panol to give 5.24 g (73%) of **8d**: mp 185–187 °C dec; NMR (Me_2SO-d_6) δ 2.80 (3, s, CH_3), 3.65 (3, s, CH_3SO_2), 7.90–8.20 (3, m, H-5, H-6, H-7), 8.30–8.60 (1, m, H-8); UV λ_{max} (MeOH) 274 nm (ε 39 590), 330 (8120); mass spectrum, *m/e* 238 (M^+). Anal. Calcd for $C_{10}H_{10}N_2O_3S$: C, 50.47; H, 4.24; N, 11.77. Found: C, 50.51; H, 4.24; N, 11.57.

4-Methyltetrazolo[1,5-*a*]quinoxaline 5-Oxide (7b). To a solution of 2-methyl-3-methylsulfonylquinoxaline 1-oxide (4.00 g, 16.8 mmol) in Me_2SO (90 mL) was added sodium azide (1.10 g, 16.8 mmol). After the solution was stirred overnight at room temperature, it was diluted with water (300 mL) and a precipitate formed that was collected by suction filtration to afford 3.02 g (89%) of **7b**: mp 205–206 °C; NMR (Me_2SO-d_6) δ 2.80 (3, s, CH_3), 7.80–8.25 (2, m, H-7, H-8), 8.40–8.70 (2, m, H-6, H-9); UV λ_{max} (MeOH) 232 nm (ε 22 200), 262 (shoulder), 317 (11 000); mass spectrum, *m/e* 201 (M^+). Anal. Calcd for $C_9H_7N_5O$: C, 53.78; H, 3.51; N, 34.84. Found: C, 53.66; H, 3.62; N, 34.62.

Acknowledgment. We wish to thank Anne Krech, Kerry Gombatz, Richard James, and Raymond Sumner for their technical assistance.

Registry No.—**1a**, 61522-60-9; **1b**, 67452-55-5; **1c**, 61522-56-3; **2a**, 67452-56-6; **2b**, 67452-57-7; **2c**, 67452-58-8; **3a**, 67452-59-9; **3b**, 67452-60-2; **3c**, 67452-61-3; **4**, 5227-59-8; **5**, 67452-62-4; **6a**, 67452-63-5; **6b**, 67452-64-6; **7a**, 61148-19-4; **7b**, 67452-65-7; **8a**, 39576-77-7; **8d**, 67464-71-5; 2-hydroxymethyl-3-methylquinoxaline 1,4-dioxide, 16915-79-0; *p*-toluenesulfonylhydrazine, 1576-35-8; 2-chloroquinoxaline, 1448-87-9.

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1,2-Diphenyl-3-azanaphtho[*b*]cyclobutadiene

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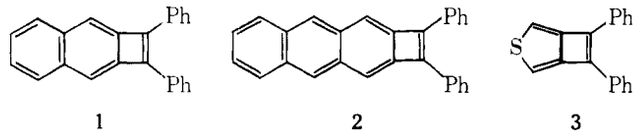
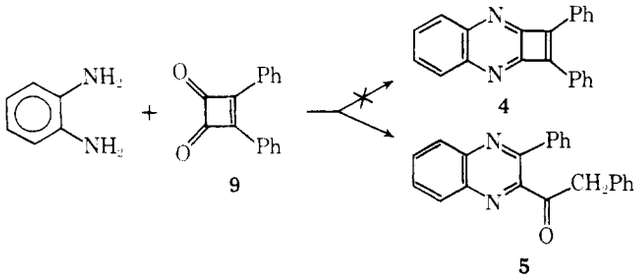
1,2-Diphenyl-3-azanaphtho[*b*]cyclobutadiene (**12**) has been synthesized. The cyclopentadienone derivative **13** and its iron tricarbonyl complex **14** were also formed during the final reduction step. The title compound, obtained as red crystals, undergoes addition reactions (reduction, oxidation) at the 1,2-double bond; it also undergoes a Diels–Alder reaction with 1,3-diphenylisobenzofuran and on heating with triiron dodecacarbonyl it is converted to a mixture of **13** and **14**. The iron tricarbonyl complex **14** is easily oxidized with Ce^{4+} to give **13**.

The synthesis of the first stable aromatic-fused cyclobutadiene, namely 1,2-diphenylnaphtho[*b*]cyclobutadiene (**1**), was reported by Cava[1] in 1963. Since then, 1,2-diphenylanthra[*b*]cyclobutadiene (**2**),[2] 6,7-diphenyl-3-thiabicyclo[3.2.0]heptatriene (**3**),[3] and a few other aromatic-fused cyclobutadienes[4,5] have been synthesized. Compound **3** represents the first known heteroaromatic-fused cyclobutadiene.



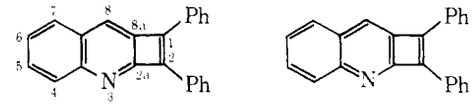
1 **2** **3**



9 **4** **5**

In 1961, Blomquist and Lalancette[6] attempted the synthesis of the diaza analogue **4** of the hydrocarbon **1** by condensation of the dione **9** with *o*-phenylenediamine; they isolated the ring cleavage product **5** rather than the desired cyclobutadiene derivative **4**.

In this paper we report the synthesis and some chemical properties of 1,2-diphenyl-3-azanaphtho[*b*]cyclobutadiene



12a **12b**

(**12**), the first example of a heteroaromatic-fused cyclobutadiene with nitrogen as the heteroatom.

Results and Discussion

o-Nitrobenzyl bromide (**6**) was converted to *o*-nitrobenzyltriphenylphosphonium bromide (**7**) in excellent yield. Wittig condensation of dione **9** with the ylide **8**, derived from the phosphonium salt **7**, afforded a mixture of *cis*- and *trans*-nitroaryls **10a** and **10b** in 85% yield. These isomers, found in the ratio of 87:13, respectively, were separated by

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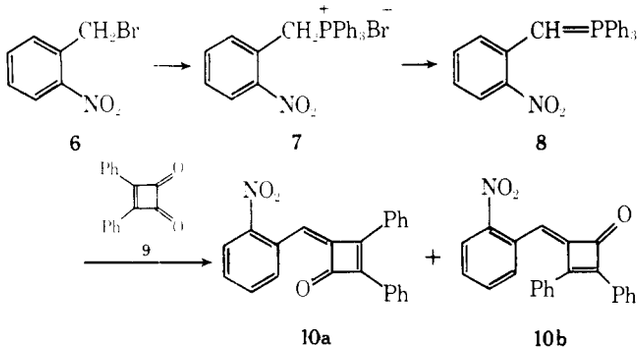
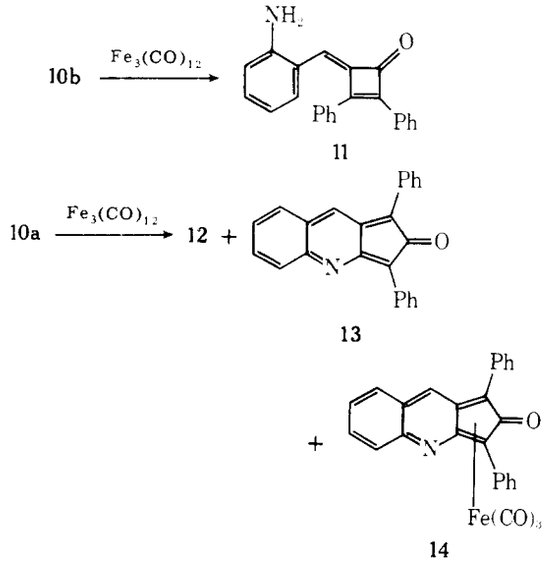


either column chromatography or fractional crystallization from ethanol.

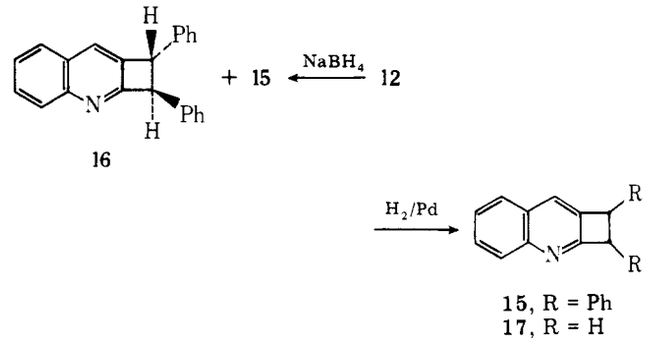
Assignment of the cis and trans geometries to **10a** and **10b** was easily achieved by reduction of these compounds and identification of the product(s) obtained in each case. Although attempts to reduce selectively the nitro group of either **10a** or **10b** by conventional reduction methods, e.g, metals and acid, failed, application of the method of Landesberg[7] to **10a** and **10b** gave the desired products in each case. Thus, reduction of **10b** with triiron dodecacarbonyl afforded the corresponding amino ketone **11**. On the other hand, reduction of **10a** under the same conditions was accompanied by spontaneous ring B closure to give the desired 1,2-diphenyl-3-azanaphtho[*b*]cyclobutadiene (**12**) in 16.5% yield, along with two



other products, the cyclopentadienone derivative **13** (13% yield) and its iron tricarbonyl complex **14** (12.5% yield).

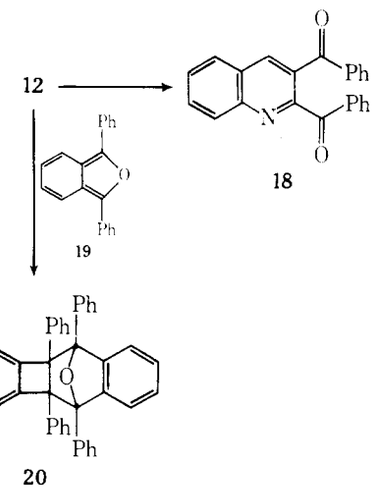
The structural assignment of the latter compounds is based upon spectral and chemical evidence. Compound **12**, isolated as red crystals, mp 163–164 °C, shows a parent ion at *m/e* 305 in its mass spectrum; in addition to a multiplet in the aromatic region in its NMR spectrum, there appears a singlet for one hydrogen at the relatively high-field position of δ 6.55. The position of this proton, undoubtedly that at C-8, is very close to that (δ 6.55) of the olefinic protons of *cis*-stilbene[8] and is strong evidence that the bonds 2a–3 and 8–8a in **12** are fixed to a remarkable degree as in **12a**. A similar suggestion was made to explain the NMR spectrum of **1**.[1] The ultraviolet–visible spectrum of **12** is quite similar to that of hydrocarbon **1**.[1]

Although 1,2-diphenyl-3-azanaphtho[*b*]cyclobutadiene (**12**) appears to be stable indefinitely, it undergoes addition reactions at its 1,2-unsaturated bond of the four-membered ring very easily. Thus, absorption of 1 molar equiv of hydrogen in the presence of palladium afforded *cis*-1,2-diphenyl-3-azanaphtho[*b*]cyclobutene (**15**), whose UV spectrum is quite



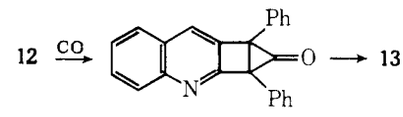
similar to that of nonphenylated analogue **17**, prepared by Wilk.[9] Compound **12** also undergoes facile reduction with sodium borohydride to give largely *trans*-1,2-diphenyl-3-azanaphtho[*b*]cyclobutene (**16**) and a trace of the cis isomer **15**.

Oxidation of **12** with potassium permanganate in dilute hydrochloric acid proceeds smoothly to give 2,3-dibenzoylquinoline (**18**). The diketone **18** could also be obtained by irradiation of a dilute acetone solution of **12** with direct sunlight for 48 h. Finally, the Diels–Alder reaction of **12** with 1,3-di-



phenylisobenzofuran (**19**) resulted in the formation of the expected adduct **20**, whose structure follows from its mass (M^+ 475) and NMR (δ 7.8, s, 1 H).

The dark violet crystalline compound **13**, mp 202–204 °C, exhibits the following spectral data; its NMR spectrum has a singlet at δ 7.3 in addition to a multiplet in the aromatic region, and shows a parent ion at *m/e* 333 in its mass spectrum. Its IR spectrum shows an intense absorption at 1700 cm^{-1} due to a carbonyl group. Compound **13** is probably formed by a chelotropic addition of carbon monoxide to the 1,2-unsaturated bond of the four-membered ring of **12**, giving the in-



termediate **21** which undergoes homolytic ring cleavage to the observed product.[10]

In fact, when **12** was heated with triiron dodecacarbonyl under the conditions of reduction, both **13** and **14** were formed.

$$12 \xrightarrow[C_6H_6,\ \text{heat}]{Fe_3(CO)_{12}} 13 + 14$$

The iron tricarbonyl complex **14** is an orange crystalline compound, mp 297–299 °C dec. It undergoes oxidation with ceric ammonium nitrate very easily, giving back the violet

compound **13**. In its IR spectrum, a carbonyl absorption appears at 1675 cm^{-1} in addition to three distinct absorptions at 2060, 2000, and 1980 cm^{-1}, attributable to three carbonyl groups attached to the iron.

Experimental Section

General. Melting points were determined with a Thomas Unimelt apparatus and are uncorrected. Ultraviolet–visible spectra were determined in ethanol. Spectra were recorded on a Perkin–Elmer 157G IR spectrophotometer, a Varian Cary 118 UV–visible spectrophotometer, a Varian T-60 NMR spectrometer, and a Varian CH5 or Varian Mat. 112 mass spectrometer. Elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratories, West Germany.

***o*-Nitrobenzyltriphenylphosphonium Bromide.**[11] A solution of *o*-nitrobenzyl bromide (2.16 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) in chloroform (20 mL) was stirred at room temperature for 48 h. Diethyl ether (20 mL) was added and the resulting solution was kept at room temperature for an additional 24 h. The deposited crystals were filtered, washed with dry diethyl ether, and air dried. Recrystallization from ethanol afforded colorless prisms (4.15 g, 87%): mp 161–162 °C; NMR ($CDCl_3$) δ 6.05 (d, 2 H, J = 7 Hz), 7.9 (m, 19 H). Anal. Calcd for $C_{25}H_{21}BrNO_2$: C, 62.76; H, 4.39; N, 2.93. Found: C, 62.55; H, 4.56; N, 2.83.

Wittig Condensation of 8 with Dione 9. A solution of dione **9**[6] (2.43 g, 10 mmol) and phosphonium salt **7** (4.78 g, 10 mmol) in dry acetonitrile (50 mL) was heated to reflux under a slight pressure of nitrogen. Triethylamine (6 mL) was added dropwise to the refluxing solution over a period of 30 min. After the addition was completed, the dark violet solution was refluxed for an additional 4 h. The solution was cooled, the solvent was evaporated on a rotary evaporator, and the oily residue was triturated under ethanol to give 3.0 g (85%) of a mixture of **10a** and **10b** as a yellow solid. The mixture was chromatographed on a column of silica gel using a 1:1 mixture of petroleum ether–benzene as eluent. The leading band afforded, after the evaporation of the solvent, 2.4 g (84% of the mixture) of **10a** as yellow solid. Crystallization from ethanol gave the analytical sample of **10a:** mp 124–126 °C; IR (KBr) 1765 cm^{-1}; NMR ($CDCl_3$) δ 7.10 (s, 1 H), 7.50 (m, 14 H); M^+ 353. Anal. Calcd for $C_{23}H_{15}NO_3$: C, 78.18; H, 4.20; N, 3.96. Found: C, 78.18; H, 4.25; N, 3.97.

The second fraction obtained from the column afforded, after evaporation of the solvent and crystallization of the solid residue from methanol, yellow needles of **10b** (450 mg, 16% of the mixture): mp 162.5–164 °C; M^+ 353; NMR ($CDCl_3$) δ 7.0 (s, 1 H), 7.50 (m, 14 H). Anal. Calcd for $C_{23}H_{15}NO_3$: C, 78.18; H, 4.20; N, 3.96. Found: C, 78.0; H, 4.34; N, 4.07.

Reduction of 10b. Triiron dodecacarbonyl (2.5 g, 5 mmol) was added to a solution of **10b** (870 mg, 2.5 mmol) in dry benzene (30 mL) containing absolute methanol (2 mL), and the resulting solution was refluxed under nitrogen for 7 h. The solvent was evaporated on a rotary evaporator and the residue was taken up into chloroform. The chloroform solution was concentrated and chromatographed on a column of silica gel using a 25:75 mixture of benzene–petroleum ether as eluent. Evaporation of the solvent and crystallization of the solid residue from ethanol afforded an analytical sample (350 mg, 54%) of **11** as orange needles: mp 164–165 °C; IR (KBr) 3400, 1765 cm^{-1}; NMR ($CDCl_3$) δ 6.55 (s, 1 H), 7.25 (m, 14 H); M^+ 323. Anal. Calcd for $C_{23}H_{17}NO$: C, 85.44; H, 5.26; N, 4.33. Found: C, 85.50; H, 5.08; N, 4.23.

Reduction of 10a. Triiron dodecacarbonyl (5.04 g, 0.01 mol) was added to a solution of **10a** (3.53 g, 0.01 mol) in dry benzene (150 mL) containing absolute methanol (2 mL) and the resulting solution was refluxed under nitrogen for 7 h. The reaction mixture was cooled to room temperature and filtered. Evaporation of the filtrate gave a dark red gummy material which was dissolved in a small amount of chloroform and chromatographed on a column of basic alumina. Elution of the column with diethyl ether afforded two different fractions. The first fraction, which was a red solution, was evaporated on a rotary evaporator. Trituration of the residue under ether gave a red solid which was crystallized from *n*-hexane to give the analytical sample of **12** (0.5 g, 16.5%): mp 163–164 °C; M^+ 305; NMR ($CDCl_3$) δ 6.5 (s, 1 H), 7.42 (m, 14 H); UV λ_{max} (EtOH) 282 (log ϵ 5.62), 444 nm (3.35). Anal. Calcd for $C_{23}H_{15}N$: C, 90.49; H, 4.91; N, 4.59. Found: C, 90.22; H, 5.06; N, 4.45.

Evaporation of the second fraction gave a deep violet solid, which was crystallized from *n*-hexane to give deep violet crystals of **13** (450 mg, 13.5%): mp 202–204 °C; IR (KBr) 1700 cm^{-1} (C=O); M^+ 333; NMR ($CDCl_3$) δ 7.32 (s, 1 H), 7.43 (m, 14 H); UV λ_{max} (EtOH) 269 (log ϵ 6.5), 477 (5.9), 552 nm (5.6). Anal. Calcd for $C_{24}H_{15}NO$: C, 86.00; H, 4.50; N, 4.20. Found: C, 85.67; H, 4.62; N, 4.15.

Further elution of the column with a 95:5 mixture of chloroform–methanol afforded, after evaporation of the solvent, an orange solid which was crystallized from ethanol to give orange needles of **14** (600 mg, 12.6%). Another crystallization from ethanol gave the analytical sample of **14:** mp 297–299 °C dec; M^+ 473; IR (KBr) 2060, 2000, 1980, 1670 cm^{-1}; NMR (CD_3CO_2H) δ 7.82 (s, 1 H), 7.11 (m, 14 H). Anal. Calcd for $C_{27}H_{15}NO_4Fe$: C, 68.49; H, 3.17; N, 2.95; Fe, 11.83. Found: C, 68.18; H, 3.28; N, 3.06; Fe, 11.94.

Hydrogenation of 1,2-Diphenyl-3-azanaphtho[*b*]cyclobutadiene (12). A solution of **12** (305 mg, 1 mmol) in a mixture of benzene (10 mL) and ethanol (8 mL) was shaken under hydrogen (atmospheric pressure, room temperature) in the presence of 5% palladium on charcoal (0.1 g) until the red color vanished (~45 min). Solvent evaporation followed by crystallization from *n*-hexane–ether gave pure *cis*-1,2-diphenyl-3-azanaphtho[*b*]cyclobutene (**15;** 200 mg, 67%): mp 107–108 °C; M^+ 356; NMR ($CDCl_3$) AB system as two doublets centered at δ 4.73 and 4.93 (2 H, J = 3 Hz), 8.53 (s, 1 H); UV λ_{max} (EtOH) 234 (log ϵ 4.77), 306 (4.07), 312 (4.04), 320 nm (4.11). Anal. Calcd for $C_{23}H_{17}N$: C, 89.90; H, 5.53; N, 4.56. Found: C, 89.97; H, 5.72; N, 4.36.

Reduction of 12 with Sodium Borohydride. Sodium borohydride (100 mg) was added portionwise to a solution of **12** (305 mg, 1 mmol) in a mixture of diethyl ether (20 mL) and ethanol (10 mL) and the resulting solution was stirred at room temperature for 30 min. The solvent was evaporated and water (50 mL) was added to the oily residue and extracted with three portions (50 mL each) of methylene chloride. The combined extracts were dried (Na_2SO_4) and evaporated on a rotary evaporator. The residue was chromatographed on a thick layer of silica gel using chloroform as eluent. Separation of the two different bands afforded **15** (10 mg) and the trans isomer **16** (180 mg, 58%): mp 127–129 °C; M^+ 356; NMR ($CDCl_3$) AB system as two doublets centered at δ 5.33 and 5.63 (2 H, J = 8 Hz), 8.37 (s, 1 H); UV λ_{max} (EtOH) 235 (log ϵ 4.75), 306 (4.07), 312 (4.05), 320 nm (4.12). Anal. Calcd for $C_{23}H_{17}N$: C, 89.90; H, 5.53; N, 4.56. Found: C, 89.76; H, 5.65; N, 4.36.

Diels–Alder Reaction of 12 with 1,3-Diphenylisobenzofuran. A solution of **12** (305 mg, 1 mmol) and 1,3-diphenylisobenzofuran (270 mg, 1 mmol) in dry benzene (50 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature and the solvent was evaporated on a rotary evaporator. Crystallization of the solid residue afforded **20** as microcrystals (305 mg, 52%). Recrystallization from ethanol gave an analytical sample of **20:** mp 278–279 °C; M^+ 575; NMR (Me_2SO-d_6) δ 8.15 (s, 1 H). Anal. Calcd for $C_{43}H_{29}NO$: C, 89.73; H, 5.04; N, 2.43. Found: C, 89.40; H, 5.25; N, 2.32.

Chemical Oxidation of 12 by Potassium Permanganate. A saturated solution of potassium permanganate in acetone (1 mL) was added to a solution of **12** (305 mg, 1 mmol) in 10 mL of acetone. Dilute hydrochloric acid (15 drops) was added and the reaction mixture was heated on a steam bath for 30 min. The solution was cooled to room temperature and basified with dilute ammonium hydroxide. The basic solution was extracted with ether, dried over anhydrous sodium sulfate, and evaporated. The residue was chromatographed on a column of basic alumina. Elution with chloroform gave, after evaporation of the solvent, a solid residue which was crystallized twice with ether to give the analytical sample of **18** (55 mg, 16.5%): mp 172–173 °C; IR (KBr) 1670 and 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.25 (s, 1 H); M^+ 337. Anal. Calcd for $C_{23}H_{15}NO_2$: C, 81.89; H, 4.45; N, 4.15. Found: C, 81.45; H, 4.32; N, 4.20.

Photochemical Oxidation of 12. A solution of **12** (305 mg, 1 mmol) in acetone (300 mL) in a 500-mL flask was stoppered and kept in direct sunlight for 48 h. The solution was then evaporated on a rotary evaporator to a solid residue which was chromatographed on a column of basic alumina. Elution with chloroform gave a solid residue which was crystallized from diethyl ether to give a crystalline compound (65 mg, 20%), identical in all respects with an authentic sample of **18** obtained from chemical oxidation of **12.**

Reaction of 12 with Triiron Dodecacarbonyl. A mixture of **12** (305 mg, 1 mmol) and triiron dodecacarbonyl (405 mg, 1 mmol) in dry benzene (20 mL) containing few drops of methanol was refluxed under nitrogen for 1 h. The reaction mixture was filtered and the filtrate was evaporated on a rotary evaporator. The residue was chromatographed on a thick layer of silica gel using a mixture of 95:5 chloroform–methanol as eluent. Isolation of the leading and slowest bands afforded compounds **13** (25 mg, 6%) and **14** (65 mg, 12%) identical in their IR and melting points with authentic samples of **13** and **14,** respectively, obtained from the reduction of **10a.**

Oxidation of 14 with Ce^{4+}. A solution of **14** (235 mg, 0.5 mmol) and ceric ammonium nitrate (270 mg, 0.5 mmol) in dry acetone was

stirred at room temperature for 1 h. The reaction mixture was filtered and the filtrate was evaporated on a rotary evaporator. The solid residue was chromatographed on a column of silica gel eluting with diethyl ether. Evaporation of the solvent afforded a deep violet solid which was crystallized from *n*-hexane to give deep violet crystals (50 mg, 30%), identical in all respects with an authentic sample of **13**.

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Registry No.—**7**, 23308-83-0; **8**, 42546-50-9; **9**, 24234-76-2; **10a**, 59625-73-9; **10b**, 66809-63-0; **11**, 66809-64-1; **12**, 66809-65-2; **13**, 66809-66-3; **14**, 66809-78-7; **15**, 66809-67-4; **16**, 66809-68-5; **18**, 52260-38-5; **19**, 5471-63-6; **20**, 66809-69-6; *o*-nitrobenzyl bromide, 3958-60-9; triphenylphosphine, 603-35-0.

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Stereocontrolled Preparation of Chiral (*E*)-1-Alkenyl Sulfoxides. Efficient Reduction of Alkenyl Sulfoxides to the Corresponding Alkenyl Sulfides

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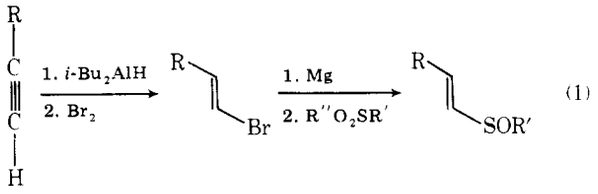
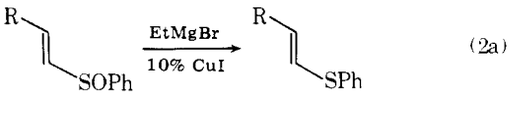
(*E*)-1-Alkenylmagnesium bromides react cleanly and stereospecifically with chiral menthyl sulfinate esters to produce chiral (*E*)-1-alkenyl sulfoxides; no alkenyl sulfide is formed in this process. 1-Alkenyl and 2-alkenyl aryl sulfoxides are easily reduced to the corresponding vinylic sulfides upon treatment with ethylmagnesium bromide/10% cuprous iodide at 0 °C for 1 h. No double bond isomerization occurs during this sulfoxide deoxygenation, and 1,3-butadienyl sulfoxides are reduced cleanly to 1,3-butadienyl sulfides. Proton NMR indicates an upfield chemical shift of about 0.1 and 0.6 ppm for H_α and H_β in the α,β-ethylenic *sulfides* relative to the corresponding *sulfoxides*.

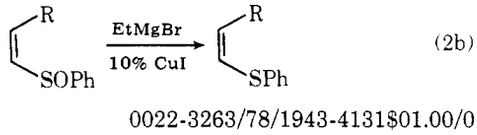
Pursuing our interest in reactions of organometallic reagents with α,β-unsaturated sulfur compounds,[1] we have sought a stereocontrolled method for preparing either (*Z*)-1-alkenyl or (*E*)-1-alkenyl sulfoxides. The Carey–Hernandez synthesis using carbonyl compounds and 1-(trimethylsilyl)-1-(phenylsulfinyl)methyllithium leads to a mixture of (*Z*)- and (*E*)-vinylic sulfoxides,[2] and the Horner–Wittig procedure using carbonyl compounds and sulfinyl methylphosphonate anions also leads to a mixture of geometrical isomers in which the *E* isomer often predominates.[3] Separation of vinylic sulfoxide geometrical isomers is often difficult and time consuming, and the overall yields of pure *E* or *Z* isomers are usually low.[2,3] We report here our recent success in stereospecifically converting (*E*)-vinylic bromides via the corresponding Grignard reagents into (*E*)-vinylic sulfoxides in good yields via eq 1. We report also our discovery that (*Z*)- and (*E*)-vinylic phenyl sulfoxides are easily reduced by ethylmagnesium bromide/10% cuprous iodide with retention of double bond configuration to the corresponding (*Z*)- and (*E*)-vinylic phenyl sulfides under mild conditions and in high yields (eq 2).



(1)



(2a)



(2b)

Results and Discussion

Preparation of (*E*)-1-Alkenyl Sulfoxides. Reaction of Grignard reagents with chiral sulfinate esters is one of the oldest and most often used procedures for preparation of chiral sulfoxides.[4] Harpp has recently summarized this area and has emphasized that a major byproduct in this type of reaction is often the sulfide derived from the initially formed sulfoxide.[5] Harpp recommends general use of organocopperlithium reagents for conversion of sulfinate esters into the corresponding sulfoxides with formation usually of only small amounts of sulfides. We have found that menthyl *p*-toluenesulfinate reacts with isopropenylmagnesium bromide/10% cuprous iodide to give substantial (e.g., 30–40%) amounts of sulfide. Surprisingly, however, we have found that vinylic Grignard reagents in the absence of any copper salts react cleanly with menthyl sulfinate esters in tetrahydrofuran to give only the corresponding vinylic sulfoxides and no detectable amounts of vinylic sulfides as indicated by the comparison with authentic sulfides (Table I).

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