The substances investigated were freshly distilled or sublimed before the measurements. Compounds **1–4, 6, 8, 11, 13, 14,** and **19** crystallized in the trans form after being kept in a refrigerator.

Physical properties and analytical data for the new compounds are collected in Table V.

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(10) Identified by its olefinic vicinal coupling constant J = 12.5 Hz, vs. J = 7.5 Hz observed for the cis isomer.
(11) For the closely related **40**, but 2.5% of the trans-s-trans isomer was found in a solution in 1,1-dichloroethylene.[12] However, because of a misprint, 25% was indicated.
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(13) Ca. 22% in a 0.1 M solution, according to a NMR spectrum; undoubtedly, the percentage of this isomer was even smaller in the 0.0001 M solution used for uv measurements.
(14) Estimated by assuming some further shift toward I in water as compared with methanol for which a 15% value was obtained by low-temperature NMR measurements.
(15) In view of the possible influence of intermolecular interactions, we considered it advisable to compare experimental data on mixtures prepared for the purpose with the results of mathematical analysis of two mixed absorption bands carried out by Vandenbelt and Henrich.[16] The agreement is quite satisfactory.
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(18) Because of low solubility of **14, 15, 16, 18,** and **19** in water, it was only possible to determine directly the percentage of the isomer IV for **12, 13,** and **17** (22, 30, and 20%, respectively, according to NMR spectra of 0.1 M solutions). On the other hand, the data on 0.1 M methanol solutions clearly demonstrate the dramatic increase in the population of IV along with increasing size of the *N*-alkyl substituents (33, 45, 62, 72, and 73% for the isopropyl ketones **12, 13, 14, 15,** and **16,** respectively, and 44, 61, and 73% for the *tert*-butyl ketones **17, 18,** and **19**).
(19) About 97% of the s-cis rotamer.[11]
(20) About 70% of the s-cis rotamer.[12]
(21) A mean value from the data on ketones which exist mainly (**13, 14, 40, 41, 42**) or entirely (**19, 43–45, 47, 48**) in the trans-s-cis form.
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Three Different Consecutive Orbital Symmetry-Controlled Reactions in the Novel Stereospecific Synthesis of 1-Phenyl-4-(1-phenylethenyl)naphthalene. The Reaction of 3,4-Diphenylthiophene 1,1-Dioxide with Ethynylbenzene

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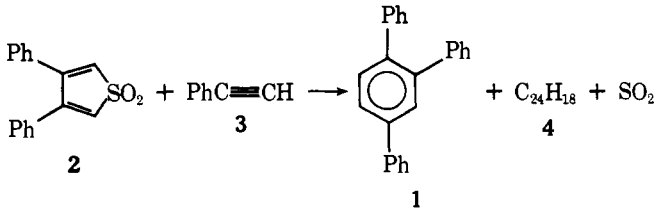
Abstract: The major product of the reaction of 3,4-diphenylthiophene 1,1-dioxide (**2**) with ethynylbenzene (**3**) was not 1,2,4-triphenylbenzene (**1**) as expected, but an isomer, 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**). Deuterium labeling studies involving 2,5-dideuterio-3,4-diphenylthiophene 1,1-dioxide (**11**) indicated that the 1-phenylethenyl moiety originated from the thiophene system in a highly stereospecific manner, giving (*E*)-3-deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)-naphthalene (**13**-*E*) as the major isomer (9:1). A mechanism for the formation of **4** has been proposed which involves three different consecutive orbital symmetry-controlled reactions.

The synthesis of the lower melting (99.1–99.6 °C) crystalline form of 1,2,4-triphenylbenzene (**1**) in low yield by the 4 + 2 cycloaddition reaction of 3,4-diphenylthiophene 1,1-dioxide (**2**) with ethynylbenzene (**3**), followed by the loss of sulfur dioxide has been reported.[1] Our own efforts to synthesize **1** resulted in the isolation of the higher melting (121–122 °C)

crystalline isomer in low yield and a $C_{24}H_{18}$ isomer of **1** (mp 102–103 °C) as the major product (**4**, 30%). The structure of **4** has now been elucidated.

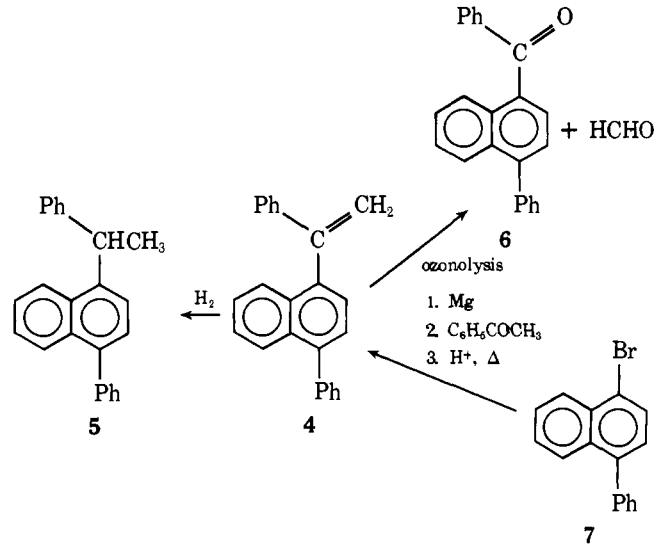


Results

The ^1H NMR spectrum of the putative triphenylbenzene **4** showed a 16 proton aromatic multiplet and two doublets (J = 1.5 Hz) at 5.35 and 5.90 ppm, each corresponding to one proton. At least 15 different types of carbon atoms were indicated by ^{13}C NMR in the 124–149 ppm region, of which seven were quaternary. A 16th resonance appeared at 116.1 ppm and was a triplet in the off-resonance decoupled spectrum. This compound was not identical with an authentic sample of **1** prepared by the cyclotrimerization[2] of ethynylbenzene (**3**).

Examination of the product **5** of quantitative hydrogenation (1.1 equiv) of **4** suggested that a vinylidene group had been converted to a $CH-CH_3$ structure (**5**). Since transition metals such as platinum often cause carbon skeleton rearrangements, **4** was also reduced by hydroboration with diborane, followed by propionic acid protonolysis to afford a product identical with **5**. Ozonolysis of **4** with 1 equiv of ozone at −78 °C in methylene chloride, followed by either oxidative or reductive decomposition gave **6**. Reduction of the ozonide also produced formaldehyde, isolated as the methylenebis(dimedone) derivative, which confirmed the presence of a vinylidene moiety in **4**. Based on these spectral and chemical properties, **4** was assigned the structure 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**) (Scheme I). This structure was unambiguously

Scheme I



verified by comparison with an authentic sample of **4** synthesized by the Grignard reaction of 1-bromo-4-phenylnaphthalene (**7**) with acetophenone, followed by dehydration.[3]

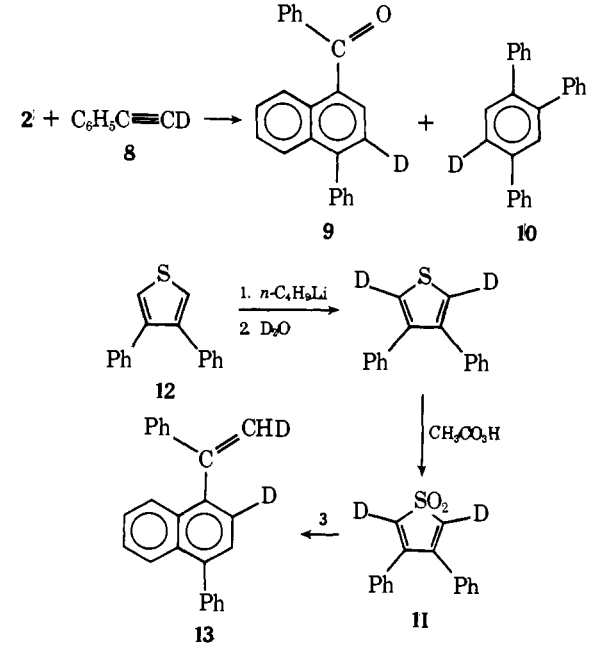
In order to elucidate the reaction mechanism leading to the unexpected appearance of **4**, deuterium labeling studies were carried out to determine the origin of the 1-phenylethenyl moiety. Reaction of **3** with excess n-butyllithium, followed by quenching with deuterium oxide afforded β-deuterioethynylbenzene (**8**) containing >95% d_1. A deuterium-containing compound **9** was then isolated from the reaction of **2** with **8**. In the ^1H NMR, the two doublets attributed to the vinylidene group at 5.35 and 5.90 ppm were unchanged, while the aromatic multiplet consisted of only 15 protons. Although the triplet due to C–D coupling could not be observed in the ^{13}C NMR, the intensity of the peak at 126.3 ppm, assigned to the β-naphthyl carbon 4, had greatly diminished relative to the spectrum of **4**. Also the doublet at 800–860 cm^{-1} in the infrared spectrum due to the naphthalene ring C–H bending had shifted to lower frequencies. These data suggest that the deuterium was located on the naphthalene ring system, and the structure assigned to this derivative was 2-deuterio-1-phenyl-4-(1-phenylethenyl)naphthalene (**9**) in which the 1-phenyl originates from the ethynylbenzene (**3** or **8**) (Scheme II).

This reaction also afforded a low yield of deuterated **1** (m/e = 307), which has been assigned the structure 5-deuterio-1,2,4-triphenylbenzene (**10**) on the basis of the disappearance of the ir band due to two adjacent aromatic hydrogens at 840 cm^{-1}. The presence of **10** precluded the formation of **1** via the thermal decomposition of the dimer of **2** which could be present in the reaction medium.[5]

The sulfone **11**, deuterated in the 2,5 positions, was prepared by treating 3,4-diphenylthiophene (**12**) with 1.1 equiv of n-butyllithium and deuterium oxide five times. Peracid oxidation of **12** afforded 2,5-dideuterio-3,4-diphenylthiophene 1,1-dioxide (**11**), 100% d_2 by ^1H NMR. The reaction of **3** with **11** was carried out and the dideuterio-derivative **13** was isolated. The resonances at 5.35 and 5.90 ppm in the ^1H NMR spectrum of **13** were observed as singlets with integrated areas corresponding to 0.9 and 0.1 H, respectively.

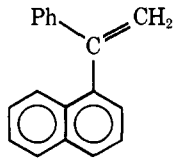
The reduction of the β-ethenyl carbon resonance at 116.1 ppm to a complex triplet and the reduction in the intensity of the ir band at 905 cm^{-1} due to vinyl C–H bending confirmed the location of one deuterium. The second deuterium atom is located on the naphthalene ring as evidenced by the ^1H NMR and the change of the doublet at 850–860 cm^{-1} to a singlet with reduced intensity. This derivative was assigned the structure 3-deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)naphthalene (**13**) (Scheme II). The conversion of the α-

Scheme II



sulfonyl carbon of **11** (or **2**) to the β-ethenyl carbon of **13** (or **4**) was quite stereospecific with 90% one isomer, E or Z, being formed; the scrambling may or may not be the result of double bond isomerization.

Although the ^1H NMR spectrum showed that the predominant isomer of **13** contained the deuterium in the position responsible for the 5.90 ppm vinylidene proton resonance, the assignment for this resonance, *E* or *Z* proton, could not be made. Empirically calculated chemical shifts[6] and comparisons with the chemical shifts of similar compounds did not lead to an unambiguous assignment; however, 1-(1-phenylethenyl)-naphthalene (**14**) has unassigned chemical shifts essentially identical with those of **4**.[7]

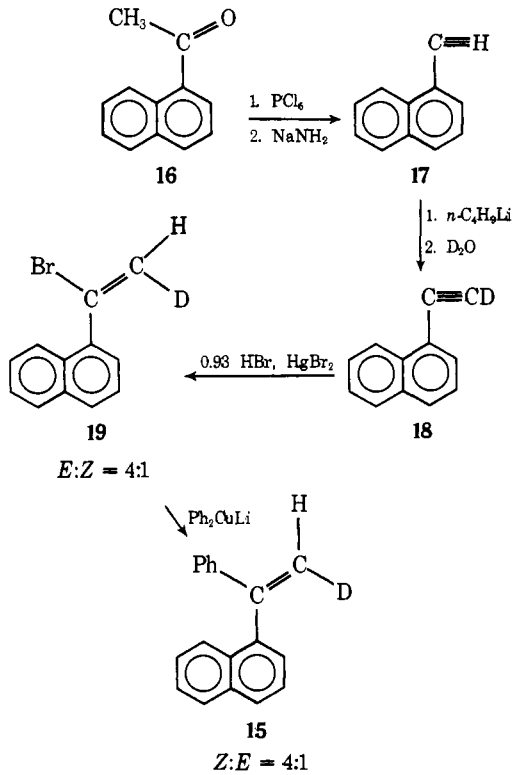


5.36, 5.92 ppm
$J = 1.5$ Hz

14

The reaction of organic halides with lithium diorganocuprates, prepared from organolithium compounds and copper(I) salts, is a relatively new method available for the synthesis of carbon–carbon bonds. Studies have shown that the reaction of lithium diarylcuprates with alkenyl bromides proceeds with little or no isomerization.[8,9] In addition, hydrogen bromide has been reported to add stereospecifically to acetylenes at low temperatures in the presence of a mercury(II) bromide catalyst.[10] These two reactions formed the basis for the stereospecific synthesis of (*Z*)-1-(2-deuterio-1-phenylethenyl)-naphthalene (**15-*Z***) (Scheme III).

Scheme III



15
Z:*E* = 4:1

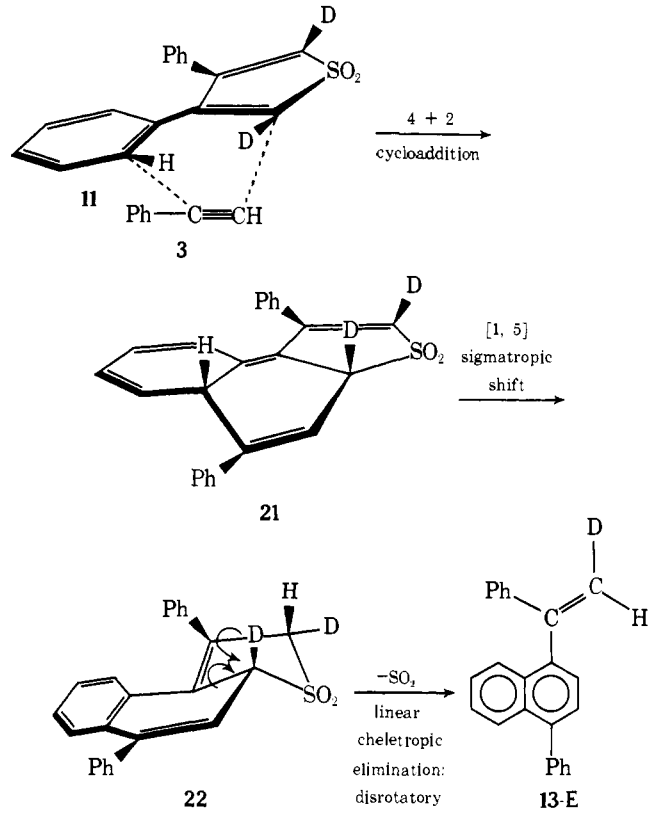
The reaction of 1-acetonaphthone (**16**) with phosphorus pentachloride, followed by sodamide dehydrohalogenation afforded 1-ethynylnaphthalene (**17**). Deuterium exchange was accomplished by a procedure similar to that used for **8** to yield 1-(β-deuterioethynyl)naphthalene (**18**), ~98% d_1. The addition of 0.93 equiv of hydrogen bromide in chloroform to a chloroform solution of **18** at −16 °C in the presence of mercury(II) bromide afforded 1-(1-bromo-2-deuterioethenyl)-naphthalene (**19**) in an *E*:*Z* isomer ratio of 4:1 by NMR analysis. This assignment, resulting from the predominantly cis addition of the hydrogen bromide, was confirmed by treating **19** with *n*-butyllithium at −40 °C to form the α-vinylcarbanion[11,12] and the subsequent addition of water. The resulting 1-(2-deuterioethenyl)naphthalene (**20**) was shown to exist in a 3:2 ratio of the **20-*Z*** and **20-*E*** isomers which were assigned by the observed coupling of the *E* and *Z* β-vinyl proton to the α-vinyl proton.

The addition of **19-*E*,*Z*** (4:1) to lithium diphenylcuprate in ether at 0 °C afforded 1-(2-deuterio-1-phenylethenyl)-naphthalene (**15**) in a 4:1 **15-*Z*:15-*E*** ratio by ^1H NMR analysis. The weaker resonance at 5.36 ppm was ascribed to the predominantly deuterium-containing *Z* position. Analogous chemical shift assignments, *E* position at 5.90 ppm and *Z* position at 5.35 ppm, could then be made for compound **4**. *These chemical shift assignments show that the almost exclusive product (90%) from the reaction of* **3** *with* **11** *was (E)-3-deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)-naphthalene* (**13-*E***).

Discussion

The first step in the proposed mechanism for the formation of **13** is the Diels–Alder 4 + 2 cycloaddition of ethynylbenzene (**3**) with the sulfone derivative **11** (Scheme IV). The expected

Scheme IV



mode of addition leading to **1** is not favored because the very electronegative sulfonyl group apparently lowers the electronic energy levels of the thiophene dioxide diene system to the point where the weak electron-donating properties of **3**[13] are no longer sufficient for this reaction to occur.[14] However, there is a second diene system in **11** comprised of one olefinic bond of the thiophene system and one Kekulé bond of a phenyl substituent. The role of this type of olefin–aromatic diene as a 4 + 2 diene partner is not uncommon.[3,14,15] In this case only one of the diene termini is α to the sulfonyl group, causing a less pronounced effect upon the electronic energy levels. The net effect is a decreased demand for an electron-donating dienophile, a function which **3** can now fulfill. The charge distributions also explain the orientation of the Diels–Alder reaction since the more negative β carbon of **3**[13] would interact

with the more positive α-sulfonyl carbon of **2**. The intermediate resulting from this reaction is **21**.

Some aromaticity is regained by the orbital symmetry allowed, suprafacial [1,5] sigmatropic shift which affords the dihydrothiophene dioxidedihydronaphthalene derivative **22**. This sigmatropic shift along a transoid π system probably has a higher activation energy than found for similar shifts along less complex π systems having simpler steric requirements. It is important to note the trans orientation of the two deuterium labels as a result of these first two reaction steps.

The final step is the cheletropic elimination of the sulfur dioxide from the dihydrothiophene derivative **22** to afford **13-*E***. Orbital symmetry ground-state cheletropic reaction classified as a $[_{\sigma}2_s + _{\sigma}2_s + _{\pi}2_s]$ fragmentation process should occur in a disrotatory manner for a linear elimination and conrotatory for a nonlinear elimination.[16]

Recent kinetic studies concerning the elimination of sulfur dioxide from cyclic sulfones have indicated that the linear mode of elimination is favored over a nonlinear mode or sequential bond cleavage by at least 10 kcal/mol.[17] The majority of investigations into the mode of elimination have involved models containing substituted α-sulfonyl carbons which may introduce steric constraints affecting the reaction products.[17-19] By replacing these bulky substituents with deuterium, any steric constraints affecting the reaction product could be eliminated. One such study has been carried out using a *cis*-2,5-dideuterio-2,5-dihydrobenzothiophene 1,1-dioxide derivative,[20] although the very high reaction temperature (500 °C) and the low stereospecificity of the product formation suggest a large amount of free radical character in the transition state. In the reaction pathway to **13-*E***, the intermediate **22** also contains a deuterium in place of a substituent on one of the α-sulfonyl carbons, but the reaction was carried out at a relatively low temperature. As **22** loses sulfur dioxide, the direction of one bond rotation during the complete aromatization of the naphthalene ring is fixed. The second bond is free to rotate as required electronically since there can be no steric discrimination between the hydrogen and the deuterium on the terminal carbon. The predicted linear, disrotatory reaction should place the deuterium in the *E* position of the product, **13-*E***, which is the experimentally observed result confirmed by the chemical shift assignment study. Thus, when the possible steric influences have been eliminated, the cheletropic elimination of sulfur dioxide from five-membered ring sulfones (4q electrons) is indeed linear and disrotatory.

The reaction sequence which affords **4** from the reaction of **2** with **3** is very unique in that of the four major classes of concerted, orbital symmetry-controlled reactions, this proposed mechanism involves three consecutively: a cycloaddition reaction, a sigmatropic rearrangement reaction, and a cheletropic elimination reaction.

Experimental Section

Reaction of 3,4-Diphenylthiophene 1,1-Dioxide (2) with Ethynylbenzene (3). A. 1-Phenyl-4-(1-phenylethenyl)naphthalene (4). A solution of 5.0 g (0.019 mol) of 3,4-diphenylthiophene 1,1-dioxide (**2**)[5,21] and 7.0 ml (6.5 g, 0.064 mol) of ethynylbenzene (**3**) in 50 ml of toluene under a nitrogen atmosphere was heated at the reflux temperature for 15 h. The solvent and excess **3** were removed under reduced pressure. The residue was chromatographed twice on Woelm neutral alumina eluting first with 1:1 benzene–Skelly F, then with 1:4 benzene–Skelly F. The light-yellow oily residue was taken up in a small amount of warm Skelly B and allowed to crystalline. Recrystallization from methanol afforded 1.84 g (31.6%) of **4** as colorless crystals: mp 102–103 °C (lit.[3] mp 99–100 °C); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.35 (d, J = 1.5 Hz, 1 H), 5.90 (d, J = 1.5 Hz, 1 H), and 7.0–7.9 ppm (m, 16 H); ^{13}C NMR δ (Me_4Si) 116.1 (t, $=CH_2$), 125.6, 126.3, 126.7, 127.1, 127.6, 128.2, 128.3, 130.1, 132.1 (s), 132.3 (s), 139.4 (s), 140.2 (s), 140.9 (s), 141.2 (s), and 148.6 ppm (s); mass spectrum (70 eV) *m/e* (rel intensity) 307 (M^+ + 1, 27.8), 306 (M^+ 100), 305 (M^+ – 1, 50), 229 ($M^+ - C_6H_5$, 47), 228 ($M^+ - C_6H_6$, 35), 202 ($M^+ - C_8H_8$, 14), and 171 (metastable 306 → 229). Anal. ($C_{24}H_{18}$): C, H.

The same product was obtained when this reaction was duplicated in the absence of solvent and in benzene or *m*-xylene solution.

B. 1,2,4-Triphenylbenzene (1). After compound **4** was eluted from the second column, the column was reeluted with 1:1 benzene–Skelly F. The residue, after solvent removal, was purified by preparative TLC on silica gel (1:2 benzene–Skelly B). Material from the band with highest R_f was isolated and allowed to crystallize from Skelly B. Two recrystallizations from methanol afforded 0.03 g (1%) of colorless prisms: mp 121–122 °C (lit.[1] mp 99.1–99.6, 119–120 °C). This product was shown to be identical with authentic 1,2,4-triphenylbenzene by ir.

C. Authentic 1,2,4-Triphenylbenzene (1). An authentic sample of 1,2,4-triphenylbenzene (**1**) was prepared by the cobalt-catalyzed cyclotrimerization of ethynylbenzene (**3**)[2] to afford colorless needles: mp 100–101 °C (lit.[1,2] mp 99.1–99.6, 120 °C); ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 10 H) and 7.2–7.7 ppm (m, 8 H); ^{13}C NMR ($CDCl_3$) δ (Me_4Si) 126.1, 126.6, 127.1, 127.4, 127.9, 128.8, 129.4, 129.9, 130.2, 131.1, 139.7 (s), 140.4 (s), 140.6 (s), 141.1 (s), 141.2 (s), and 141.6 ppm (s); mass spectrum (70 eV) *m/e* (rel intensity) 307 (M^+ + 1, 27.5), and 306 (M^+, 100).

Anal. ($C_{24}H_{18}$): C, H.

When a solution of this 100 °C melting form was seeded with the 121 °C melting form, colorless prisms were obtained, mp 122–123.5 °C.

1-Phenyl-4-(1-phenylethyl)naphthalene (5). A. Quantitative Hydrogenation of 4. The hydrogenation catalyst was prepared by reducing 0.0257 g (1.17×10^{-5} mol Pt) of platinum oxide (88.5% Pt) in ethyl acetate at 24 °C for 12 h under 1 atm of hydrogen. An ethyl acetate solution containing 0.2017 g (6.591×10^{-4} mol) of 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**) was added through an addition funnel. Hydrogen uptake was rapid during the first 2 h, and a final reading was taken after 36 h. The 20.6 ml of hydrogen absorbed contained 7.54×10^{-4} mol or 1.14 equiv after correcting for the vapor pressure of ethyl acetate (88 mmHg at 24 °C).

The reduction was also carried out on a preparative scale. Platinum oxide (0.224 g, 1.02 mmol Pt) was prereduced by bubbling hydrogen gas through an ethyl acetate suspension for 1 h at 28 °C. A solution of 1.02 g (3.34 mmol) of **4** in ethyl acetate was added and hydrogen gas was bubbled through the reaction mixture for 2½ h. The catalyst was removed by filtration through a bed of Celite. The solvent was removed from the filtrate, and the resulting product was recrystallized twice from methanol to afford 0.686 g (66.7%) of a colorless crystalline product: mp 93–95 °C (lit.[3] mp 88–89 °C); ^{1}H NMR ($CDCl_3$) δ 1.74 (d, J = 7 Hz, 3 H), 4.90 (q, J = 7 Hz, 1 H), and 7.0–8.2 ppm (m, 16 H); ^{13}C NMR ($CDCl_3$) δ (Me_4Si) 22.4 (q, CH_3), 40.7 (d, CH), 124.0, 124.2, 125.4, 125.7, 126.0, 126.6, 127.0, 127.7, 128.2, 128.5, 130.2, 132.2 (s), 132.4 (s), 139.2 (s), 141.3 (s), and 146.7 ppm (s); mass spectrum (70 eV) *m/e* (rel intensity) 309 (M^+ + 1, 26.8), 308 (M^+, 100), 293 ($M^+ - CH_3$, 99), 216, ($M^+ - C_7H_8$, 78).

Anal. ($C_{24}H_{20}$): C, H.

B. Hydroboration–Protonolysis of 4. To a stirred solution containing 0.924 g (3.02 mmol) of 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**) and 0.181 g (4.77 mmol) of sodium borohydride in 25 ml of dry diglyme under a nitrogen atmosphere was added dropwise over 1½ h, a solution of 0.81 ml (0.94 g, 6.6 mmol) boron trifluoride etherate in 25 ml of dry diglyme. After an additional 2 h, 1.6 ml (1.6 g, 22 mmol) of propionic acid was added, and the solution was heated at the reflux temperature for 3 h. The reaction mixture was poured into water and was extracted with ether which, after drying and the removal of the ether, afforded a brown oil. Chromatography on Woelm neutral alumina, eluting with 1:1 benzene–Skelly F, afforded a colorless oil which was crystallized from methanol to afford 0.265 g (28.5%) of a yellowish crystalline product. Two recrystallizations from methanol yielded colorless needles: mp 89–91 °C (lit.[3] mp 88–89 °C); ^{1}H NMR ($CDCl_3$) δ 1.73 (d, J = 7 Hz, 3 H), 4.90 (q, J = 7 Hz, 1 H) and 7.0–8.2 ppm (m, 16 H); ir identical with the compound obtained from hydrogenation with a platinum catalyst.

1-Benzoyl-4-phenylnaphthalene (6). A. Oxidative Ozonolysis of 4. In a Ruben ozonization apparatus[22] a saturated solution of ozone in 60 ml of methylene chloride (0.040 M, 2.4 mmol of ozone) was prepared at −78 °C. This solution was transferred to a methylene chloride solution containing 0.612 g (2.00 mmol) of 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**) at −78 °C. After 1 h at −78 °C, the solution was slowly warmed to room temperature. The solvent was removed

under reduced pressure, and 25 ml of 88% formic acid and 13 ml of 30% hydrogen peroxide were added to the ozonide, and the mixture was heated to the reflux temperature for 1 h. The solvent was removed under reduced pressure. Preparative TLC on silica gel using 1:1 benzene–Skelly B resulted in one major band which was isolated. The product was recrystallized from hexane to afford 0.130 g (21.1%) of colorless needles: mp 105–107 °C; ^{1}H NMR ($CDCl_3$) δ 7.0–8.2 ppm (m); ^{13}C NMR ($CDCl_3$) δ (Me_4Si) 125.4, 126.2, 126.5, 127.0, 127.7, 128.4, 130.0, 130.4, 131.6, 132.3, 133.0, 136.2, 138.8, 140.4, 143.6, and 197.7 ppm (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 309 ($M^+ + 1$, 25), 308 (M^+, 100), 307 ($M^+ - 1$, 26), 231 ($M^+ - C_6H_5$, 83), 203 ($M^+ - C_7H_5O$, 33), 202 ($M^+ - C_7H_6O$, 45), metastable peaks 178.3 (231 → 203) and 173 (308 → 231); ir (KBr) 1660–1665 cm^{-1} ($-COC_6H_5$).

Anal. ($C_{23}H_{16}O$): C, H.

B. Reductive Ozonolysis of 4. In a Ruben ozonization apparatus a saturated solution of ozone in 45 ml of methylene chloride (0.040 M, 1.8 mmol of ozone) was prepared at −78 °C. This solution was transferred to a solution of 0.502 g (1.64 mmol) of 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**) in 5 ml of methanol and 5 ml of methylene chloride at −78 °C. After 15 min, the reaction mixture was flushed with nitrogen and was warmed to ice bath temperature. Dimethyl sulfide (1 ml) was added,[23] and the solution was allowed to warm to room temperature over several hours. The volatiles were removed under reduced pressure, and the residue was dissolved in chloroform and was washed with water to remove the dimethyl sulfoxide. Removal of the dried chloroform afforded a yellow oil. Crystallization from methanol gave 0.14 g (28%) of recovered **4**. Purification of the remainder by silica gel preparative TLC (10% methanol in Skelly B) yielded 0.026 g (5.1%) of **6** as white needles when recrystallized from methanol: mp 106.5–107.5 °C. The ir of this product is identical with that obtained under oxidative conditions, and the melting point of a mixture of this product and that obtained under oxidative conditions was unchanged.

Anal. ($C_{23}H_{16}O$): C, H.

C. Detection of Formaldehyde[24] as a Product of the Reductive Ozonolysis of 4. To a saturated solution of ozone in 65 ml of methylene chloride at −78 °C (0.040 M, 2.6 mmol ozone) was added 0.500 g (1.63 mmol) of 1-phenyl-4-(1-phenylethenyl)naphthalene (**4**). After 5 min at −78 °C, the solution was allowed to warm to ice bath temperatures over 20 min. The ozonide solution was slowly added to a suspension of 0.62 g of zinc dust in 25 ml of acetic acid at 0 °C. The mixture was stirred at room temperature for 1 h. The methylene chloride was then distilled into a solution containing 0.21 g (1.5 mmol) of dimedone and one drop piperidine in 10 ml of 75% aqueous ethanol. The equivalent amount of dimedone (3.26 mmol) was not used to simplify the purification of the derivative. The methylene chloride was removed by distillation, and ethanol–water was removed under reduced pressure until crystallization occurred. After cooling, fine colorless needles of methylenebis(dimedone) were collected: mp 192–193 °C (lit.[3] mp 190–191 °C). The melting point of a mixture of this product and an authentic sample prepared from aqueous formaldehyde and dimedone was unchanged.

Authentic Sample of 1-Phenyl-4-(1-phenylethenyl)naphthalene (4). A. 1-Bromo-4-phenylnaphthalene (7). A solution of 5.32 g (26.1 mmol) of 1-phenylnaphthalene and 4.29 g (26.8 mmol) of bromine in 80 ml of carbon disulfide was stirred for 70 h at room temperature, utilizing a nitrogen stream to remove the hydrogen bromide formed. The reaction mixture was washed twice with dilute sulfurous acid and twice with water. After drying the organic portion with calcium chloride, the solvent was removed, and the residual yellow oil was purified by short-path distillation: bp 145–153 °C (1 mm). Recrystallization from methanol afforded 2.16 g (29.2%) of a colorless crystalline compound: mp 67–68 °C (lit.[25] mp 70 °C).

B. 1-Phenyl-4-(1-phenylethenyl)naphthalene (4). A Grignard reagent was prepared from 1.42 g (5.02 mmol) of 1-bromo-4-phenylnaphthalene (**7**) and 0.120 g (4.94 mmol) of magnesium in 10 ml of anhydrous ether. A solution of 0.682 (5.68 mmol) of acetophenone in 10 ml of anhydrous ether was then added dropwise, and the mixture was heated to the reflux temperature for 2 h. The reaction mixture was hydrolyzed in cold ammonium chloride solution, and the carbinol was isolated by ether extraction. Dehydration of the crude carbinol was accomplished using a mixture of concentrated sulfuric acid and glacial acetic acid.[26] The product, a yellow oil, was isolated by ether extraction. The oil was taken up in a small amount of warm Skelly B and was allowed to crystallize overnight. Recrystallization from methanol afforded 0.244 g (15.9%) of colorless needles: mp 99–100.5 °C (lit.[4] mp 99–100 °C); ^{1}H NMR ($CDCl_3$) δ 5.35 (d, J = 1.5 Hz, 1 H), 5.91 (d, J = 1.5 Hz, 1 H), and 7.0–8.0 ppm (m, 16 H). The melting point of a mixture of **4** and this authentic sample was unchanged.

Deuterium Labeling Studies. A. β-Deuterioethynylbenzene (8). To a solution of 27.2 g (0.266 mol) of ethynylbenzene (**3**) in 150 ml of anhydrous ether at −78 °C under a nitrogen atmosphere was added 175 ml (0.420 mol) of a 2.4 M *n*-butyllithium solution. After 10 min, 48 ml (48 g, 2.4 mol) of deuterium oxide was added, and the reaction mixture was allowed to warm to room temperature. The ether layer was washed with water and saturated sodium chloride solution and was dried. After the removal of the solvent, **8** was purified by distillation: bp 51–53 °C (30 mm), 22.0 g (80.3%); ^{1}H NMR <5% ≡CH; mass spectrum (70 eV) *m/e* (rel intensity) 103 (M^+, 100).

B. 2-Deuterio-1-phenyl-4-(1-phenylethenyl)naphthalene (9). A solution of 5.00 g (18.7 mmol) of 3,4-diphenylthiophene 1,1-dioxide (**2**) and 5.2 ml (4.8 g, 46 mmol) of β-deuterioethynylbenzene (**8**) in 50 ml of toluene was heated at the reflux temperature for 12 h. The product, **9**, was isolated and purified as previosuly described for **4** to yield 1.37 g (23.9%) of colorless crystals: mp 102.5–103 °C; ^{1}H NMR ($CDCl_3$) δ 5.35 (d, J = 1.5 Hz, 1 H), 5.91 (d, J = 1.5 Hz, 1 H), and 7.0–8.0 ppm (m, 15 H); mass spectrum (70 eV) *m/e* (rel intensity) 307 (M^+, 100); ir (KBr) 848 and 856 cm^{-1} absent, additional peak at 730 cm^{-1} when compared with **4**.

C. 5-Deuterio-1,2,4-triphenylbenzene (10). This compound was isolated from the above reaction of **2** with **8** by preparative TLC as described previously to afford 0.11 g (1.9%) of colorless prisms after recrystallization from methanol: mp 121–122 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 10 H) and 7.2–7.7 ppm (m, 7 H); mass spectrum (70 eV) *m/e* (rel intensity) 307 (M^+, 100); ir (KBr) band at 840 cm^{-1} absent when compared with **1**.

D. 2,5-Dideuterio-3,4-diphenylthiophene 1,1-Dioxide (11). To 15 g (66 mmol) of 3,4-diphenylthiophene (**12**) in 200 ml of anhydrous ether at −78 °C under nitrogen was added 35 ml (74 mmol) of a 2.1 M *n*-butyllithium solution. The reaction mixture was allowed to warm to room temperature, followed by the addition of 5.0 ml (5.0 g, 0.25 mol) of deuterium oxide with cooling. The ether layer was washed with water and was dried; removal of the ether afforded a white crystalline product. The exchange was repeated five times. The product (11.5 g) was oxidized[21] with peracetic acid to afford 8.2 g (45% overall) of **11:** mp 166–168 dec (lit.[5] mp 171.5–172.5). The ^{1}H NMR showed no signal at 6.5–6.6 ppm due to any 2,5 protons; ir (KBr): strong C–D stretch at 2300 cm^{-1} replaces C–H stretch at 3300 cm^{-1}.

E. 3-Deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)naphthalene (13). A solution of 2.5 g (9.3 mmol) of 2,5-dideuterio-3,4-diphenylthiophene 1,1-dioxide (**11**) and 3.0 ml (2.0 g, 20 mmol) of ethynylbenzene (**3**) in 33 ml of toluene under a nitrogen atmosphere was heated at the reflux temperature for 12 h. The product, **13,** was isolated and was purified as previously described for **4** to afford 0.77 g (29%) of a colorless crystalline product: mp 102–104 °C; ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 0.9 H), 5.91 (s, 0.1 H), and 7.0–8.2 ppm (m, 15 H); mass spectrum (70 eV) *m/e* (rel intensity) 308 (M^+, 100); ir (KBr) 3090, 1390 and 600 cm^{-1} peaks absent, 850–860 and 910 cm^{-1} reduced in intensity, and 2260, 970, 735, and 590 cm^{-1} peaks additional when compared with **4**.

Stereospecific Synthesis of (*Z*)-1-(2-Deuterio-1-phenylethenyl)-naphthalene (15-*Z*). A. 1-Ethynylnaphthalene (17). To a suspension of 84.0 g (40.0 mmol) of phosphorus pentachloride in 100 ml of anhydrous benzene at 0 °C under a nitrogen atmosphere was added a solution of 68.0 g (40.0 mmol) of 1-acetonaphthone (**16**)[27] in 50 ml of anhydrous benzene, and the reaction mixture was allowed to warm to room temperature. After the disappearance of the solid, the solution was poured into ice water and was extracted with ether. The ether solution was washed once with ice–water, and then it was dried over anhydrous magnesium sulfate and was filtered to afford a red solution of 1-(α,α-dichloroethyl)naphthalene which was used without further purification.

A suspension of sodamide in liquid ammonia was prepared from 26 g (1.1 g-atom) of sodium metal and 1 l. of liquid ammonia using 0.5 g of ferric nitrate as a catalyst. After the blue color had discharged, the previously prepared solution of 1-(α,α-dichloroethyl)naphthalene was slowly added. After an additional 1½ h, the reaction mixture was hydrolyzed carefully with 500 ml of water, and then the mixture was extracted with ether. The ether layer was washed with water, dilute hydrochloric acid, and saturated sodium chloride solution and was

dried. Removal of the solvent and distillation afforded **44** g (72% overall) of **17**: bp 118–120 °C (8 mm), [lit.[28,29] bp 135 °C (20 mm), 143–144 °C (25 mm)]; ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 1 H) and 6.9–8.6 ppm (m, 7 H); ir (neat) 3300 (≡C–H) and 2100 cm^{-1} (C≡C).

B. 1-(β-Deuterioethynyl)naphthalene (18). To a solution of 15.2 g (0.100 mol) of 1-ethynylnaphthalene (**17**) in 30 ml of anhydrous ether maintained at −50 °C under a nitrogen atmosphere was slowly added 120 ml (0.20 mol) of 1.65 M *n*-butyllithium solution. The reaction mixture was warmed to room temperature over 30–40 min before 20 ml (20 g, 1.0 mol) of deuterium oxide was slowly added with cooling. After 0.5 h, the organic layer was separated, was washed with water and saturated sodium chloride solution, and was dried. Solvent removal afforded **18** which was purified by distillation: bp 65–68 °C (1 mm); ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 0.02 H) and 6.9–8.6 ppm (m, 7 H); ir (neat) 2600 cm^{-1} (≡C–D).

C. 1-(1-Bromo-2-deuterioethenyl)naphthalene (19). A solution of hydrogen bromide in anhydrous chloroform was prepared by passing hydrogen bromide gas through chloroform at room temperature. The concentration of hydrogen bromide was determined by the Volhard titration for bromide ion.[30]

To a vigorously stirred mixture of 8.5161 g (55.66 mmol) of 1-(β-deuterioethynyl)naphthalene (**18**) and 0.358 g (9.94×10^{-4} mol) of freshly sublimed mercury(II) bromide[31] in 225 ml anhydrous chloroform under nitrogen, maintained at −16 °C, was slowly added 150 ml (51.5 mmol) of a 0.343 M hydrogen bromide solution over a 1¼ h period. The pale-green reaction mixture was maintained at −16 °C for an additional hour. The chloroform solution was rapidly washed with ice water, cold dilute sodium bicarbonate solution, cold sodium chloride solution, and was dried. Removal of the chloroform afforded a light-yellow oil which was purified by short-path distillation: bp 89–96 °C (2 mm); 10.3 g (85.5% based on HBr added); ^{1}H NMR (neat) δ 5.54 (s, 0.2 H) (E =CH), 5.79 (s, 0.8 H) (Z =CH), and 6.8–8.2 ppm (m, 7 H). This product was a 4:1 mixture of **19-*E*:19-*Z***.

D. 1-(2-Deuterioethenyl)naphthalene (20). To a solution of 1.40 g (5.98 mmol) of 1-(1-bromo-2-deuterioethenyl)naphthalene (**19-*E*:19-*Z*** = 4.1) in 15 ml of anhydrous ether under a nitrogen atmosphere at −40 °C was added 4.0 ml (6.6 mmol) of 1.65 M *n*-butyllithium solution. After 5 min, water (10 ml, 10 g, 0.56 mol) was added, and the reaction mixture was warmed to room temperature. The ether layer was separated, was washed with saturated sodium chloride, and was dried. Removal of the solvent afforded a light-yellow oil which was analyzed without further purification: ^{1}H NMR ($CDCl_3$) δ 5.18 (d, J = 11 Hz, 0.6 H) (E =CH), 5.55 (d, J = 17.5 Hz, 0.4 H) (Z =CH), and 7.0–8.2 ppm (m, 7 H). The *Z* isomer of **20** resulting from the cis addition of hydrogen bromide predominates.

E. 1-(2-Deuterio-1-phenylethenyl)naphthalene (15). Lithium diphenylcuprate was prepared at 0 °C by slowly adding 25.0 ml (46.5 mmol) of 1.86 M phenyllithium solution to a suspension of 5.03 g (24.4 mmol) of bromo(dimethyl sulfide)copper(I)[32] in 20 ml of anhydrous ether. A yellow precipitate formed initially which changed to a homogeneous green solution after complete addition. After an additional 40 min at 0 °C, a solution of 1.36 g (5.81 mmol) of 1-(1-bromo-2-deuterioethenyl)naphthalene (**19-*E*:19-*Z*** = 4:1) in 3 ml of anhydrous ether was then added. After 4½ h at 0 °C, the reaction mixture was poured into aqueous saturated ammonium chloride solution (pH 9 by addition of ammonium hydroxide), and this was stirred for 1½ h. The ether layer was separated, was washed twice with saturated sodium chloride solution, and was dried. Removal of the solvent afforded a light-yellow oil which was purified by short-path distillation, collecting the fraction with bp 124–134 °C (1 mm). The yield was 0.80 g (60%) of **15** as an oil which was crystallized from methanol: mp 57.5–58.5 °C (lit.[26] mp 60 °C); ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 0.2 H) (Z =CH), 5.93 (s, 0.8 H) (E =CH), and 6.8–7.9 ppm (m, 12 H). The **15-*Z*** isomer predominates 4:1; ir (KBr) 910, 715, 685 cm^{-1} peaks absent (=CH_2), 2860 and 860 cm^{-1} peaks additional when compared with ir of undeuterated compound **15**.

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