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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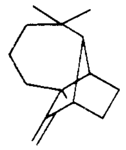
(+)-Longifolene (1) and (+)-3-carene (2) have exhibited useful properties as chiral auxiliaries for asymmetric synthesis.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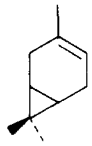
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For example, we established that dilongifolylborane (Lgf$_2$BH) hydroborates cis and trisubstituted prochiral olefins (acyclic and cyclic) to provide, after oxidation of the intermediate organoboranes, alcohols of 60–80% ee.[2] Recently we reported 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$_2$BH, which is sparingly soluble in common organic solvents, such as pentane, THF, CCl$_4$, CH$_2$Cl$_2$, or CHCl$_3$. We discovered that simple preparation of Lgf$_2$BH, 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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[1] Postdoctoral research associate on Grant GM 10937-22 from the National Institutes of Health.

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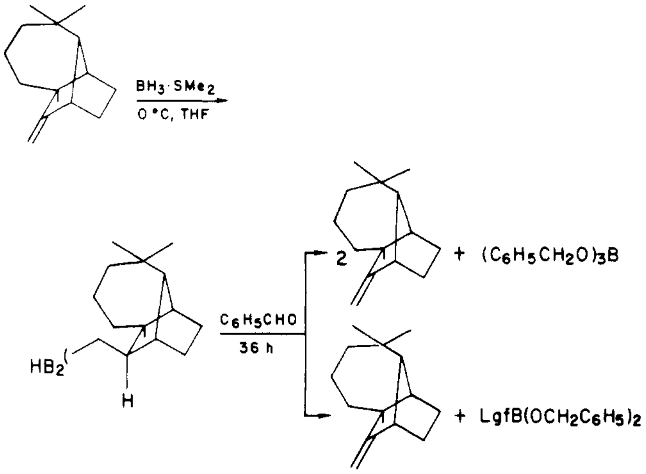
Table I. Upgrading the Optical Purities of (+)-Longifolene and (+)-3-Carene

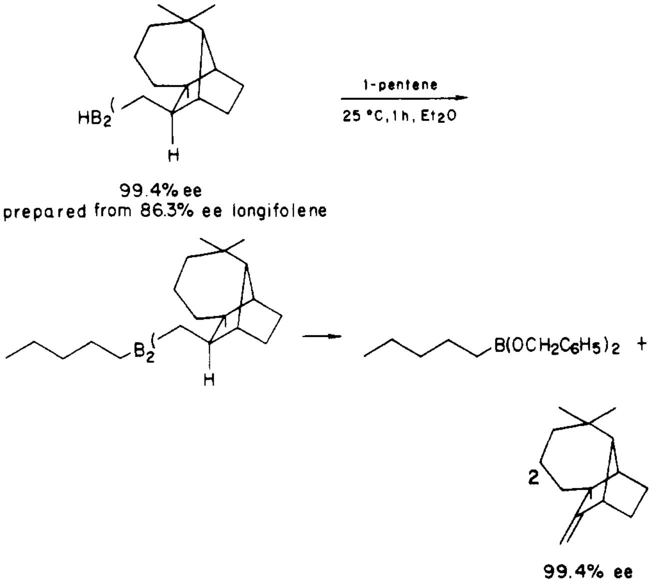
dialkylborane	solvent	molarity of borane soln	aldehyde	temp during eliminatn step,[e] °C	overall isolated yield, %	$[\alpha]^{23}_{D}$ (neat), deg	% ee[f]
Lgf$_2$BH[a]	ether	0.75	CH$_3$CHO	25	12	+41.6	86.7
Lgf$_2$BH	THF	0.75	CH$_3$CHO	25	10	+45.7	95.2
Lgf$_2$BH	THF	0.50	C$_6$H$_5$CHO	75	26	+47.7	99.4
Lgf$_2$BH[b]	THF	0.50	C$_6$H$_5$CHO	75	56	+48.0	100
Lgf$_2$BH	THF	0.75	C$_6$H$_5$CHO	75	44	+47.3	98.5
Lgf$_2$BH	THF	1.00	C$_6$H$_5$CHO	75	56	+43.3	90.2
Car$_2$BH[c]	ether	0.7	C$_6$H$_5$CHO	60	46	+17.1	96.5
Car$_2$BH[c]	THF	0.7	C$_6$H$_5$CHO	60	53	+17.7	100
Car$_2$BH[d]	THF	0.7	C$_6$H$_5$CHO	60	49	+17.7	100

[a] In all cases the starting material, (+)-longifolene, has an optical rotation of $[\alpha]^{23}_{D}$ +41.1° (neat) (86.3% ee). [b] Purified longifolene of $[\alpha]^{23}_{D}$ +47.7° was used. [c] The starting material, (+)-3-carene, has an optical rotation of $[\alpha]^{23}_{D}$ +16.7° (neat) (94.5% ee). [d] The starting material, (+)-3-carene, has an optical rotation of $[\alpha]^{23}_{D}$ +14.9° (neat) (84.2% ee). [e] In all cases the 1-pentyl derivatives were treated with the aldehyde. [f] The % ee of (+)-longifolene and (+)-3-carene based on maximum rotation $[\alpha]^{23}_{D}$ +48° (neat) and $[\alpha]^{23}_{D}$ +17.7° (neat), respectively.

Scheme I



Scheme II



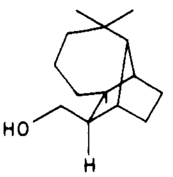
a 0.5 M concentration in THF at 0 °C. The results are summarized in Table I.

Quantitative elimination of longifolene from Lgf$_2$BH proved extremely difficult and treatment of Lgf$_2$BH with excess benzaldehyde at 75 °C for 36 h afforded only dibenzyl longifolylboronate (Scheme I).

Fortunately, an alternative procedure solved the problem. The purified Lgf$_2$BH was used to hydroborate 1-pentene at 25 °C in Et$_2$O. The trialkylborane thus obtained was treated with benzaldehyde at 75 °C for 36 h under neat conditions, providing (+)-longifolene in satisfactory conversion (Scheme II). After a single crystallization and washing, longifolene, $[\alpha]^{23}_{D}$ of +41.4° (neat), gives longifolene, $[\alpha]^{23}_{D}$ of +47.7° (neat). Further rehydroboration gave material with a slightly higher rotation, $[\alpha]^{23}_{D}$ +48.0°. Consequently, this is the value we assign to longifolene of 100% ee.[7]

The use of acetaldehyde to lower the elimination temperature was not helpful, with only one longifolyl group being eliminated at 25 °C.

Lgf$_2$BH, obtained after crystallization from THF (0.75 M solution), was oxidized with alkaline hydrogen peroxide. The longifolol, **3**, thus obtained, showed $[\alpha]^{23}_{D}$ −22.7° (*c* 2.5, chloroform) of 98.5% ee, based on the optical purity of the longifolene utilized. Further oxidation of the mother liquor provided longifolol of $[\alpha]^{23}_{D}$ −15.4° (*c* 2.5, chloroform), corresponding to 66.8% ee.



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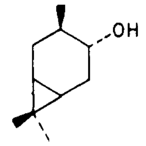

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In a similar manner (+)-3-carene (**2**) was hydroborated[8] with BH$_3$·SMe$_2$ and selective crystallization of pure Car$_2$BH was achieved in THF. Next, the Car$_2$BH thus obtained was used to hydroborate 1-pentene at 0 °C in Et$_2$O and the trialkylborane obtained was treated with benzaldehyde to yield (+)-3-carene of 100% ee.[9] By this method, (+)-3-carene of 84% and 94% ee could be upgraded to 100% ee.

The crystallized Car$_2$BH was methanolyzed and then oxidized by using alkaline hydrogen peroxide to 4-isocaranol, **4**, $[\alpha]^{23}_{D}$ −70.1° (*c* 3.2, chloroform) of 100% ee, as

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[7] Optical purity was determined by measuring the rotation and comparing the values with the maximum reported rotations.[7a–e] (a) Simonsen, J. L. *J. Chem. Soc.* **1920**, *117*, 570: $[\alpha]_{D}$ +42.7° (neat). (b) Commercial sample available from Fluka has $[\alpha]^{20}_{D}$ +45° (neat). (c) Commercial sample available from Aldrich has $[\alpha]^{22}_{D}$ +45.7° (neat). (d) Ourisson, G.; Munavalli, S.; Ehret, C. In "Data Relative to Sesquiterpenoids"; Pergamon Press: Elmsford, NY, 1966: $[\alpha]_{D}$ +45 ± 1° (neat). (e) Matsuo, A.; Nakayama, M.; Hayashi, S. *Chem. Lett.* **1973**, 769: $[\alpha]_{D}$ −46.9° (neat).

[8] Brown, H. C.; Suzuki, A. *J. Am. Chem. Soc.* **1967**, *89*, 1933.

[9] Optical purity was based on ^{19}F NMR examination of the Mosher ester of 4-isocaranol. The rotation for (+)-3-carene is higher than any reported value.[9a–c] (a) Commercial sample available from Fluka has $[\alpha]^{20}_{D}$ +17° (neat). (b) Simonsen, J. L. In "The Terpenes", 2nd ed.; revised by Simonsen, J. L. and Owen, L. N.; Cambridge University Press: New York, 1949–1957: $[\alpha]_{D}$ +17°. (c) Gollnick, K.; Schroeter, S.; Ohloff, G.; Schade, G.; Schenck, G. *Justus Liebigs Ann. Chem.* **1965**, *687*, 14: $[\alpha]^{25}_{D}$ +17.5° (*c* 3.7, benzene).

indicated by ^{19}F NMR examination of the Mosher ester.[10] Oxidation of the mother liquor afforded 4-isocaranol of $[\alpha]^{23}_{\mathrm{D}}$ −55.5° (*c* 3.2, chloroform) of 79% ee.

The present method therefore makes readily available Lgf$_2$BH and Car$_2$BH of very high optical purity, which can be used for the asymmetric hydroboration of prochiral olefins. However, the hydroboration of prochiral olefins using Car$_2$BH is yet to be explored. These procedures for upgrading the optical purities of (+)-longifolene and (+)-3-carene, together with the earlier procedure we reported for upgrading the optical purity of α-pinene, may be useful for upgrading the optical purities of other terpenes.

Experimental Section

The reaction flasks and glass equipment were stored in an oven at 150 °C overnight and assembled in a stream of dry nitrogen gas. Syringes were assembled and fitted with needles while hot and cooled in a stream of dry nitrogen gas. Special techniques used in handling air-sensitive materials are described in detail elsewhere.[11] ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in δ relative to BF$_3$·Et$_2$O. GC analyses were carried out with a Hewlett-Packard 5750 chromatograph using 12 ft × 0.125 in. columns with (a) 10% Carbowax 20M on Chromosorb W (100–120 mesh) and (b) 10% SE-30 on Chromosorb W (100–120 mesh). Rotations were measured on a Rudolph Polarimeter Autopol III.

Materials. Tetrahydrofuran (THF) was distilled over benzophenone ketyl and stored under nitrogen atmosphere in an ampule. Borane–methyl sulfide (BMS) was purchased from Aldrich Chemical Co. BMS was estimated according to the standard procedures.[10] (+)-Longifolene and (+)-3-carene were distilled from a small excess of lithium aluminum hydride.

Preparation of Dilongifolylborane (Lgf$_2$BH) of High Optical Purity (~99% ee). A 250-mL flask equipped with a side arm, magnetic stirring bar, and gas lead was flushed with nitrogen. In this flask was placed 5.57 mL (8.98 M, 50 mmol) of BH$_3$·SMe$_2$ and 39 mL of THF and maintained under magnetic stirring. To the reaction mixture was added 22.02 mL (100 mmol) of (+)-longifolene, $[\alpha]^{23}_{\mathrm{D}}$ +41.4° (neat), via a syringe, and the reaction mixture was kept at 0 °C for 24 h. A white crystalline solid, Lgf$_2$BH, crystallized out. The supernatant solution was removed by a double-ended needle and the solid washed with diethyl ether (3 × 15 mL). The crystals were dried under vacuum (12 mmHg) at room temperature for 1 h to obtain 18.5 g (72% yield) of Lgf$_2$BH.

(a) The solid thus obtained was suspended in 30 mL of THF and methanolyzed (^{11}B NMR, δ 54). The reaction mixture was oxidized by using 24 mL of 3 N sodium hydroxide and 9 mL of 30% hydrogen peroxide. The reaction mixture was further stirred at 55 °C for 2 h and cooled to room temperature. It was saturated with anhydrous potassium carbonate and extracted with diethyl ether (3 × 25 mL). The ether extract was washed with water (2 × 20 mL), followed by brine (2 × 20 mL), and then dried over MgSO$_4$. Evaporation of the solvent afforded longifolol: 13.3 g (60% overall yield); mp 83–84 °C [lit.[12] (mp 78.5–80.5 °C; lit.[6] mp 84–85 °C); $[\alpha]^{23}_{\mathrm{D}}$ −22.7° (*c* 2.5, chloroform) [lit.[12] $[\alpha]_{\mathrm{D}}$ +23.5° (in 95% ethanol); lit.[6] $[\alpha]_{\mathrm{D}}$ −28° (in chloroform)].

(b) The mother liquor from the experiment was oxidized by using 18.6 mL of 3 N sodium hydroxide and 7 mL of 30% hydrogen peroxide as above. Logifolol obtained showed optical rotation of $[\alpha]^{23}_{\mathrm{D}}$ −15.4° (*c* 2.5, chloroform), 66.8% ee.

(c) In another experiment, Lgf$_2$BH was prepared as above. The reaction mixture (without isolating the solid Lgf$_2$BH) was methanolyzed and oxidized as described in a. Compound **2** obtained has shown $[\alpha]^{23}_{\mathrm{D}}$ −19.7° (*c* 2.5, chloroform), (85.5% ee).

Liberation of (+)-Longifolene of ~99% ee. The crystalline Lgf$_2$BH, as described above, 18.5 g (36 mmol), was suspended in 32 mL of diethyl ether. To it was added 4.5 mL (40 mmol) of 1-pentene. After the mixture was stirred at room temperature for 1 h, the solid Lgf$_2$BH had disappeared. ^{11}B NMR of the reaction mixture showed a signal at δ 84, indicating the formation of a R$_3$B species. The solvent was removed under vacuum (12 mmHg). To the product was added 14.7 mL (144 mmol) of benzaldehyde, and the reaction mixture was kept at 75 °C for 36 h. Then the crude reaction mixture was distilled under vacuum (0.08 mmHg) to afford benzaldehyde (at 40 °C) and (+)-longifolene (at 53 °C). The latter fraction was dissolved in 50 mL of ether, and traces of residual benzaldehyde were removed by washing with 3 × 25 mL of 10% aqueous sodium bisulfite solution. The organic layer was dried over MgSO$_4$ and the solvent removed. The residue was distilled over a small quantity of lithium aluminum hydride under vacuum: bp 53 °C (0.03 mm) [lit.[12] bp 144–146 °C (30 mm)]; 9 g, 61% yield) (44% overall yield); chemical purity of the sample >99% (as indicated by GC); $[\alpha]^{23}_{\mathrm{D}}$ +47° (neat). It was further purified by preparative GC (20% Carbowax 20M column) to obtain a 100% chemically pure sample: $[\alpha]^{23}_{\mathrm{D}}$ +47.3° (neat) [lit.[7a] $[\alpha]_{\mathrm{D}}$ +42.7° (neat)]; n^{20}_{D} 1.5035 [lit.[12] n^{25}_{D} 1.5000].

Preparation of Dicaranylborane (Car$_2$BH) of High Optical Purity (~100% ee). A 250-mL flask equipped with a side arm, magnetic stirring bar, and gas lead was charged with 5.57 mL (8.98 M, 50 mmol) of BH$_3$·SMe$_2$ and 50 mL of THF. It was cooled to 0 °C in an ice bath, and 15.8 mL (100 mmol) of (+)-3-carene, $[\alpha]^{23}_{\mathrm{D}}$ +14.9° (neat), was added dropwise with magnetic stirring. The flask was maintained at 0 °C without stirring for 18 h. A white crystalline solid separated out. The supernatant liquid was removed by double-ended needle, and the crystals were washed with ice-cold ethyl ether (3 × 15 mL). The solid Car$_2$BH was dried under vacuum (12 mmHg) at room temperature for 1 h to obtain 9.12 g (64% yield) of Car$_2$BH.

(a) The solid thus obtained was suspended in 25 mL of THF and methanolyzed. The reaction mixture was oxidized by using 21.3 mL of 3 N sodium hydroxide and 8 mL of 30% hydrogen peroxide. The reaction mixture was further stirred at 55 °C for 2 h and cooled to room temperature. It was saturated with anhydrous potassium carbonate and extracted with diethyl ether (3 × 25 mL). The ether extract was washed with water (2 × 20 mL), followed by brine (2 × 20 mL), and then dried over MgSO$_4$. Evaporation of the solvent afforded (−)-4-isocaranol isolated by distillation: bp 70–72 °C (15 mm) [lit.[8] bp 89–90 °C (35 mm)]; 7.8 g 51% yield; n^{20}_{D} 1.4814 (lit.[8] n_{D} 1.4816); $[\alpha]^{23}_{\mathrm{D}}$ −70.1° (*c* 3.2, chloroform); [lit.[9c] $[\alpha]^{25}_{\mathrm{D}}$ −69.7° (*c* 3.2, chloroform)]. Its Mosher ester was prepared according to the literature procedures.[10] The ^{19}F NMR indicated the compound to be 100% ee.

(b) The mother liquor from the above experiment was oxidized by using 12 mL of 3 N sodium hydroxide and 4.5 mL of 30% hydrogen peroxide as above. (−)-4-Isocaranol obtained showed optical rotation of $[\alpha]^{23}_{\mathrm{D}}$ −55.5° (*c* 3.2, chloroform) (79% ee).

(c) In another experiment, Car$_2$BH was prepared as above. The reaction mixture (without isolating the solid) was methanolyzed and oxidized as described in a. (−)-4-Isocaranol thus obtained showed an optical rotation of $[\alpha]^{23}_{\mathrm{D}}$ −67.0° (*c* 3.2, chloroform) (96% ee).

Liberation of (+)-3-Carene of High Optical Purity (~100% ee). The solid Car$_2$BH, prepared as above, was suspended in 25 mL of THF at 0 °C and treated with 4 mL of 1-pentene (35 mmol) under magnetic stirring. After 2 h the reaction mixture became homogeneous and the ^{11}B NMR spectrum indicated absorption at δ 84, corresponding to the presence of trialkylborane. The trialkylborane was freed from solvents under vacuum (12 mmHg), and to it was added 8.16 mL of benzaldehyde (80 mmol). The reaction mixture was kept at 60 °C for 4 h. From the crude reaction mixture, (+)-3-carene was recovered by distillation: 70 °C (27 mm). It was dissolved in 50 mL of ether and excess benzaldehyde removed by washing with 4 × 30 mL of 10% sodium bisulfite solution. The organic layer was dried over MgSO$_4$ and the ether evaporated. The residue was distilled over LiAlH$_4$ under vacuum: bp 58–60 °C (12 mm) [lit.[7a] bp 123–124 °C (200 mm)]; 6.6 g, 75% yield (49% overall yield); GC purity ≥98%. A small portion of the sample was further purified by preparative GC to obtain a 100% GC pure sample: $[\alpha]^{23}_{\mathrm{D}}$ +17.7° (neat) [lit.[9c] $[\alpha]_{\mathrm{D}}$ +17.5° (neat)].

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Registry No. 3, 96705-75-8; 4, 4017-88-3; Lgf$_2$BH, 96705-76-9; Lgf$_3$B, 96705-77-0; Car$_2$BH, 96705-78-1; Car$_3$B, 96705-79-2; (+)-longifolene, 475-20-7; (+)-3-carene, 498-15-7.

1,3-Dipolar Cycloadditions of 3,5-Dichloro-2,4,6-trimethylbenzonitrile Oxide to (Phenylsulfonyl)allenes

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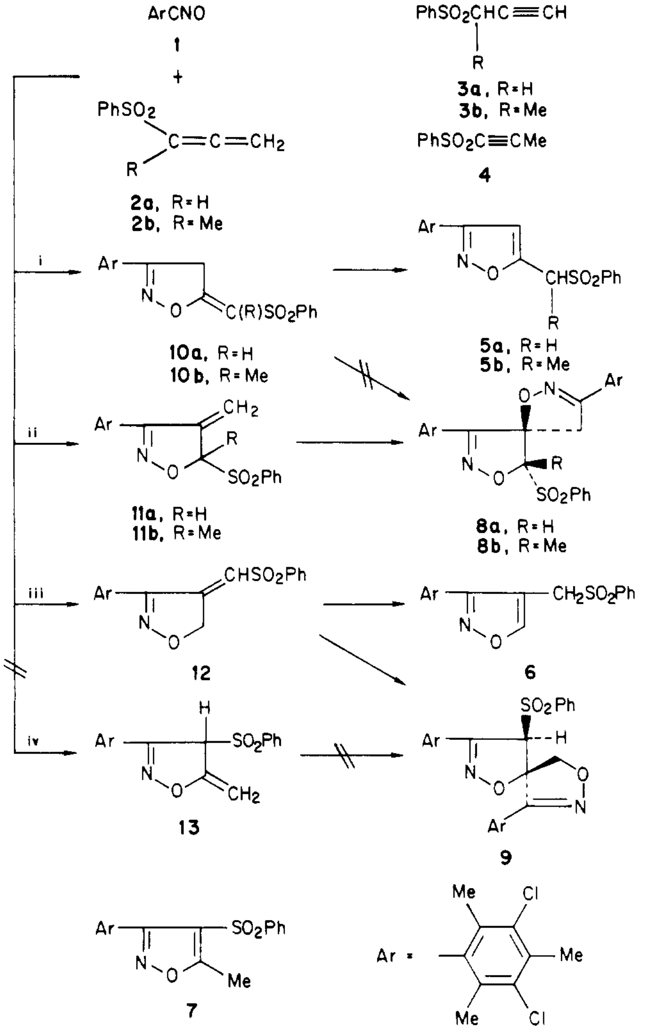
1,3-Dipolar cycloadditions to allenes present a number of synthetic and mechanistic possiblities.[2-10] In previous papers, we have described the reaction of 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide (1) with 1,1-diphenylallene, phenoxyallene, and 1-methyl-1-phenoxyallene. These substrates give exclusively cycloadducts due to bond formation between the carbon of the 1,3-dipole and the central carbon of the allenic function. To gain information about the generality and the origin of this pattern of behavior, we have now studied the reaction of the same nitrile oxide with strongly polarized, electron-deficient allenes such as the phenylsulfonyl-substituted substrates **2a,b**.

The reactions of nitrile oxide 1 with allenes **2a,b** were carried out in boiling carbon tetrachloride using equimolar amounts of the reactants. The time necessary to complete disappearance of starting 1, as shown by periodic TLC and IR analyses, was 9 and 21 h, respectively. In the case of allene **2a**, the chromatographic treatment of the complex product mixture gave, apart from recovered **2a** (28%) and side products due to isomerization or dimerization of 1, the monoadducts **5a** (23%), **6** (21%), and **7** (2.5%) and the diadducts **8a** (4%) and **9** (1.8%).[11] Compounds **5a** and **7** were obtained as the only products by treating 1 with the alkyne derivatives **3a** and **4**, respectively. The reaction of 1 with **2b** resulted in a less complex mixture than that arising from **2a**. The monoadduct **5b** (55%) and the diadduct **8b** (11%) were obtained. Minor quantities of unchanged allene and of unidentified side products were also present. Compound **5b** was found to be the exclusive product of the reaction between 1 and **3b**.

Scheme I



Structural assignments for the products rely upon analytical data, spectral properties, and chemical evidence. The formulas **5a,b** and **6** were readily established on the basis of the chemical shifts of the isoxazolic protons. The fully substituted isoxazole **7** was prepared independently by treatment of 1 with (phenylsulfonyl)acetone in the presence of sodium hydroxide; the proposed regiochemical course of this reaction is highly probable in light of the well-known behavior of nitrile oxides toward active methylene compounds.[12]

The diadduct structures come from the following evidence. Both ^{1}H and ^{13}C chemical shifts as well as the geminal coupling constants are consistent with the endocyclic methylene group being adjacent to carbon in **8a,b** and to oxygen in **9**. On the other hand, the methine sp^3 carbon resonates at δ 73.1 in **9**, while it is much more deshielded in **8a** (δ 96.1). Moreover, the chemical shifts of the spiro carbons of the three diadducts are practically coincident, in harmony with the assigned structures which present similar chemical environments at the spiro center. It is to be noticed that each diadduct was obtained as one diastereoisomer; the marked NMR nonequivalence of the geminal protons may reflect a spatial influence of the sulfonyl moiety, thus indicating a cis relationship between the endocyclic methylene group and the PhSO$_2$ substitu-

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