Ia, 1.3% *endo*-Ia, 2.6% *exo*-IIIa, and 6.3% of the homoallylic acetate corresponding to Ia. Acetolysis of the *exo*-tosylate yields 90.0% of *exo*-Ia and 10.0% of the homoallylic acetate. Separation of the homoallylic acetate from the mixture is a comparatively easy procedure compared to separation of the unopened products.

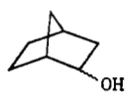
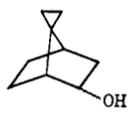
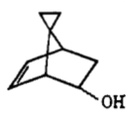
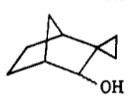
(5) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

(6) Z. Rappaport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, **42**, 3719 (1965).

(7) Melting and boiling points are uncorrected. Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., Scandinavian Microanalytical Laboratories, Denmark, and Schwarzkopf Microanalytical Laboratories, N. Y. Proton nmr spectra were obtained on a Varian A-60 spectrometer. The nmr spectra were in all cases rather complex but fully consistent with the structures assigned. Specific spectral features not reported here are reproduced in the thesis of R. G. Jesaitis.[1] Infrared spectra were run on a Perkin-Elmer Infracord spectrometer. Gas chromatographic analyses were performed on either an Aerograph A-90P (thermal conductivity detector) or an Aerograph Hy-Fi (flame ionization detector). The retention times on a 10 ft × 1/8 in. 5% FFAP/Chromosorb G column at 145° were *exo* IIIb, 31 min; *exo* Ib, 41 min; *endo* Ib, 43 min; *endo* IIIb, 49 min.

TABLE I

BICYCLIC ALCOHOLS EQUILIBRATION WITH Al(*i*-OPr)$_3$[a]

Compound	T, °C	% exo	% endo	exo/endo[b]	ΔF, kcal
	116	78	22	3.54	1.0[a]
	136	59.3	40.7	1.46 ± 0.11	0.3
	124	40.5	59.5	0.68 ± 0.02	−0.3
	124	66.4	33.6	1.98 ± 0.06	0.5

[a] These equilibrations were carried out at a concentration of 0.3 *M* aluminum isopropoxide [C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1097 (1963)]. The compositions might differ at lower concentrations. [b] The limits refer to the precision of duplicate determinations.

Anal. Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.77, H, 6.90, S, 10.75.

Reduction of this tosylate with lithium aluminum hydride in ether yielded the saturated hydrocarbon of the 7-spiro series, mp 46–47°. The 60-mc nmr spectrum (carbon tetrachloride) of the product showed a complex pattern between 81.2 and 1.91 ppm and a sharp spike at δ 0.4 ppm representing the cyclopropyl hydrogens. The infrared spectrum had characteristic absorptions at 2930 cm (CH) and 1005 cm^{-1} (cyclopropyl (?)).

The dinitrobenzoate of *endo* IIIb was made by the standard method, mp 135–136°.

Anal. Calcd for $C_{10}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.62; H, 5.01; N, 8.39.

The brosylate of *endo* IIIb was made by the standard method, mp 60–61°.

Anal. Calcd for $C_{15}H_{17}O_3SBr$: C, 50.43; H, 4.80; S, 8.97; Br, 22.37. Found: C, 50.22, H, 4.74; S, 9.03; Br, 21.59.

The nosylate of *endo* IIIb was made by the standard method, mp 90–91° dec.

Anal. Calcd for $C_{15}H_{17}NO_5S$: C, 55.71; H, 5.30; N, 4.33; S, 9.92. Found: C, 55.71; H, 5.15; N, 4.21; S, 9.72.

***exo*-Spiro[cyclopropane-1,7′-norbornanol-2′]** (*exo* **IIIb**).—Aluminum isopropoxide (25 g), 150 ml of isopropyl alcohol, 10 g of the *endo*-alcohol, IIIb, and 0.5 ml of acetone were placed in a closed 500-ml Carius combustion tube (Fischer & Porter) and heated at 140° for 11 days. The excess aluminum isopropoxide was removed by filtration and washed with ether. The liquids were combined and 200 ml of a 50:50 mixture of ice–10% hydrochloride acid was added. This mixture was extracted four times with a total of 300 ml of ether. The ether extract was washed with 100 ml of 10% hydrochloric acid, 200 ml of saturated aqueous sodium bicarbonate, and 200 ml of water, and then placed over anhydrous potassium carbonate to dry. The solution was then evaporated to 30 ml in a rotary evaporator. The *exo* and *endo* isomers were separated by preparative gas chromatography on a 10 ft × 3/8 in. 20% FFAP on Chromosorb W column at 135°. A yield (*exo*) of 4.0 g (40%) was obtained: mp (*exo*) 125–127°; mp (recovered *endo*) 112° (compare with 114° by fractional sublimation). The infrared spectrum shows strong characteristic bands at 3040 (CH) and 1010 cm^{-1} (cyclopropyl (?)).

Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 78.1, H, 10.3.

The tosylate of this alcohol was prepared in the standard manner, mp 57–58°.

Anal. Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.98; H, 7.04; S, 11.08.

***endo*-Spiro[cyclopropane-1,7′-[5]norbornenol-2′]** (*endo* **IIb**).—The unsaturated alcohol, IIb, was prepared by a method identical with that used to prepare the saturated alcohol, IIIb: bp 97° (13 mm) (lit.[3] bp 97° (13 mm)): mp 39–40.5° (purified by vpc); no melting point reported.

The tosylate was prepared in the standard manner, mp 47–48°.

Anal. Calcd for $C_{16}H_{18}SO_3$: C, 66.17; H, 6.24; S, 11.04. Found: C, 65.94; H, 6.16; S, 11.12.

***exo*-Spiro[cyclopropane-1,7′-[5]norbornenol-2′]** (*exo* **IIb**).—To 3.1 g of the unsaturated alcohol, *endo* IIb, was added 20 ml of isopropyl alcohol, 50 μl of acetone, and 4 g of aluminum isopropoxide. This was placed into a sealed Carius tube and heated at 133° for 3 days. The solution was then poured into 500 ml of 10% hydrochloric acid and extracted four times with a total of 350 ml of ether. The ether solution was washed with 125 ml of aqueous saturated sodium bicarbonate and then dried over anhydrous potassium carbonate. The solution was evaporated to 10 ml and separated by preparative vpc by two passes through a 15 ft × 3/8 in. 5% bentone–5% diisodecyl pthalate on Chromosorb W column at 150°. Approximately 300 g (93% isomeric purity) was collected. The compound appears to be a low-melting solid (*ca.* 30°). The infrared spectrum shows characteristic bands at 3040 (OH) and 710 cm^{-1} (*cis* double bond).

The tosylate of the alcohol was prepared in the standard manner. An analysis of the ester could not be obtained because of the facile decomposition at room temperature. However, an infinity titer of a solvolysis of this compound in acetic acid showed a purity of (97 ± 3) %, mp 32–33°.

Spiro[cyclopropane-1,3′-norbornanone-2′] (**V**).—Cupric acetate (2.4 g) was dissolved in 120 ml of boiling acetic acid and 44 g of zinc dust was added to the solution. After 30 sec the acid was decanted off and the couple was washed with 100 ml of acetic acid and three times with 100 ml of anhydrous ether.[8] Anhydrous ether (120 ml) was then added to the couple. 3-Methylenenorbornanone-2 (25 g) (Aldrich-80% purity) and 75 g of methylene iodide were combined and added dropwise to the stirred couple mixture over a period of 20 min. The mixture was then refluxed with stirring for 6.5 hr. The mixture was filtered and the couple washed several times with ether. The ether solution was extracted with 300 ml of a 50:50 mixture of ice–10% hydrochloric acid. The ether layer was washed with 200 ml of ice–acid mixture and then washed three times with 250 ml of a saturated aqueous sodium bicarbonate. The ether solution was then placed over anhydrous potassium carbonate to dry overnight. The potassium carbonate was then removed by filtration and the solution was evaporated to 25 ml in a rotary evaporator. The solution was distilled on a spinning band column and 9 g (40%) of the ketone was obtained, bp 66° (7 mm). The infrared spectrum shows a characteristic carbonyl absorption at 1743 cm^{-1} (0.36% in carbon tetrachloride). The compound absorbed 203 (4350) mμ.[9]

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 78.98; H, 8.96.

***endo*-Spiro[cyclopropane-1,3′-norbornanol-2′]** (*endo* **Ib**).—A 3.0-g portion of the ketone, V, was dissolved in 150 ml of anhydrous ether and 1.3 g of lithium aluminum hydride was added to a separate 250-ml portion of anhydrous ether. The ketone solution was added slowly to the lithium aluminum hydride mixture and then stirred for 1 hr. A 5.2-ml portion of water was then added very slowly and the mixture stirred for 6 hr. The solids were then filtered off, washed with ether, and the ether solution evaporated to 10 ml. Crystallization was performed at low temperature and an almost quantitative yield of the alcohol was obtained, mp 37–38°, bp 73° (4.8 mm). The infrared spectrum shows characteristic bands at 3035 (OH) and 1010 cm^{-1} (cyclopropyl (?)).

Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 77.9; H, 10.1.

The *p*-nitrobenzoate of the alcohol was prepared by the standard method, mp 91–91.5°.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.86. Found: C, 66.73; H, 5.94; N, 4.78.

The 3,5-dinitrobenzoate was prepared by the standard method, mp 128–129°.

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.85; H, 4.95; N, 8.45.

***exo*-Spiro[cyclopropane-1,3′-norbornanol-2′]** (*exo* **Ib**). **A.**—To prepare a sample of this alcohol, the same procedure was used

(8) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(9) Kindly measured for us in the laboratory of W. G. Dauben by J. Frei.

as to prepare the other two *exo*-alcohols, IIb and IIIb. However, it was not possible to get any reasonable separation by preparative vpc, though one could separate the isomers (*exo* and *endo*) sufficiently on an analytical column (10 ft × 1/8 in. 5% FFAP/Chromosorb G) and collect enough alcohol for identification purposes.

B.—To prepare large scale quantities of pure alcohol, Ib, it was necessary to use a more roundabout route. The *endo*-7-spiro saturated tosylate (12 g) and 5.0 g of sodium acetate were dissolved in 500 ml of anhydrous acetic acid. The solution was heated at 75.0° in a closed vessel without stirring for 68 hr. The liquid was allowed to cool to room temperature and mixed with 500 ml of pentane. This solution was mixed with 500 ml of water, shaken, and the phases were separated. The water phase was washed with an additional 250 ml of pentane and then the pentane phases were combined. The pentane phase was washed with 300-ml portions of water and saturated aqueous sodium bicarbonate. The organic phase was placed over Drierite to dry for several hours. After the solid dessicant was removed by filtration, the solution was evaporated to ~25 ml. This solution was mixed with 350 ml of anhydrous ether and then 3.5 g of lithium aluminum hydride was slowly added. The mixture was stirred for 1 hr, whereupon 14 ml of water was added slowly and the mixture stirred for an additional 3 hr. The precipitate was removed by filtration and extracted with an additional 20 ml of ether. The ether phases were combined and dried over anhydrous potassium carbonate. The drying agent was removed by filtration and the solution was evaporated to approximately 10 ml with a rotary evaporator. The remaining solvent was removed at low pressure in a sublimator and the solid was sublimed and then resublimed. This yielded 4.1 g (72%) of the *exo*-alcohol, mp 50–51°. The infrared spectrum had characteristic absorptions at 3040 (OH) and 1025 cm^{-1} (cyclopropyl (?)).

Anal. Calcd for C_9H_{14}: C, 78.21, H, 10.21. Found: C, 78.50; H, 10.21.

The dinitrobenzoate of this compound was prepared by the standard procedure, mp 100–101.5°.

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.76; H, 4.89; N, 8.39.

The *p*-nitrobenzoate was prepared by the standard procedure, mp 68.5–70°.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.86. Found: C, 66.95; H, 5.84; N, 4.82.

Norcamphene.—Methylene norbornylene (100 g), 0.3 g of 10% palladium on charcoal catalyst, 2 cc of quinoline, and 100 ml of methanol were placed into a Parr hydrogenation apparatus. Hydrogen at 3 atm was let into the constantly shaking apparatus until the reaction had virtually ceased. This took about 3 hr. The reaction without the added quinoline had no clear dividing line where only one double bond had been reduced, but the quinoline decreased the rate of hydrogenation of the *exo* double bond to such an extent that the break was clearly visible. The catalyst was removed by filtration and 1 l. of water and 250 ml of pentane were added (norcamphene azeotropes with methanol). The pentane phase was dried over potassium carbonate and then the solid was removed and the solution distilled. The fraction boiling from 120.5 to 123° was collected to yield 95 g (95%) of norcamphene, bp 122° (740 mm) (lit.[8] bp 123°).

This was compared with a sample made by xanthate ester pyrolysis as reported by Diels and Alder[10] and the two were found to have identical ir spectra.

Spiro[cyclopropane-1,2′-norbornane].—Cupric acetate (2 g) was dissolved in 100 ml of stirred boiling acetic acid. Zinc dust (35 g) was added and then the mixture was allowed to stand for 1 min. The acetic acid was decanted off and the residue was washed with a 100-ml portion of acetic acid and three 100-ml portions of anhydrous ether. Another 100 ml of ether was then added to the residue. Methylene iodide (2 ml) was added and bubbling ensued. A mixture of 27 g of norcamphene and 93 g of methylene iodide was added over a period of 30 min with rapid stirring and light reflux. Stirring was continued for 3 hr whereupon the solution turned reddish purple and was decanted off the residue into a separatory funnel containing 300 ml of mixture of 1 *N* hydrochloric acid and ice. The residue was washed with 200 ml of ether, which was added to the separatory funnel. The ether layer was washed with 100 ml of 1 *N* hydrochloric acid and three times with 100-ml portions of water and then dried over potassium carbonate. Distillation yielded 24 g (78%) of the polycyclic alkane, bp 114–145°. The infrared spectrum had characteristic bands at 2915 (CH) and 1005 cm^{-1} (cyclopropyl (?)).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.63; H, 11.50; C, 88.49; H, 11.47.

Reaction of Mercuric Acetate with Norcamphene.—To 1 l. of acetic acid was added 50 g of norcamphene and 296 g of mercuric acetate. The solution turned bright yellow. The temperature of the stirred solution was raised from 25 to 85° in 24 min and then heating was continued for an additional 65 min at 85–90°. A white precipitate of mercurous acetate was formed as well as a small amount of mercury. The precipitate was removed by filtration and the 2 l. of pentane was added to the acetic acid solution. Water (4 l.) was then added and the mixture shaken. The pentane phase was washed twice with 1-l. portions of saturated aqueous sodium bicarbonate solution. The solution was then evaporated down to a volume of approximately 1 l. and washed with 500-ml portions of cold (0°) dilute nitric acid and saturated aqueous sodium bicarbonate. The liquid was dried over anhydrous potassium carbonate and then evaporated down to *ca.* 45 ml. Analytical chromatography (13 ft × 0.25 in. 15% FFAP/Chromosorb W) at 120° showed a mixture of three products, which when separated by preparative vpc (10 ft × 3/8 in. 20% FFAP/Chromosorb W at 160° were identified as 2-*exo*-acetoxy-2-*endo*-methylnorbornane (*ca.* 50%), 3-methylenenorcamphor (*ca.* 30%), and 3-methylene *exo*-norbornylacetate (*ca.* 20%). Preparative vpc of these products proved to be difficult for large samples so this approach to the spiro-3 compounds was abandoned.

Preparation of Tosylates (and Other Arenesulfonates).—Alcohol (0.01 mol) was mixed with *p*-toluenesulfonyl chloride (0.01 mol) in 20 ml of pyridine (dried over potassium hydroxide and allowed to stand for 1 day at 50° and then poured into 200 ml of an ice–water mixture. The ice–water mixture was then extracted twice with about 200 ml total of pentane. The pentane solution was washed with 100 ml of 10% hydrochloric acid and 100 ml of saturated aqueous sodium bicarbonate. It was then placed over magnesium sulfate to dry. The solution was evaporated to low volume and the tosylate ester was crystallized and recrystallized from ether–pentane at Dry Ice temperatures. In the case of the two *endo*-7-spiro esters it was found that 90% methanol–10% pentane was an excellent solvent for recrystallization. Yields averaged around 60%.

Brosylates (*p*-bromobenzenesulfonates) and nosylates (*p*-nitrobenzenesulfonates) were similarly prepared using the corresponding acid chlorides.

Preparation of 3,5-Dinitrobenzoates and Paranitrobenzoates.—To 20 ml of anhydrous pyridine at 0° was added 1.0 g of alcohol and then 1.7 g of 3,5-dinitrobenzoyl chloride (or the corresponding *p*-nitro compound) with constant stirring. The solution was allowed to stand 6 hr at 0°. Crystals of pyridine hydrochloride were seen to form. The solution was poured into 500 ml of an ice–water mixture and extracted three times with a total of 600 ml of ether. The ether solution was washed with 200 ml of 10% hydrochloric acid and then 200 ml of saturated aqueous sodium bicarbonate. The ether solution was then placed over magnesium sulfate to dry for 1 hr. The drying agent was removed by filtration and the solvent was removed on the rotary evaporator until approximately 20 ml of solution remained. This was placed in a freezer at −10° and allowed to crystallize. The crystals were collected and recrystallized from 95% ethanol. Yields averaged 60%, though crude yields were considerably higher.

Registry No.—*endo* Ib, 16133-53-2; *exo* Ib, 16170-24-4; *p*-nitrobenzoate of *endo* Ib, 16133-54-3; *p*-nitrobenzoate of *exo* Ib, 16133-55-4; 3,5-dinitrobenzoate of *endo* Ib, 16133-56-5; 3,5-dinitrobenzoate of *exo* Ib, 16133-57-6; tosylate of *endo* IIb, 16170-25-5; *exo* IIIb, 1633-58-7; 3,5-dinitrobenzoate of *endo* IIIb, 16133-59-8; brosylate of *endo* IIIb, 16133-60-1; nosylate of *endo* IIIb, 16133-61-2; tosylate of *exo* IIIb, 16133-62-3; tosylate of *endo* IIIb, 16133-63-4; V, 16133-64-5; spiro-[cyclopropane-1,2′-norbornane], 173-89-7.

(10) O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).