absence of hydrazone yielded no detectable hydroxylation products (less than 6×10^{-4} of the yield of reactions run as described above).

Hydroxylation of Toluene in Methylene Chloride. In a typical reaction, acetone hydrazone (3.00 mL, 0.0373 mol) and TPP (11.2 mg, 0.0182 mmol) were dissolved in methylene chloride, which was diluted to 50.00 mL in a volumetric flask. A 20.00-mL aliquot was removed, precooled to low temperature in a dry ice–acetone cold bath, and reacted by irradiating for 1 h under a stream of oxygen. After 1 h the reaction was stopped, and 20.00 mL of precooled toluene was added to the reaction vessel. The toluene and methylene chloride were removed under vacuum and the products analyzed as described above.

Attempted Observation of Chemiluminescence. Acetone hydrazone (2.0 mL, 0.025 mol) and TPP (17 mg, 2.7×10^{-5} mol) were dissolved in 50 mL of methylene chloride. A portion (25 mL) of this solution was precooled in a dry ice–acetone cold bath and reacted under the photooxygenation conditions for 30 min. The reaction was stopped, and 25 mL of a precooled solution of diphenylanthracene (8.5 mg, 2.6×10^{-5} mol) was added. The solution was allowed to warm to room temperature under observation in a darkened room. In a separate experiment, the remaining 25 mL of the above acetone hydrazone solution was reacted as above. A precooled solution of dibromoanthracene (8.6 mg, 2.6×10^{-5} mol) in 25 mL of methylene chloride was added and observed as above. No light was seen in either experiment.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The mass spectral facility was support by NIH Grant RR00954 from the Division of Research Resources.

Registry No. 1 ($R = CF_3$, $R' = CH_3$, $R'' = H$), 97315-16-7; **2**, 97315-14-5; **3**, 50265-80-0; **10**, 97315-15-6; $CH_3C(CF_3)=NNH_2$, 6257-45-0; $CF_3C(O)CH_3$, 421-50-1; $PhCH_3$, 108-88-3; PhCHO, 100-52-7; $PhCH_2OH$, 100-51-6; acetone, 67-64-1; acetone azine, 627-70-3; acetone hydrazone, 5281-20-9; hydrazine, 302-01-2; benzophenone azine, 983-79-9; cyclohexanone methylhydrazone, 1567-83-5; benzophenone hydrazone, 5350-57-2; benzophenone, 119-61-9; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5.

Notes

2,5-Disubstituted Benzotricyclo[4.2.1.$0^{2,5}$]nonanes: Photochemical Precursors to Substituted Bridged *o*-Xylylene Derivatives

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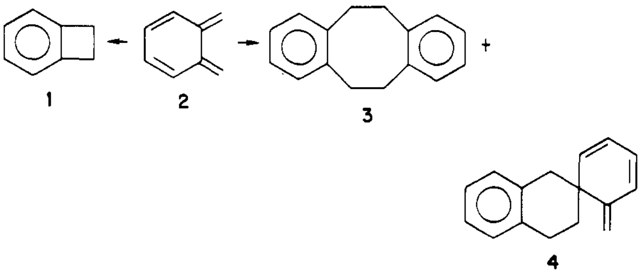
o-Xylylene (**2**) is a highly reactive intermediate which has attracted considerable theoretical and experimental attention.[1] This material when generated in fluid solution is unstable both with regard to dimerization and also internal cycloaddition to form dihydrobenzocyclobutene (**1**).



The electrocyclic ring closure, which presumably occurs via a symmetry allowed conrotatory mode,[2] is particularly interesting, and recently Roth and co-workers[3] have measured the activation energy (29 kcal/mol) for this process by flash photolytic techniques. In this regard, we have previously demonstrated that bridging the *o*-xylylene moiety with a bulky bicyclic group not only prevents dimerization but also inhibits the electrocyclic reaction presumably by forcing a symmetry forbidden disrotatory ring closure.[4] The bridged, bicyclic *o*-xylylene **6** is available by the photolysis of either *exo*- or *endo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]nonane in rigid media.

There has been considerable theoretical interest recently in the effects of substituents on the rate of electrocyclic reactions. Carpenter and co-workers,[5c,d] using a conceptually simple perturbational approach, have predicted relative substituent effects for a wide variety of pericyclic processes and have further suggested that these effects should be maximized for symmetry forbidden processes. This, coupled with the bimolecular stability of the bicyclic derivative **6**, suggested that substituted derivatives would be ideal candidates for the study of the disrotatory 8π electrocyclic ring closure. The synthesis of appropriately substituted derivatives of **6** reduces to developing a technique for selectively introducing substituents into positions 2 and/or 5 of the parent tricyclononanes **5** or **7**. We report here our synthetic efforts in this area.

The parent hydrocarbons **5** and **7** have been prepared either by the Diels–Alder cycloaddition of benzocyclobutadiene with cyclopentadiene[6] or by the 2 + 2 cycloaddition of benzyne to norbornene,[7] respectively. Since the former approach seemed to lack synthetic versatility,[8]

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[1] McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270 and references therein.

[2] Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry", Academic Press: New York, 1970.

[3] (a) Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.; Mosselman, C. Hermann, H. *Chem. Ber.* **1978**, *111*, 3892. (b) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741.

[4] (a) Miller, R. D.; Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1976**, *98*, 8510. (b) Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 1820.

[5] Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1200. (b) Epiotis, N. D. *Angew, Chem., Int. Ed. Engl.* **1974**, *86*, 825. (c) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (d) Wilcox, C. F., Jr.; Carpenter, B. K.; Dolbier, W. R. *Tetrahedron* **1979**, *35*, 707. (e) Jensen, A.; Kunz, H. *Theoret. Chim. Acta* **1984**, *65*, 33.

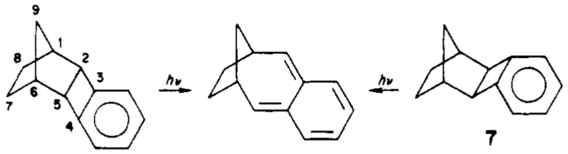
[6] Cava, M. P.; Mitchell, M. J. *J. Am. Chem. Soc.* **1959**, *81*, 5409.

[7] Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *83*, 1657.

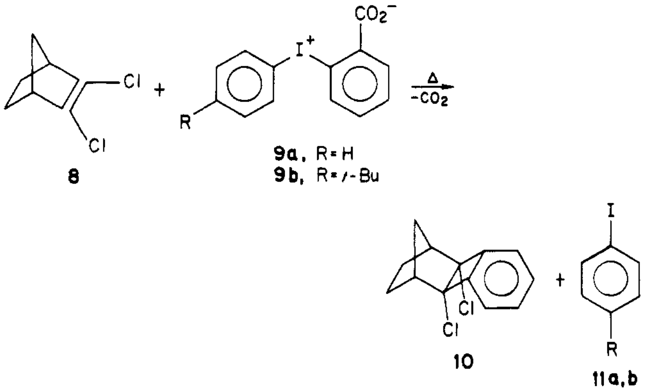
[8] Very recently the preparation of 2-chloro-*endo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]non-7-ene by the Diels–Adler trapping of chlorobenzocyclobutadiene generated in situ has been reported: Ghenciulescu, A.; Georghiu, M. D.; Enescu, L.; Dinulescu, I. G.; Avram, M. *Revue Roumaine de Chemie* **1984**, *29*, 49.

0022-3263/85/1950-3200$01.50/0

we concentrated on the latter. Unfortunately, the presence of two substituents on the double bond of the norbornene derivative often caused the cycloaddition to fail even though the corresponding monosubstituted norbornene was quite reactive.[9] In hopes of finding an unhindered, disubstituted norbornene derivative which was also capable of further chemical transformation subsequent to the cycloaddition, we concentrated our efforts on the readily available 2,3-dichloronorbornene 8.[10]



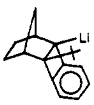
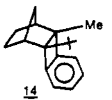
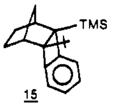
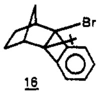
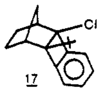
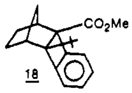
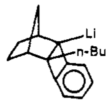
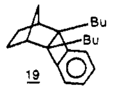
5 **6** **7**



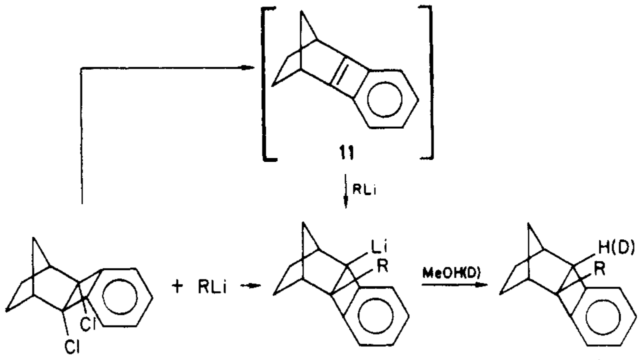
This material was unreactive toward benzyne generated by the more usual low-temperature processes.[11] We found, however, that the use of a high-temperature source such as 9[12] produces the adduct 10 in 20–25% yield. Initial attempts to recycle the olefin 8 were complicated by the presence of the byproduct iodobenzene which was difficult to remove and whose presence adversely affected the yield of 10 in subsequent reactions. The problem was alleviated by the use of the substituted derivative **9b**. Using this procedure, unreacted 8 was easily recovered from the *p*-*tert*-butyliodobenzene by distillation. An X-ray structural analysis[13] of the crystalline adduct 10 formed in this manner confirmed that the benzyne had attacked from the least hindered exo face as expected.

Dichloride 10 is remarkably unreactive and was recovered unchanged after treatment with lithium dimethylcuprate, methyllithium, dimethyltitanium dichloride, silver nitrate in ethanol, and silver acetate in acetic acid. It was, however, readily dehalogenated by a variety of other organolithium reagents. In this regard, when 10 was treated at low temperatures with *tert*-butyllithium in pentane, a dark and persistent yellow color resulted which disappeared immediately upon quenching with water or acetic acid. The major[14] product isolated in this case was *exo*-2-*tert*-butyl-*endo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]nonane (**13a**).[15] The organolithium derivative **12a** appears to be an intermediate in this process, since quenching the reaction mixture with methanol-d_1 resulted in the formation of **13a** which was >90% deuterated at the benzylic methine position (^{1}H NMR and mass spectroscopic analysis). Use of less than 3 mmol of *tert*-butyllithium/mmol of **10** results in a substantially decreased yield of **13a** and the recovery of unreacted starting material.

Table I. 2,5-Disubstituted *endo*-3,4-Benzotricyclo[4.2.1.$0^{2,5}$]nonane Derivatives

Starting Material	Quenching Reagent	Product (Yield)
 Li 12a	$(Me)_2SO_4$	 Me 14 (47)ᵃ
	$(Me)_3SiCl$	 TMS 15 (80)
	$BrCH_2CH_2Br$	 Br 16 (35)
	CCl_3CCl_3	 Cl 17 (25)
	MeOCOCl	 CO_2Me 18 (35)
 Li, n-Bu 12b	n-BuBr	 Bu, Bu 19 (25)

a. Isolated Product Yields



10 **12a**, R=*t*-Bu **12b**, R=*n*-Bu **13a, b**

The inversion in the configuration of the benzocyclobutene moiety from the exo position in the starting material to the endo configuration in **13a** suggests the possible intermediacy of the highly strained benzocyclobutadiene **11**. The addition of *tert*-butyllithium to a substituted cyclobutadiene has been reported[16] and in the case of **11** would be expected to occur from the least hindered exo face to yield the observed product upon quenching.

The formation of the anion **12a** in the dehalogenation process provides a route to a number of disubstituted

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[9] Miller, R. D., Franz, L., unpublished observations.

[10] Nagendrappa, G. *Org. Synth.* **1973**, *53*, 1855.

[11] (a) Logullo, F. M; Seitz, A. H.; Friedman, L. *J. Org. Chem.* **1968**, *48*, 12. (b) Newman, M. S.; Cella, J. A. *J. Org. Chem.* **1973**, *38*, 3482. (c) Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 3881.

[12] (a) LeGoff, E. *J. Am. Chem. Soc.* **1962**, *84*, 3786. (b) Fieser, L. F.; Haddadin, M. J. *Org. Synth.* **1966**, *46*, 107.

[13] X-ray crystallographic data: **10**, $C_{13}H_{12}Cl_2$; orthohombic space group *P21* 21 21, a = 8.200 (4) Å, b = 11.059 (5) Å, c = 12.570 (4) Å, ρ = 1.39 g/cm^3.

[14] A small amount (~7%) of the saturated hydrocarbon *exo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]nonane (**7**) was also isolated from the reaction mixture. None of the corresponding endo derivative **5** was detected.

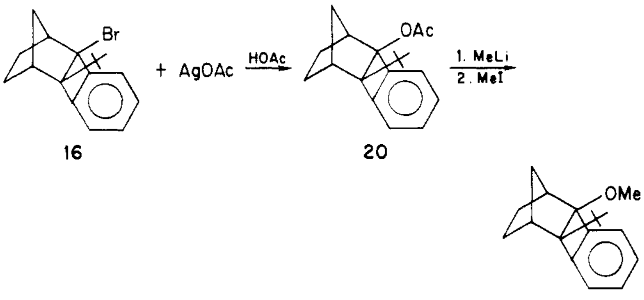
[15] The configuration of **13a** is assigned on the basis of its ^{1}H NMR spectrum.[7] In this case the exo benzylic methine hydrogen appeared at δ 3.42 as a doublet (J = 5 Hz) which is consistent with the structural assignment.

[16] Maier, G.; Köhler, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 308.

derivatives simply by changing the nature of the quenching electrophile (see Table I). In each case, the formation of the disubstituted derivatives was accompanied by the isolation of variable amounts of **13a**. All of the products shown in Table I are presumed to have the benzocyclobutene group in the endo position by analogy with the formation of **13a**.

Treatment of **10** with *n*-butyllithium also results in dehalogenation to produce the *n*-butyl derivative **13b**. In this case, however, there is a complicating feature. The crude reaction mixture obtained upon protic quench contained an additional higher boiling component which was tentatively identified as the di-*n*-butyl derivative **19** by GC-MS. This structural assignment was confirmed by deliberately quenching **12b** with *n*-butyl bromide to produce **19** which was identical in every way with the high boiling contaminant. The formation of **19**, even in the case of a protic quench, presumably results from the alkylation of **12b** by the *n*-butyl chloride generated in situ. Interestingly, the presence of **19** persists even when large excesses of butyllithium are employed.

The generation of derivatives containing oxygen substituents at the 2 or 5 position of **5** requires a different procedure. For this purpose, derivatives such as **16** and **17** were useful due to their solvolytic lability. After 3 days (25 °C) in the presence of silver acetate–acetic acid, the bromide **16** was completely converted into the desired acetate **20** (38% overall from **10**). The structure of **20** was consistent with the spectral data and the configuration was confirmed by X-ray analysis. Interestingly, the dichloride **10** is stable under these solvolytic conditions. The corresponding methyl ether **21** was produced by the treatment of **20** with methyllithium followed by alkylation with methyl iodide.



16

20

21

In summary, the formation of **10** by high-temperature cycloaddition of benzyne to **8** provides a valuable starting material for the synthesis of 2,5-substituted derivatives of **5**. By alkylative dehalogenation, a variety of materials containing either donor or acceptor substituents can be prepared. Preliminary studies indicate that **10**, **14–19**, and **21** all rapidly open to the desired *o*-xylylene derivatives, which are characterized by a strong, structured absorption in the visible around 400 nm, upon irradiation (254 nm)[18] in a 3-methylpentane matrix at 77 K. Although these *o*-xylylenes vary considerably in their thermal stability, all reclose to the corresponding benzocyclobutenes rapidly and in quantitative yield at temperatures below 110 °C.

Experimental Section

All solvents were routinely dried before use. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer using tetramethylsilane as an internal standard. ^{13}C NMR spectra were run on a Varian CFT-20 machine. Infrared spectra were taken on a Perkin-Elmer 297 machine. GLC analyses were accomplished with a Hewlett-Packard 5750 machine using a glass column ($^1/_4$ in. × 6 ft) packed with 10% SE-30 on Gas-Chrom Q. UV spectra were recorded on a Hewlett Packard 8450A instrument.

Phenyl(*p-tert*-butylphenyl)iodonium-2-carboxylate (9b). Concentrated sulfuric acid (30 mL) was cooled in an ice bath before pouring into a mixture of 7.4 g (0.03 mmol) of *o*-iodobenzoic acid and 9.7 g (0.036 mol) of potassium persulfate. The reaction mixture was cooled in an ice bath for 5 min and then allowed to warm to room temperature for 20 min. The reaction was recooled to ~10 °C and 13 mL of *tert*-butylbenzene (11.3 g, 0.08 mol) was added with stirring. After stirring at 10 °C for 1 h, the temperature was reduced to −15 °C and 180 mL of cold water was added in a steady stream. At this point, 150 mL of methylene chloride was added followed by 90 mL of concentrated ammonia while maintaining the reaction temperature below 20 °C. The layers were separated, the alkaline aqueous phase was reextracted with additional methylene chloride, and the organic material was dried over $MgSO_4$. After removal of the solvent the crude product was recrystallized from methanol, 6.3 g (55%). **9b**: mp 248 °C; ^{1}H NMR ($CDCl_3$) δ 8.3–6.5 (m, 8 H), and 1.38 (s, 9 H); IR (KBr) 2960 and 1610 cm^{-1}. Anal. Calcd for $C_{17}H_{17}IO_2$: C, 53.70; H, 4.51; I, 33.38; Found: C, 53.46; H, 4.53; I, 33.26.

2,5-Dichloro-*exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nonane (10). Into a round-bottomed flask equipped with a reflux condenser was placed 7.2 g (44 mmol) of 2,3-dichloronorbornene **8**[10] and 4.2 g (10 mmol) of the iodonium salt **9b**. The flask was heated to 200 °C (bath temperature) for 15 min and a second 3.8-g portion of **9b** was added. The mixture was heated at 200 °C for a total of 2 h. The excess dichloronorbornene **8** was recovered by distillation (bp 95 °C, 30 mm, 5.9 g), and the residue was purified by flash chromatography[17] over silica gel (250 g) using hexane as the eluant. In this manner 1.03 g (22%) of the product **10** was obtained: mp 86–88 °C; ^{1}H NMR ($CDCl_3$) δ 7.55–7.05 (m, 4 H), 2.5 (m, 2 H), 2.2–1.83 (m, 2 H), 1.75–1.6 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 141.8, 129.15, 119.65, 79.49, 42.56, 34.03 and 20.65; UV λ_{max} (3-methylpentane) 263 (sh 1589), 269 (2378), 276 (2621); high-resolution mass spectroscopic molecular weight calcd for $C_{13}H_{12}Cl_2$, 238.0316, found 238.0316. Anal. Calcd for $C_{13}H_{12}Cl_2$: C, 65.56; H, 5.08; Cl, 29.78. Found: C, 65.14; H, 5.04; Cl, 29.48.

2-*tert*-Butyl-*endo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nonane (13a). Into a dry flask sealed with a rubber septum containing a magnetic stirrer was placed 148 mg (0.62 mmol) of the dichloride **10** and 10 mL of THF. After cooling to −78 °C, 1.3 mL of *tert*-butyllithium in pentane (1.8 M, 2.3 mmol) was added, and the stirring was continued for 2 h. At this point, the temperature was raised to −40 °C and maintained for 2 h (yellow solution). After being recooled to −78 °C, the mixture was quenched with saturated NH_4Cl, 10 mL of ether were added, and the layers were separated. After the organic layer was washed with brine, it was dried over $MgSO_4$. Removal of the solvent yielded 121 mg of a mobile oil. GLPC analysis indicated the presence of two products (ratio ~1:8). The products were separated by preparative GLPC (10% SE-30). The minor lower boiling contaminant was identified as *exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nonane (**7**)[7] while the major one was the mono *tert*-butyl derivative **13a**.

13a (75%): ^{1}H NMR (CCl_4) δ 6.98 (m, 4 H), 3.42 (d, J = 5, 1 H), 2.4 (m, 2 H), 2.1–1.85 (m, 1 H), 1.65–0.6 (m, s at 0.93, 14 H); ^{13}C NMR ($CDCl_3$) δ 152.16, 147.92, 126.28, 125.79, 124.21, 123.43, 69.82, 52.92, 44.08, 50.05, 39.93, 34.30, 28.63, 27.86, 26.00; high-resolution mass spectroscopic molecular weight, calcd for $C_{17}H_{22}$ 226.1721, found 226.1709; UV λ_{max} (3-methylpentane) 262 (sh, 1486), 269 (2010), 275 (2244) nm.

A variety of *tert*-butyl-substituted derivatives were prepared simply by varying the electrophile used to quench the anion **12a** (see Table I).

14 (47%): ^{1}H NMR (CCl_4) δ 7.18–6.97 (m, 4 H), 2.48 (m, 2 H), 2.2–1.92 (m, 2 H), 1.6 (s, 3 H), 1.5–0.6 (m, s at 1.05, 14 H); mass spectroscopic molecular weight 240; UV λ_{max} (3-methyl pentane) 266 (sh 1214), 273 (2179), 278 (2429) nm.

15 (80%): ^{1}H NMR (CCl_4) δ 7.03 (m, 4 H), 2.58–2.38 (m, 2 H), 2.3–0.9 (m, s at 1.08, 17 H), 0.21 (s, 9 H); high-resolution mass spectroscopic molecular weight, calcd for $C_{20}H_{13}Si$ 298.2117, found 298.2119; UV λ_{max} (3-methyl pentane) 266 (sh 1599), 272 (2330), 279 (2499) nm.

16 (35%): mp 67 °C; ^{1}H NMR ($CDCl_3$) δ 7.27–6.9 (m, 4 H), 2.87–2.73 (m, 1 H), 2.6–2.3 (2 H, m), 1.7–0.85 (m, 3 H), 1.13 (s,

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[17] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[18] See ref 4 for a representative photochemical procedure.

9 H); ^{13}C NMR ($CDCl_3$) δ 147.83, 147.45, 128.29, 127.68, 124.14, 122.23, 77.92, 75.02, 53.89, 43.76, 42.84, 36.25, 28.07, 27.63, 27.35; IR (KBr) 3080, 3060, 2980, 2960, 2880, 645 cm^{-1}; high-resolution mass spectroscopic molecular weight, calcd for $C_{17}H_{21}Br$ 304.0827, found 304.0825. Anal. Calcd for $C_{17}H_{21}Br$: C, 66.89; H, 6.93; Br 26.18. Found C, 67.04; H, 6.92; Br, 25.77.

17 (25%): ^{1}H NMR (CCl_4) δ 7.14 (m, 4 H), 2.7–2.34 (m, 3 H), 1.72–0.96 (m, s at 1.12, 14 H); high-resolution mass spectroscopic molecular weight, calcd for $C_{13}H_{21}Cl$ 260.1331, found 260.1340; UV λ_{max} (3-methylpentane) 265 (1580), 271 (2435), 278 (2714) nm.

18 (35%): ^{1}H NMR δ 7.0–6.77 (m, 4 H), 3.57 (s, 3 H), 2.8 (m, 1 H), 2.43 (m, 2 H)8 1.7–0.8 (m, s at 0.98, 14 H); ^{13}C NMR ($CDCl_3$) δ 174.9, 150.0, 145.28, 126.68, 126.49, 124.29, 124.03, 79.36, 68.05, 51.69, 46.66, 45.89, 40.89, 35.69, 28.35, 27.64, 26.56; IR (neat) 3070, 2970–2920, 2880, 1725, 1600, 1270, 1200, 1150, 1115, 730 cm^{-1}; high-resolution mass spectroscopic molecular weight, calcd for $C_{19}H_{24}O_2$ 284.1776, found 284.1786, UV λ_{max} (3-methylpentane) 262 (1073), 268 (1630), 275 (1724) nm.

2,5-Di-*n*-butyl-*endo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nonane (19). The dichloro derivative **10** 127.6 mg (0.53 mmol) was dissolved in 10 mL of THF and cooled to −78 °C. At this point 2.7 mL (3.78 mmol) of butyllithium in hexane was added and the mixture was stirred for 15 min at 78 °C and 2 h at room temperature. After recooling to −78 °C, 1 mL (1.276 g, 9.25 mmol) of *n*-butyl bromide was added with stirring. The reaction was maintained at −78 °C for 25 °C for 1 h. After quenching with saturated brine, the aqueous phase was extracted with hexane. The hexane solution was dried over $MgSO_4$ and removed on the rotary evaporatory. The residue was prepurified by TLC (SiO_2, hexane) and separated by preparative GLPC to yield pure **19** (18%): mp 46 °C; ^{1}H NMR (CCl_4) δ 6.97 (m, 4 H), 2.22 (m, 2 H), 2.0–1.08 (m, 18 H), 1.02–0.63 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 151.19, 126.56, 124.03, 64.38, 43.72, 41.29, 32.04, 29.72, 27.08, 23.79, 14.21; UV λ_{max} (cyclohexane) 261 (1316), 267 (1929), 274 (1991) nm. Anal. Calcd for $C_{21}H_{30}$: C, 89.30; H, 10.70. Found: C, 89.44; H, 10.96.

2-Acetoxy-5-*tert*-butyl-*endo*-benzotricyclo[4.2.1.0^{2,5}]nonane (20). Into a flask placed 415.4 mg (1.74 mmol) of **10** and 40 mL of THF. After cooling to −78 °C, 5 mL (7.5 mmol) of *tert*-butyllithium in pentane was added. The reaction was stirred at −78 °C for 1 h and −45 °C for 2 h and quenched with 2 mL (4.36 g, 23.2 mmol) of 1,2-dibromoethane (−78 °C). After workup in the usual fashion, the crude reaction product, which contained mainly **16** contaminated with a small amount of the mono *tert*-butyl derivative **13a**, was dissolved in 100 mL of acetic acid containing 2.0 g of silver acetate. The mixture was stirred for 3 days at 25 °C, filtered, and diluted with hexane. The hexane solution was poured into 300 mL of cold 3 N NaOH and extracted with additional hexane. After drying over $MgSO_4$, the residue was purified by TLC (SiO_2, hexane) to yield 30 mg (8%) of **13a** and 95 mg (20%) of the desired acetate **20**: mp 79 °C; ^{1}H NMR (CCl_4) δ 7.23–6.77 (m, 4 H), 2.57 (br s, 1 H), 2.43 (br s, 1 H), 2.02 (s, 3 H), 1.57–0.67 (m, 6 H), 1.03 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 169.18, 148.13, 145.0, 127.19, 126.10, 124.88, 122.68, 95.0, 73.12, 44.12, 41.75, 40.29, 34.19, 27.46, 26.37, 25.03, 20.63; IR (neat) 3070, 2980–60, 2880, 1740, 1605, 1450, 1250, 1210, 740 cm^{-1}; high resolution mass spectroscopic molecular weight, calcd for $C_{19}H_{24}O_2$ 284.1776, found 284.1799; UV λ_{max} (3-methylpentane) 262 (1156), 268 (1751), 275 (1873) nm. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.38; H, 8.44.

2-Methoxy-5-*tert*-butyl-*endo*-benzotricyclo[4.2.1.0^{2,5}]nonane (21). A flask was charged with 89 mg (0.31 mmol) of **20** and 15 mL of THF. After cooling to −78 °C, 1.5 mL (2.01 mmol) of methyllithium in ether was added, and the reaction maintained at −78 °C for 0.5 h. The mixture was warmed to 25 °C and stirred for 3 h, and 1 mL (2.89 g, 16 mmol) of methyl iodide was added. After 15 h at room temperature, the reaction was diluted with hexane and washed with brine solution. The hexane solution was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by TLC (SiO_2, hexane) to yield 65 mg (80%) of **21**: mp 61 °C; ^{1}H NMR ($CDCl_3$) δ 7.1 (br s, 4 H), 3.5 (s, 3 H), 2.57–2.17 (m, 3 H), 1.57–0.93 (m, s at 1.05, 16 H); ^{13}C NMR δ 149.84, 146.01, 127.41, 126.32, 124.43, 123.64, 98.44, 73.23, 54.18, 43.19, 42.81, 41.25, 35.09, 28.53, 27.70, 25.85; IR (KBr) 3060, 2990, 2960, 2880, 2820, 1100 cm^{-1}; UV λ_{max} (3-methylpentane) 263 (1369), 270 (2249), 276 (2308) nm. Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 83.90; H, 9.50.

Registry No. 7, 31641-96-0; 8, 21604-74-0; **9b**, 96430-04-5; **10**, 96430-05-6; **13a**, 96430-06-7; **14**, 96430-07-8; **15**, 96430-08-9; **16**, 96430-09-0; **17**, 96430-10-3; **18**, 96430-11-4; **19**, 96430-12-5; **20**, 96430-13-6; **21**, 96430-14-7.

Supplementary Material Available: X-ray structural data for 2,5-dichloro-*exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nonane (16 pages). Ordering information is given on any current masthead page.

A Convenient Method for Upgrading the Enantiomeric Purities of (+)-Longifolene and (+)-3-Carene to Materials Approaching 100% ee

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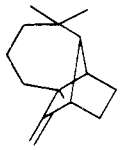
(+)-Longifolene (1) and (+)-3-carene (2) have exhibited useful properties as chiral auxiliaries for asymmetric synthesis.



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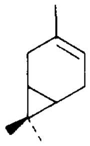

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For example, we established that dilongifolylborane (Lgf_2BH) hydroborates cis and trisubstituted prochiral olefins (acyclic and cyclic) to provide, after oxidation of the intermediate organoboranes, alcohols of 60–80% ee.[2] Recently we reported that *B*-allyldicaranylborane, on condensation with aldehydes, yields secondary homoallylic alcohols of very high optical purities.[3] However, the optical purities of (+)-longifolene and (+)-3-carene available from many of the natural sources are only in the range of 80–95% ee. We had previously developed an efficient procedure for upgrading α-pinene from 92% to 99% ee.[4,5] Consequently, we concluded that it would be desirable to have these new chiral ligands longifolene and 3-carene available in higher optical purities. We hoped that a simple procedure such as had served to upgrade the optical purity of α-pinene would also make it possible to upgrade the optical purities of (+)-3-carene and (+)-longifolene. Hence we undertook to develop simple and efficient methods for upgrading the optical purities of these olefins.

(+)-Longifolene undergoes hydroboration[6,8] readily to yield crystalline Lgf_2BH, which is sparingly soluble in common organic solvents, such as pentane, THF, CCl_4, CH_2Cl_2, or $CHCl_3$. We discovered that simple preparation of Lgf_2BH, followed by separation of the mother liquor, provided an improved product. For this purpose, THF proved to be preferable and the concentration of the solution used is critical. Best results were obtained using

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