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Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decane Ring System[1]

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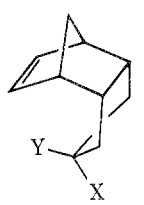
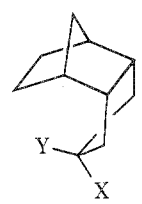
The tosylates of *endo*-5,6-trimethylene-2-norbornen-9-ol have been prepared and solvolyses carried out in acetic acid. This has led to *exo*-tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-9-ol. Solvolysis of the tosylate of this compound leads to a degenerate rearrangement with migration of the C_4–C_8 bond.

Participation of π electrons in the solvolysis of norbornyl derivatives has led to new norbornyl-type ring systems in many cases.[3] We were interested in the solvolysis of *endo*-5,6-trimethylene-2-norbornen-9-yl tosylates (**2**, **4**) as a source of new ring systems.[4] Compound **3** was prepared by treatment of 4-hydroxycyclopentene with cyclopentadiene, oxidation of the product with chromium trioxide in pyridine, and reduction with lithium aluminum hydride.[5] Treatment of **4** with tetraethylammonium acetate and saponification of the resulting acetate yielded **1**. Hydrogenation of **1** and **3** led to the known saturated alcohols,[6] which served to prove the configuration at C_9 was well as confirm the structure of the ring skeleton. Rate data for the acetolysis of **2** and **4** are given in Table I.



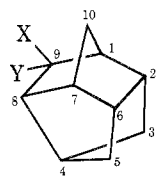


	X	Y
1	OH	H
2	OTos	H
3	H	OH
4	H	OTos
8	Cl	H

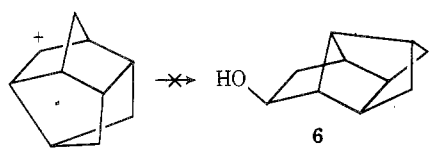
	X	Y
2a	OTos	H
4a	H	OTos

The exo/endo rate ratio of 27 at 25° is probably indicative of a small rate enhancement of the exo isomer due to participation of the π electrons. An alternate explanation of steric hindrance to ionization[6] of the endo isomer **4** seems unreasonable. The analogous saturated tosylates **2a** and **4a** exhibit an exo/endo acetolysis rate ratio of 0.62 at 25°.[6] It does not appear likely that introduction of the double bond would drastically change the relative rates for steric reasons. The rate for acetolysis of the saturated endo tosylate[6] **4a** is 7.19×10^{-7} sec^{-1}, while that of the unsaturated is 2.49×10^{-7} sec^{-1}. The decrease in rate of the unsaturated endo tosylate **4** compared to the saturated could be largely attributed to the electron-withdrawing character of the double bond. The exo-unsaturated tosylate **2** exhibits a rate of 66.4×10^{-7} sec^{-1}, while the saturated analog **2a** has a rate of 4.48×10^{-7} sec^{-1}. The fact that the unsaturated tosylate solvolyzes 15 times faster than the saturated is most reasonably explained by participation of the double bond.

Both exo and endo isomers gave excellent straight lines for first-order kinetics to over 80% of reaction. Examination of the products from acetolysis at 75° shows a 2:1 ratio of acetate to olefinic products from both **2** and **4**. Dicyclopentadiene was the only olefinic product. The acetate from **4** after saponification showed 70% of **1** and 30% of rearranged alcohol **5**. The product resulting from sapon-



	X	Y
5	OH	H
9	OTos	H
10	H	OH
11	H	OTos
13	D	OH

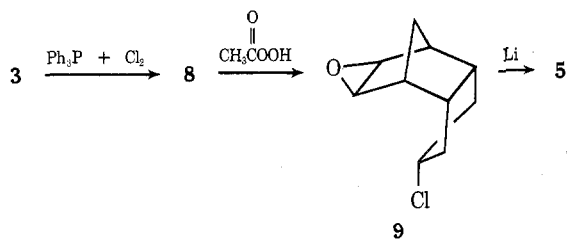


7 6

ification of the acetate derived from **2** was greater than 95% *exo*-tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decan-9-ol (**5**). We did not find any of **6** which would have resulted from Wagner-Meerwein rearrangement of ion **7**.

Structure **5** was proven by an alternate synthesis and by its chemical and physical properties. The alternate synthesis is outlined in Chart I.

Chart I



Treatment of **3** with thionyl chloride led to a mixture of chlorides, which consisted of about 50% of rearranged chloride resulting from participation of the double bond. Reaction with triphenylphosphine and chlorine gave a very clean product with no signs of rearrangement. Treatment of epoxide **9** with lithium dispersion succeeded in closing the ring.[7]

The nmr spectrum of **5** is very suggestive of the structure. The methine proton of **5** shows a broadened singlet with a width at half-height of 4 Hz. The approximate dihedral angles that the methine proton makes with adjacent protons on C_1 and C_8 are 70 and 90°, respectively, leading to calculated[8] coupling constants of less than 1 Hz in both cases. This is very similar to the spectrum reported for *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol.[7a] The epimeric alcohol **10** was prepared by chromic acid oxidation of **5** to ketone **12** and reduction with lithium aluminum hydride. The nmr spectrum of **10** and **11** showed a broadened doublet (J = 6.5 Hz) for the methine proton. The methine hydrogen makes approximate dihedral angles with the C_1 and C_8 protons of 60 and 27°, which would lead to calculated couplings of less than 2 and 6.5 Hz, respectively. One interesting feature of the nmr spectrum of **5** and **10** is the chemical shift for the methine protons. The endo methine proton of **5** is at δ 4.0 while the exo methine proton of **10** is at δ 3.67. This is the opposite of what is usually found in norbornyl systems; the exo proton is in the usual case downfield from the endo proton.[9] This same reversal of the relative positions of the exo and endo methine protons is also found in the tosylates and *p*-nitrobenzoates. This resembles the type of behavior found in the highly hindered half-cage and related compounds.[9]

Relative rates of chromic acid oxidation of **5** and **10** were also highly indicative of the structure. In 40% aqueous acetic acid at 25° (1.79×10^{-3} M in chromic acid and 2.68×10^{-3} M in alcohol) the rates of oxidation were 3.50×10^{-3} l. mol^{-1} sec^{-1} for **5** and 0.27 l. mol^{-1} sec^{-1} for **10**. The endo alcohol is being oxidized to ketone faster than the exo by a factor of 73, a $\Delta\Delta F^*$ difference of 2.5 kcal/mol. The rate ratio is reasonably similar to that found for the *endo*-5,6-trimethylene-2-norbornanols.[10] This is to be expected, since models show that the steric interactions of the endo alcohols seem to be approximately similar.

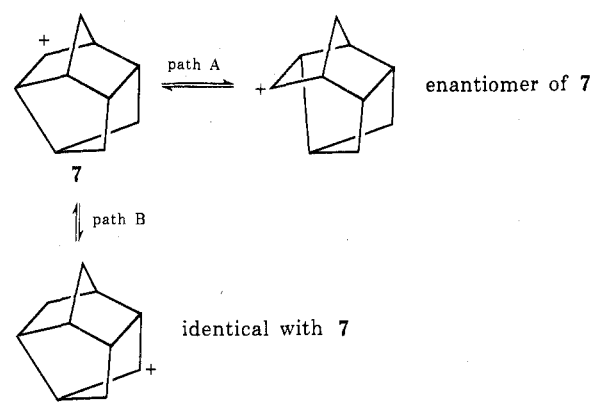
The kinetic results of acetolysis of tosylates **9** and **11** have previously[1] been reported, exhibiting an exo/endo rate ratio of 0.33 at 25°. The nmr spectrum of tosylate **9** shows essentially an identical pattern for the methine proton as was present for the alcohol precursor **5**, a broadened singlet with a width at half-height of 5 Hz. Alcohol, which showed no signs of skeletal rearrangement,[11] could be regenerated from **9** in 85% yield by treatment with sodium and naphthalene in tetrahydrofuran.[12,13]

Table I
Titrimetric Acetolysis Rates of Tosylates (Solutions 0.013 M in Tosylate and 0.015 M in Sodium Acetate)

Tosylate	Temp, °C	$k \times 10^7$, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu (25°)
2	50.0	1640 ± 19	24.0	−1.8
	25.0	66.4 ± 1.3		
4	75.0	1700 ± 32	26.3	−0.80
	50.0	83.8 ± 1.2		
	25 (calcd)	2.49		
Cyclopentyl	25.0	17.9 ± 0.34		

The product of acetolyses from both **9** and **11** after saponification is largely **5**. The yield of **5** by vpc using dodecyl alcohol as an internal standard was 83% from **9** and 85% from **11** with less than 5% of **10** present in both cases. Samples collected by preparative vpc were identical with authentic alcohol. There were 8–10% of unidentified alcohols from both tosylate solvolyses.

The possibility of degenerate rearrangements exists. These could involve C_4–C_8 bond migration (path A), migration of endo 3-hydride to C_9 (path B), and possibly other more complex pathways.



These were investigated as follows. Ketone **12** was reduced with lithium aluminum deuteride to give **13**. Nmr spectroscopy showed a complete absence of methine proton and mass spectroscopy indicated a greater than 98.4% incorporation of deuterium at C_9. Solvolysis of the tosylate in acetic acid with sodium acetate and saponification led to exo alcohol whose nmr spectrum showed 0.25 ± 0.03 methine protons. Mass spectroscopy showed that all of the deuterium was still in the molecule. Preparation of tosylate from this sample of exo alcohol, acetolysis, and saponification led to exo alcohol which showed essentially no loss of deuterium by mass spectroscopy, but the methine proton by nmr was 0.48 ± 0.04. Preparation of tosylate from this alcohol, acetolysis, and saponification gave exo alcohol in which there was no further change. Treatment of the tosylate of **13** with tetraethylammonium acetate gave essentially the same result as acetolysis.

The data indicate that in the solvolysis of endo tosylate from **13** attack of nucleophile occurs before complete equilibration takes place. However, the exo isomer **9** solvolyzes with complete equilibration of **7** or formation of a delocalized ion from **7** before attack of nucleophile can occur. Clearly, **9** is solvolyzing with a degenerate rearrangement taking place by path A, path B, or some other pathway leading to the same results.

Oxidation of exo alcohol with 0.48 methine protons led to ketone that had lost 49.6% of its deuterium content

(mass spectroscopy). A combination of both path A and path B can be excluded at this point because less than 49.6% of deuterium would have been lost if both pathways were involved. Lithium aluminum hydride reduction of this ketone led to endo alcohol whose nmr spectrum permitted determination of the rearrangement path. If path A were the reaction process there should be approximately 50% of deuterium at C_8. The nmr spectrum should show a doublet for the methine hydrogen with a broadened singlet superimposed in the middle of the doublet. The doublet and singlet should be in a 1:1 ratio.

Path B should lead to product which should show a doublet for the methine hydrogen, since there should be no deuterium at C_8. Experimentally the nmr spectrum of the endo alcohol shows quite clearly a broadened singlet superimposed in the middle of a doublet estimated to be in a 1:1 ratio. Path A is the predominant process by which the degenerate rearrangement takes place.

Experimental Section

Melting points were determined in capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Glpc was carried out on a Hewlett-Packard 5750 gas chromatograph with flame ionization detectors. Analytical measurements were on 10 ft × 0.125 in. columns and preparative work was on 10 ft × 0.25 in columns. The columns used were 10% of stationary phase on 60–80 mesh Chromosorb W. The stationary phases were UCW-98, Carbowax 20M, FFAP, and UCON LB-550X. Nmr spectra were recorded on a Varian A-60 instrument using deuteriochloroform as solvent and tetramethylsilane as internal standard. The spectra are reported in δ units as parts per million downfield from TMS. Ir spectra were measured with a Beckman IR-10 instrument.

All tosylates were prepared by treatment of alcohol with a 100% excess of *p*-toluenesulfonyl chloride in pyridine at 0° for 2 days and worked up in the usual way. Recrystallization was from ether–pentane.

Impure *endo*-5,6-Trimethylene-2-norbornen-*exo*-9-ol (1). The procedure of Webb[5] was followed. This involved heating of equimolar quantities of 4-hydroxycyclopentene[14] and freshly cracked cyclopentadiene at 180° for 18 hr. This procedure in our hands gave after distillation [82–94° (2 mm)] material with about 50% of impurities resulting from higher molecular weight Diels–Alder reaction products of cyclopentadiene, as well as *exo*-5,6-trimethylene-2-norbornen-9-ol as an impurity. Glpc (FFAP) showed 45% of **1**, 8% of *exo*-5,6-trimethylene-2-norbornen-9-ol, and 47% of cyclopentadiene adducts. This material proved to be intractable in further synthetic work and required purification. A crude distilled mixture (15.0 g) was dissolved in 200 ml of ether and extracted with 50-ml portions of 10% silver nitrate solution until glpc showed essentially no alcohol in the ether (eight extractions). To the aqueous silver nitrate at 0° was added 100 ml of ammonium hydroxide. The ammonia solution was extracted with ether, and the ether was dried (magnesium sulfate) and evaporated to give 7.0 g of product, which by glpc consisted of 81% of **1**, 17% of its isomer, and 2% of cyclopentadiene adducts.

***endo*-5,6-Trimethylene-2-norbornen-*endo*-9-ol (3).** Impure **1** (containing only **1** and its isomer) was oxidized to ketone with chromium trioxide in pyridine and reduced with lithium aluminum hydride, according to the procedure of Webb,[5] to give **3**: mp 64–65° (lit.[5] mp 65.5–66.5°); ir 3650, 3350 (broad), 3060 cm^{-1}; nmr δ 6.18 (2, t, J = 2 Hz), 4.02 (1, m), 2.7 (2, m), 2.3 (2, broad m), 2.0–0.97 (6, complex m).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.72; H, 9.30.

Hydrogenation of 3. Compound **3** (50 mg) was hydrogenated in ethanol using 5% palladium on charcoal to give after work-up 40 mg (79%) of *endo*-5,6-trimethylene-*endo*-9-norbornanol identical after recrystallization (ether–pentane) with authentic material (ir, glpc, melting point, mixture melting point).

Tosylate 4 had mp 83–85°.

Anal. Calcd for $C_{17}H_{20}SO_3$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.38; H, 6.42; S, 10.33.

***endo*-5,6-Trimethylene-2-norbornen-*exo*-9-ol (1).** Tosylate **4** (1.6 g, 5.3 mmol) and 3.0 g of tetraethylammonium acetate[15] were dissolved in 30 ml of acetone and refluxed for 24 hr. The acetone distilled off and the residue was added to 100 ml of water and extracted with ether. The ether was dried (magnesium sulfate) and evaporated, and the residue was refluxed for 1 hr with 1 g of potassium hydroxide in methanol. The reaction mixture was worked up in the usual way to give 450 mg (57%) of alcohol **1**. Glpc (FFAP) showed a purity of 98%. An analytical sample was obtained by recrystallization from ether–pentane: mp 69.5–70.0°; ir 3650, 3350 (broad), 3075, 1660 cm^{-1}; nmr δ 6.10 (2, t, J = 2 Hz), 4.25 (1, broad m), 2.7 (4, broad m), 1.8–0.8 (6, complex m).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.80; H, 9.28.

Tosylate 2 had mp 59–61°.

Anal. Calcd for $C_{17}H_{20}SO_3$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.25; H, 6.61; S, 10.38.

Hydrogenation of 1. Compound **1** (40 mg) was hydrogenated in 81% yield in the same way as described for **3** to give *endo*-5,6-trimethylene-*exo*-9-norbornanol identical with authentic material.

***exo*-Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-9-ol (5) (Preparative Scale).** Tosylate (21.1 g) from impure **1** (containing 80% **1** and 20% of *exo*-5,6-trimethylene-2-norbornen-9-ol) was made 0.5 M in acetic acid which was 1.0 M in sodium acetate. The reaction mixture was heated at 50° for 24 hr, then poured into water and extracted with pentane. The pentane was washed with sodium carbonate solution, dried, and evaporated. The residue was dissolved in 100 ml of methanol (3 g of potassium hydroxide added), refluxed for 1 hour, and worked up in the usual way. An ether solution showed 80% of **5** and 20% of *exo*-5,6-trimethylene-2-norbornen-9-ol. The ether solution was extracted with 10% aqueous silver nitrate until glpc showed greater than 95% of **5**. The ether solution was then dried and evaporated, and the residue was chromatographed on alumina using gradient elution (pentane–ether) to give 4.0 g of product. An analytical sample was prepared by recrystallization from ether–pentane: mp 179–180°; ir (CCl_4) 3650, 3400 (broad), 1080 cm^{-1}; nmr δ 4.00 (1, s, CH methine), 2.2 (6, m, CH tertiary), 1.9–0.8 (6, m, CH_2); mass spectrum mol wt calcd 150, found 150.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.90; H, 9.25.

***p*-Nitrobenzoate Derivative of 5** had mp 102–103°.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.07; H, 5.80; N, 4.86.

***exo*-Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]dec-9-yl Tosylate (9)** had mp 80–81°; ir 1170, 1360 cm^{-1}; nmr δ 7.6 (4, q, center of an AB pattern, CH aromatic), 4.80 (1, s, CH methine), 2.46 (3, s, CH_3), 2.3 (6, m, CH tertiary), 2.0–0.8 (6, m, CH_2).

Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.38; H, 6.88; S, 10.53.

Reaction of Tosylate 9 with Sodium. Sodium (46 mg, 2.0 mmol) was added, with stirring, to 270 mg (21 mmol) of naphthalene in 7 ml of tetrahydrofuran which had been flushed with nitrogen and then kept under a static pressure of nitrogen. After the solution had become dark green and all traces of sodium had disappeared (1 hr), it was cooled to −78° and 100 mg of tosylate **9** in 5 ml of tetrahydrofuran was added. The solution immediately became colorless and was stirred for an additional 10 min. Water was added and the solution was poured into saturated sodium chloride. The layers were separated and the aqueous portion was extracted with ether. Examination by glpc (UCW-98) with an external standard showed an 85% yield of tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-9-ols. A sample collected by preparative glpc showed by ir spectroscopy 85% of **5** and 15% of **10**. Compound **10** had an absorption at 1110 cm^{-1} that was completely absent in **5**. With the use of standards, a quantitative evaluation of the relative amounts of **5** and **10** could be made. Glpc on five columns would not separate the isomers.

Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-9-one (12). Alcohol **5** was oxidized essentially according to the procedure of Brown, Garg, and Liu[16] to give a 96% yield of ketone, 94% pure by glpc. Chromatography on alumina, using gradient elution (pentane–ether), and recrystallization (pentane) gave an analytical sample >99% pure, mp 184–185°, ir 1753 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.82; H, 7.95.

***endo*-Tetracyclo[5.2.1.$0^{2,6}$.$0^{4,8}$]decan-9-ol (10).** Ketone **12** was reduced with lithium aluminum hydride in the usual way to give a 98% yield of alcohol, 97% pure. Recrystallization (ether–pentane) gave an analytical sample: mp 209–210°; ir (CCl_4) 3650, 3500 (broad), 1110, 1080 cm^{-1}; nmr δ 3.67 (1, d, J = 6.5 Hz, CH methine), 2.55 (1, d, J = 11 Hz, CH endo C_3), 2.17 (6, m, CH tertiary), 1.6–0.85 (5, complex m, CH_2).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.19; H, 9.22.

p-**Nitrobenzoate Derivative of 10** had mp 125–126°.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.02; H, 5.87; N, 4.95.

Tosylate 11 had mp 59–61°; nmr δ 7.69 (4, center AB quartet, J = 8 Hz), 4.30 (1, d, J = 6 Hz, CH methine), 2.50 (3, s, CH_3), 2.22 (7, complex m, CH tertiary and endo C_3 H), 1.8–0.9 (5, complex m, CH_2).

Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 67.48; H, 6.88; S, 10.33.

endo-**5,6-Trimethylene-***exo*-**9-chloro-2-norbornene (8).** Triphenylphosphine (3.74 g, 14.3 mmol) was dissolved in 10 ml of carbon tetrachloride and chlorine was bubbled in with stirring. A solid immediately precipitated. This became an oil as addition of chlorine continued. The solvent was removed by rotary evaporation and the residue was dissolved in 10 ml of acetonitrile (distilled from phosphorus pentoxide). The solvent was again evaporated off to remove chlorine. The residue was triturated with anhydrous ether, the ether was poured off, and the residue was dried at 2 mm for 30 min. The residue was dissolved in 10 ml of acetonitrile and a solution of 1.0 g (6.65 mmol) of **3** and 0.55 ml (6.65 mmol) of pyridine in 5 ml of acetonitrile was added at 0°. After addition the reaction was stirred for 10 min, allowed to warm to room temperature, and stirred for 1 hr. The solvent was removed at reduced pressure and the residue was triturated well with pentane. The pentane was washed with water, dried, and evaporated, and the residue was distilled to give 0.45 g (2.7 mmol, 40%) of oily product: bp 50–53° (0.3 mm); n^{29}D 1.5174; ir 3060, 1650, 730 cm^{-1}; nmr δ 6.18 (2, t, J = 1.5 Hz, CH vinyl), 4.47 (1, m, CH methine), 3.0–2.82 (4, m, CH tertiary), 2.6–1.3 (6, m, CH_2).

Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.20; H, 7.77; Cl, 21.02. Found: C, 71.04; H, 7.95; Cl, 21.30.

exo-**4-Chloro-9-oxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane (9).** Chloride **8** (0.330 g, 1.97 mmol) was dissolved in 7 ml of chloroform and cooled to −5°, and 1.60 ml of 40% peracetic acid buffered with 0.30 g of sodium acetate was added over 2 min. The solution was kept at 0°, stirred for 3 hr, and then worked up in the usual way to give 0.30 g of white solid. Recrystallization (pentane) gave 170 mg of analytical material: mp 76–77°; ir 3040, 1270, 910, 840 cm^{-1}; nmr δ 4.56 (1, m, CH methine), 3.20 (2, s, CH epoxide), 2.87–2.51 (4, m, CH tertiary), 2.05–0.85 (6, m, CH_2).

Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.03; H, 7.09; Cl, 19.20. Found: C, 65.35; H, 7.35; Cl, 19.34.

Reaction of Epoxide 9 with Lithium.[7] A three-neck flask was fitted with a gas inlet tube, a condenser, and an injection port covered with a serum stopple and connected to a mercury bubbler. The apparatus was flame dried with a helium stream and to the flask was added 0.40 g (0.036 mol) of lithium dispersion (50% dispersion in hexane) and 5 ml of tetrahydrofuran. A solution of 80 mg (0.43 mmol) of chloro epoxide **9** in 5 ml of tetrahydrofuran was added and the mixture was stirred and refluxed for 45 hr under a static pressure of helium. The work-up was carried out, essentially as described by Sauers,[7] to give a 64% yield of product (glpc with an external standard). Preparative glpc (UCW-98) yielded a sample that was identical with authentic material (ir, melting point, mixture melting point, nmr, glpc).

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Registry No.—**1,** 50506-62-2; **2,** 50506-63-3; **3,** 50506-64-4; **4,** 50506-65-5; **5,** 28029-30-3; **5** *p*-nitrobenzoate, 50506-67-7; **8,** 50506-68-8; **9,** 27743-80-2; **10,** 27786-03-4; **10** *p*-nitrobenzoate, 50506-71-3; **11,** 27743-81-3; **12,** 27852-55-7; *exo*-4-chloro-9-oxatetracyclo-[5.3.1.0^{2,6}.0^{8,10}]undecane, 50506-74-6; *p*-toluenesulfonyl chloride, 98-59-9; 4-hydroxycyclopentene, 14320-38-8; cyclopentadiene, 542-92-7.

References and Notes

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