radical, while generally observed to be the least selective and hence most reactive of the three abstracting radicals considered in this study, has the largest computed energy of activation.

Conclusions

The generally accepted explanations of the polar effect in hydrogen-abstraction reactions are based upon enthalpic arguments. On the basis of the empirical results obtained by us[13] and others[24] for the bromination reaction, it appears that these arguments are unsatisfactory and that an entropic effect must be considered. Now, based upon the semiempirical MNDO method, theoretical results are presented that also suggest that reasoning based upon only enthalpic arguments is inadequate.

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Registry No. H_2, 1333-74-0; PhMe, 108-88-3; *p*-MeC_6H_4Me, 106-42-3; *p*-ClC_6H_4Me, 106-43-4; Cl, 22537-15-1; Br, 10097-32-2; Me·, 2229-07-4.

(24) Kim, S. S.; Kang, C. H.; Choi, S. Y. "Abstracts of Papers", 187th National Meeting the American Chemical Society, St. Louis, April 1984; American Chemical Society: Washington, DC, 1984; ORGN 171.

(25) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142.

7-Oxabicyclo[2.2.1]hept-2-ene and Related Materials by Reductive Elimination

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The cycloadduct 1 of furan and (*E*)-1,2-bis(phenylsulfonyl)ethylene has been converted to various derivatives, which in turn have been subjected to sodium amalgam reductive elimination conditions. Some of these procedures constitute useful methods for the preparation of the title olefin. The amalgam reduction of 1 provides modest yields of 7-oxabicyclo[2.2.1]hepta-2,5-diene. The cycloadduct of isobenzofuran and the reactive dienophile was prepared and subjected to analogous reactions. Various reaction steps which compete with reductive elimination have been identified.

The oxygen analogue of norbornene, 7-oxabicyclo-[2.2.1]hept-2-ene (**3**), is potentially useful as a dienophile and in other applications. It has received little attention, however, since it is relatively inaccessible. The only open literature preparative method,[1] the direct Diels–Alder reaction of furan and ethylene, requires the use of pressure apparatus and suffers from very low yield and a tedious isolation procedure.[2]

De Lucchi and co-workers have recently reported the use of (*E*)-1,2-bis(phenylsulfonyl)ethylene as a very reactive "acetylene equivalent" dienophile[3] and shown that it will react cleanly with furan to form the adduct **1**. Since at least three distinct pathways (all of which have been described by De Lucchi for carbocyclic materials) could be envisioned (see Scheme I) for converting **1** to **3**, this obvious extension seemed worth pursuing. It was recognized that cleavage of the oxa bridge in **1** might intervene, since there is precedent for such behavior in reactions involving presumed anionic intermediates with the analogous 1,4-dihydro-1,4-epoxynaphthalene[4] and reductive elimination of β-alkoxy sulfones occurs readily under the conditions needed to effect removal of a phenylsulfonyl group.[5] We report here conditions which are useful for the preparation of **3** as well as the results of studies which shed some light on the various reactions that **1** and related materials undergo.

Results and Discussion

The most direct method by which **1** can be converted to **3** involves catalytic reduction of the double bond to give **2**, followed by reductive elimination (path A, Scheme I). The first step was accomplished in $CHCl_3$ solvent, Parr shaker, with Pd/C catalyst (quantitative). De Lucchi[3] has commented on the failure of several reducing agents to effect reductive elimination of a model bis-sulfone and settled on sodium amalgam (6% Na, used in large excess) with solid $NaH_2PO_4 \cdot H_2O$ as a buffer in methanol solvent as the most efficient method for carrying out this step. When we employed this procedure with **2**, the desired product **3** was indeed formed, along with the overreduced material 7-oxabicyclo[2.2.1]heptane (**6**) in combined 30–50% yield. The yields were determined, after pentane extraction and careful evaporation of most of the solvent,

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(1) Nudenberg, W.; Butz, L. W. *J. Am. Chem. Soc.* **1944**, *66*, 307. The preparation of **3** by an electrochemical oxidation method is also claimed in a Japanese patent (T. Shono, Japan Patent 72 27 511; *Chem. Abstr.* **1972**, *77*: 139803x), but details, including starting material, are not obvious from the abstract.

(2) Several years ago we repeated the literature procedure[1] and obtained **1** in ca. 1 % yield, contaminated with furan (unpublished work with J. Staroscik). Considerable furan polymerization occurs, and careful fractionation is needed to isolate **1** from the large excess of furan that is employed.

(3) (a) De Lucchi, O.; Modena, G. *Tetrahedron Lett.* **1983**, *24*, 1653. (b) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596. (c) De Lucchi, O.; Pasquato, L. *Gazz. Chim. Ital.* **1984**, *114*, 349.

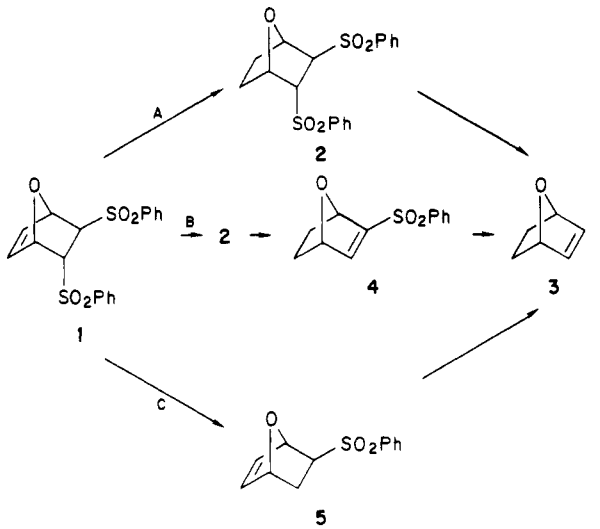
(4) Caple, R.; Chen, G. M. S.; Nelson, J. D. *J. Org. Chem.* **1971**, *36*, 2874. See also: Jeffrey, A. M.; Yeh, H. J. C.; Jerina, D. M.; DeMarinis, R. M.; Foster, C. H.; Piccolo, D. E.; Berchtold, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6929. Brion, F. *Tetrahedron Lett.* **1982**, *23*, 5299.

(5) For example, Kocienski[6] has utilized this approach to convert epoxy sulfones to allylic alcohols. We have also been unable to prevent reductive elimination of a cyclic β-methoxy sulfone when the desired reaction was simple reduction (unpublished work with R. J. Moss).

(6) Kocienski, P. J. *Tetrahedron. Lett.* **1979**, 441.

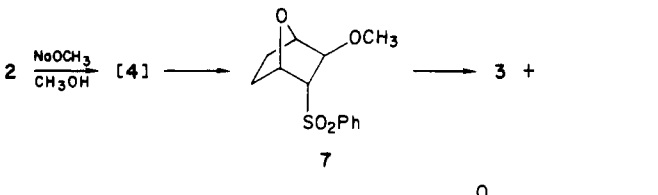
0022-3263/85/1950-4340$01.50/0

Scheme I



by NMR using durene as an internal standard. The ratio of **3**/**6** was typically 90/10, with the remainder of the material either water soluble or nonvolatile and not characterized. Slow spinning band distillation of the crude product caused extensive decomposition of **3** with the formation of viscous pot residue, and vacuum distillation was used to obtain material (**3**/**6**) contaminated only by small amounts of pentane. A change from methanol to ethanol solvent gave a similar yield and ratio of **3**/**6**. In an effort to minimize the available proton source which might be important for overreduction, DMF solvent was employed (with the buffer present), and this gave a better result, 70% of **3** containing <5% of **6**. However, repetition on larger scale (ca. 10 g) gave somewhat diminished yields (40–60%).

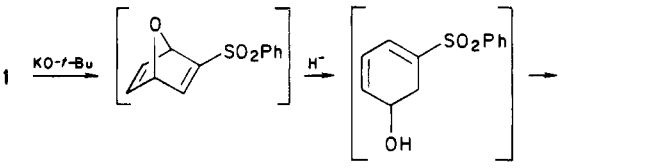
Path B, Scheme I, differs from A in that a base is intentionally used to cause elimination to form the unsaturated sulfone **4**. This eliminiation occurs readily with moderately strong bases, although not with triethylamine. Treatment of **2** with excess sodium methoxide in methanol was examined, and this led to the formation (94%) of product **7** (eq 1). This material is almost certainly formed



by initial elimination to **4**, followed by Michael addition (exo face) of methoxide and protonation; the endo configuration of the phenyl sulfone probably reflects the equilibrium position for this group when the adjacent position bears an exo substituent. The stereochemical features are based on NMR analysis. Compound **7** was of interest since it might be formed in the methanol/amalgam reduction of **2**, possibly accounting for the modest yields in this reaction. On the other hand, **7** in principle could also serve as a substrate for reductive elimination to **3**. To test this possibility, **7** was subjected to the amalgam/DMF conditions. The desired product **3** was formed in ca. 48% yield; thus **7** does serve as a substrate for formation of **3** (free of **6**) but offers no advantage in yield compared with the direct reduction of **2**. The major side product in this sequence is compound **8**, which is formed in 25% yield in DMF and becomes the preferred product when the reduction is carried out in methanol (**3**/**8** = 30%/47%).

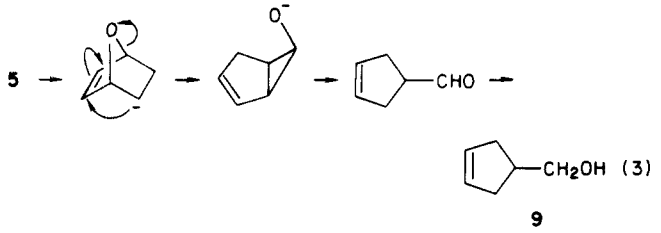
Choosing a base which will not undergo Michael addition to the unsaturated sulfone **4** is no easy matter, since even "nonnucleophilic" species such as lithium diisopropylamide are known to undergo 1,4-addition reactions.[7] We examined the use of KO-*t*-Bu in DMF, and this gave sufficient **4** (25%) for further examination of the path B procedure. When **4** was subjected to the best conditions developed for the conversion of **2** to **3**, the desired olefin was observed in only 20% yield (NMR). Since this result was substantially poorer than the direct reaction of **2**, or the conversion via **7**, further efforts to improve the yield of **4** were abandoned.

De Lucchi has reported that the treatment of a carbocyclic analogue of **4** with $NaBH_4$ (in THF) caused reduction of the double bond and noted that direct reaction of the precursor bis-sulfone gave the same product.[3c] This suggested that we might employ the alternative path C, Scheme I, which differs from A and B in that the double bond in the product **3** is that originally present in **1**. We chose DMF again to attempt the hydride reduction of **1**, since both the substrate and $NaBH_4$ are quite soluble in this medium. No reaction was observed after stirring at room temperature for several hours; methanol was then added to this mixture, causing methanolysis of the borohydride, but again no reaction of **1** (high recovery). Reasoning that elimination must precede reduction, KO-*t*-Bu was added to a mixture of **1** and $NaBH_4$ in DMF. Rapid reaction occurred, but after workup the major product (59% isolated by chromatography) proved to be diphenyl sulfone. A rational mechanism for the formation of this material is shown in eq 2.



It was possible to circumvent this problem by careful control of the amount of base used. Thus addition of 1 equiv of KO-*t*-Bu to an acetonitrile solution (0 °C) of **1** and excess $NaBH_4$ gave product in over 90% yield; NMR analysis indicated that the major isomer (55–86% in three reactions) had the exo phenyl sulfone structure shown for **5** in Scheme I, path C. This stereochemistry is thought to reflect equilibration (base-catalyzed epimerization), and exo preference for the substituent when the adjacent methylene group is unsubstituted. When **5** was subjected to the amalgam (methanol, buffer, ice bath) in a small-scale (0.5 g) reaction, **3** was formed in 65% yield, accompanied by 8% of benzene. Repetition on a larger scale gave a poorer yield (30%) of **3**, 4% of benzene, and over 40% (some lost in aqueous wash) of a new product, 3-cyclopentenylmethanol (**9**).[8] This ring contracted material presumably arises as outlined in eq 3, although certain features remain unclear (e.g., no 2-cyclopentenylmethanol[9] is observed in the Favorski-like sequence proposed). In the hope of avoiding the oxa ring cleavage processes which lead to benzene and **9**, the reduction of **5** was repeated at

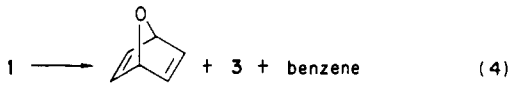
(7) Little, R. D.; Dawson, J. R. *Tetrahedron. Lett.* **1980**, *21*, 2609.
(8) Paasivirta, J.; Hakli, H.; Widen, K. *Org. Magn. Reson.* **1974**, *6*, 380.
(9) Maercker, A.; Geuss, R. *Chem. Ber.* **1973**, *106*, 773.



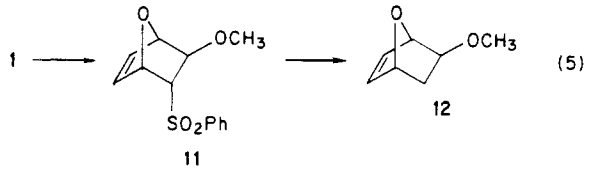
−20 °C. These side reactions appear to be suppressed at the lower temperature, since only a trace of benzene, and no **9**, were detected. However, the yield of **3** was only 48%, and the fate of the remainder of the material could not be ascertained.

To summarize, **3** can be made from **1** in several ways, at least three of which represent improvement over the literature procedure,[1] in spite of moderate yields which are adversely affected by scale-up, for reasons that are not completely understood.

Compound **1** can also in principle serve as a precursor to 7-oxabicyclo[2.2.1]hepta-2,5-diene (**10**). This interesting oxa analogue of norbornadiene has been prepared previously by Prinzbach and Babsch in a multistep sequence starting with the cycloadduct of furan and vinylene carbonate.[10] When the reductive elimination procedure was applied directly to **1**, **10** was indeed formed (as judged by NMR analysis of the crude reaction mixture), along with **3** and benzene. The ratio of **10**/**3** varied from ca. 50/50 to 65/35 when the amalgam reaction was done in methanol, at room temperature and reflux, respectively. The combined yields of **10** and **3** were estimated (NMR) to be 40–50%. Similar treatment in ethanol solvent gave a somewhat poorer yield (30–40%) and a less favorable ratio of **10**/**3** (40/60). As noted in the amalgam reduction of **2**, the use of DMF solvent greatly diminished (<5%) the formation of overreduction product (**3** in this instance), but the yield of **10** was not improved (25%).



When **1** was stirred for 12 h as a slurry in methanol containing excess potassium methoxide, it was recovered unchanged with minimal loss (in contrast to the saturated analogue **2**, which gave **7** under these conditions); this failure to react is attributed to the very low solubility of **1**, for when the reaction was repeated in 60/40 vol % acetonitrile/methanol, **11** was formed in excellent yield.

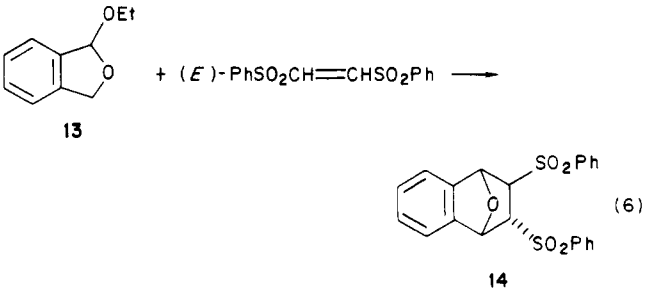


The amalgam reduction (methanol) of **11** gave **12** in 48% yield, accompanied by a small amount of **10** (4%), and a trace of benzene as the only distinguishable products. Although this route is not useful for the preparation of **10**, materials such as **12** are difficult to prepare by other methods and have interesting potential applications.

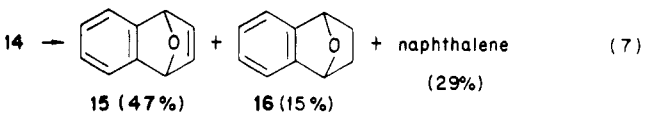
In order to study some aspects of these reactions with a substrate leading to less volatile products, the isobenzofuran analogue of **1** was prepared (compound **14**).

(10) Prinzbach, H.; Babsch, H. *Angew. Chem., Int. Edit. Engl.* **1975**, *40*, 753.

The acid-catalyzed method[11] for generating isobenzofuran from the acetal **13** was employed, with mesitoic acid catalyst in refluxing toluene (eq 6). The cycloadduct was



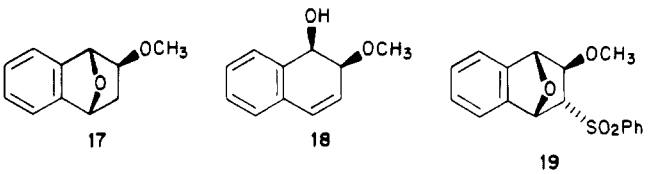
formed in essentially quantitative yield. The amalgam reduction (buffer, methanol) of **14** gave the three products **15**, **16**, and naphthalene in the yields shown in eq 7. When



the amount of Na·Hg used was reduced from ca. 12 to 4 molar equiv, the overall yield fell to 25%, without significant change in the product ratio, and a sizeable amount of starting material was recovered.

Treatment of **14** with amalgam (12 equiv)/buffer in DMF—one of the better ways found to prepare **3** from **2**—gave a complex mixture which was not further investigated. Use of only 3 equiv of amalgam gave partial reaction (70% of **14** recovered), with the remainder consisting of a ca. 1:1 mixture of naphthalene and 2-(phenylsulfonyl)naphthalene.[12] Thus this solvent has a deleterious effect on the formation of **15**.

When the solvent was changed to DMF/methanol (80/20), again with 12 equiv of amalgam but without the buffer, four products were formed in combined 92% yield. These are the olefin **15** (20%), naphthalene (5%), and compounds **17** (55%) and **18** (12%). Both **17** and **18**

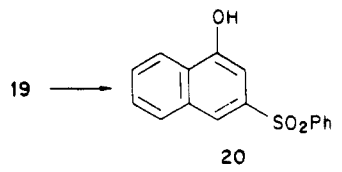


presumably arise from **19**, which is a reasonable intermediate that would be expected under the basic conditions which arise in amalgam/methanol solutions in the absence of the acidic buffer. The cis stereochemistry of **18** is assigned on the basis of the vicinal (1,2) coupling constant (5 Hz), which is in good agreement with values reported for similar structures.[13] It is also anticipated from the *exo*-methoxy structures of the (proposed) intermediate **19** and the major product **17**.

Compound **19** was prepared (quantitative yield) in a separate experiment by subjecting **14** to excess methoxide/methanol (24 h, ambient). Amalgam reduction of **19** in methanol/buffer gave **17** as the major product (75%), along with 16% of the olefin **15**. In DMF/buffer the products found are naphthalene (20%), **15** (22%), and the phenol **20**, which was isolated in 54% yield (eq 8).

Although the mechanism of formation of **20** has not been studied, a reasonable pathway would involve oxa bridge

(11) Mir-Mohamed-Sadeghy, B.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 2237.
(12) Baarschers, W. H. *Can. J. Chem.* **1976**, *54*, 3056.
(13) Anet, F. A. L. *Can. J. Chem.* **1961**, *39*, 789; see also ref 4.



(8)

cleavage via the sulfone-stabilized carbanion generated, e.g., by proton abstraction from **19**. The formation of **20** (and other sulfone-containing ring-opened products) would thus imply at least a localized basic environment; note that the NaH_2PO_4 "buffer" is only slightly soluble in the media employed in this study and neutralization may not be a rapid process. This mechanism is supported by the formation of diphenyl sulfone when **1** was subjected to excess *tert*-butoxide (noted earlier). Once the ring is opened, further elimination to the aromatic system should be relatively facile. The isolation of a sensitive material such as **18** requires careful pH control, in this instance obtained through somewhat arbitrary choice of conditions.

The formation of phenolic product(s) may well explain the modest material balances obtained in the reactions of the simpler bis-sulfone **1**.

Two control experiments were carried out with olefin **15** which established that it is stable (>95% recovered) to treatment with excess amalgam/buffer/methanol (reflux, 16 h) and methoxide/methanol (ambient, 12 h), respectively. This demonstrates, among other features, that the simple aromatics (naphthalene, and by analogy benzene) do not arise from further reaction of the desired olefin products.

In conclusion, this work shows that the Na·Hg reductive elimination of the bis-sulfone **2** and some of its derivatives is a viable method for the formation of **3**, but this approach is less useful for the formation of the diene **10** (although still competitive with the literature procedure[10]), and yields of **15** are such that the alternative aryne–furan cycloaddition would generally be preferred if the precursors are available for variants of this structure. Some of the many possible competing processes have been delineated by consideration of the alternative products formed under various reaction conditions. These are the following: direct reductive displacement of the phenyl sulfone group(s); facile elimination to form vinyl sulfones, which undergo rapid Michael addition reactions; reductive cleavage of the oxa bridge; sulfone-stabilized anionic cleavage of the oxa bridge; subsequent aromatization processes of various intermediates; and the unusual ring contraction to form compound **9**. Some of these competing reactions are shared by carbocyclic analogues, but it is clear that the oxa bridge introduces a greater level of complexity to these reductive eliminations. Experiments designed to circumvent one undesirable pathway often led to the introduction of another.

Experimental Section

The 6% sodium amalgam was prepared by adding the appropriate weight of mercury to molten sodium in a round-bottomed flask under nitrogen, with continuous shaking and heating (Bunsen burner). The liquid was poured onto an asbestos sheet (hood, in the air), and upon cooling the amalgam was broken into small pieces and stored in a capped bottle. (*E*)-1,2-Bis(phenylsulfonyl)ethylene was prepared essentially as described by De Lucchi,[3b] using commercial (*Z*)-1,2-dichloroethylene to form (*Z*)-1,2-bis(phenylmercapto)ethylene according to the Parham procedure,[14] followed by the Truce method[15] for oxidation, and subsequent I_2/sunlight conversion of the *Z* to the *E* isomer.

The general reductive elimination procedure was as follows: ca. 10–15 molar equiv (based on Na) of the 6 wt % amalgam was added to a mechanically stirred slurry of 4 molar equiv of $NaH_2PO_4 \cdot H_2O$ and 1 equiv of substrate in 10–15 mL of solvent per mmol of substrate. Reactions were carried out at room temperature under N_2 unless otherwise specified.

Melting points were taken on a Mel-Temp apparatus in open capillary tubes and are uncorrected. NMR spectra were obtained on Varian EM-360 and Nicolet NT-300 instruments in $CDCl_3$ (Me_4Si standard), and MS (electron impact) and MS-CI (chemically induced, methane flow gas) spectra were obtained on a VG ZAB-2F instrument. Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN.

2-*endo*,3-*exo*-Bis(phenylsulfonyl)-7-oxabicyclo[2.2.1]-hept-5-ene (1). The general procedure of De Lucchi[3b] was followed by using 75.5 g of (*E*)-1,2-bis(phenylsulfonyl)ethylene and 53 mL of furan (3 equiv) in 600 mL of CH_2Cl_2 to give 92.0 g (100%) of **1**, mp 229–230 °C (lit.[3b] mp 216–226 °C): ^1H NMR δ 3.65 (d, J = 5 Hz, 1 H, endo methine), 4.22 (dd, apparent t, J = 5 Hz, 1 H, exo methine), 5.25 (dd, J = 5 and 1.5 Hz, 1 H, bridgehead adjacent to endo sulfone), 5.43 (br s, 1 H, other bridgehead), 6.7 (m, 2 H, vinyl), and 7.4–8.0 (m, 10 H).

2-*endo*,3-*exo*-Bis(phenylsulfonyl)-7-oxabicyclo[2.2.1]-heptane (2). A Parr shaker was charged with **1** (21.0 g), 400 mL of $CHCl_3$, and ca. 100 mg of 10% Pd/C. The reduction was carried out under 50 psig of H_2 and was complete within a few minutes. Gravity filtration and evaporation of the solvent gave in quantitative yield **2**, mp 216–217 °C (recrystallized from benzene/petroleum ether): ^1H NMR δ 1.6–2.7 (m, 4 H), 3.75 (d, J = 5 Hz, 1 H, endo methine), 4.10 (dd, apparent t, J = 5 Hz, 1 H, exo methine), 4.90 (m, 2 H, bridgehead protons), and 7.5–8.0 (m, 10 H); MS-CI, m/z calcd for (P + H) 379.0672, found 379.0671. Anal. Calcd for $C_{18}H_{18}O_5S_2$: C, 57.13; H, 4.79. Found: C, 56.82; H, 4.74.

Reductive Elimination of 2 to 3. (a) In Methanol. The general procedure was used, with 4.39 g of **2**. After 24 h the mixture was poured into 250 mL of saturated brine and extracted with pentane (4 × 20 mL). The organic phase was dried over K_2CO_3, and the majority of the pentane was removed by slow distillation through a 25-cm column packed with glass helices. Yields were determined at this stage by adding known weight of durene to the residue and integration of the downfield product peaks vs. the aromatic proton singlet of the internal standard. The pot residue was then vacuum distilled (ca. 25/torr, room temperature, cooled receiver) to give 530 mg (48%) of material which consisted of **3** (90%), **6** (10%), and a trace of pentane. A sample of **3** was isolated by preparative VPC, using a 20 m × 6.4 mm Carbowax 6M column at 110 °C; injector and detector temperatures were held at 150 °C to avoid the decomposition of **3** which was observed (formation of furan) when the detector was at 275 °C. Pure **3** obtained in this manner had ^1H NMR δ 1.15 (m, 2 H), 1.77 (m, 2 H), 4.99 (br s, 2 H, bridgeheads), and 6.25 (s, 2 H, vinyl); it has a very disagreeable and pervasive odor.

A sample of **3** was reduced (pentane, 10% Pd/C, 1 atm) to **6**, which had the identical NMR spectrum and pleasant odor of an authentic commercial specimen.

(b) In DMF. The general procedure was used, with 1.20 g of **2** and 5-h reaction time. The yield of **3** was 70% by NMR, and this spectrum indicated that a small amount (ca. 5%) of **6** was also present.

(c) In DMF/Methanol (80/20), No Buffer. The general procedure was followed except that the buffer was omitted; 4.92 g of **2**, a reaction time of 12 h, and ether extraction were used. Workup as above gave 605 mg (48%) of **3** which contained ca. 2% (VPC) of **6**.

2-*exo*-Methoxy-3-*endo*-(phenylsulfonyl)-7-oxabicyclo-[2.2.1]heptane (7). To a suspension of 3.86 g of **2** in 100 mL of methanol was added 1.5 g of KOH dissolved in 50 mL of methanol. After stirring for 3 h, most of the methanol was removed under reduced pressure, and the crude product was taken up in CH_2Cl_2, washed with water, dried, and rotary evaporated to give 2.54 g (94%) of essentially pure **7**. After recrystallization from $CHCl_3$/hexane, **7** had the following: mp 118–119 °C; ^1H NMR δ 1.56–1.75 (m, 2 H), 1.85 (m, 1 H), 2.46 (m, 1 H), 3.14 (s, 3 H, methoxy), 3.49 (m, 1 H, exo methine), 3.86 (d, 1 H, J = 3 Hz, endo methine), 4.63 (m, 2 H, bridgeheads), 7.65 (m, 3 H), and 7.92 (m,

(14) Parham, W. E.; Heberling, J. *J. Am. Chem. Soc.* **1955**, *77*, 1175.
(15) Truce, W. E.; McManimie, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 5745.

2 H); MS-CI, calcd for (P + C_2H_5) 297.1159, found 297.1150. Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. Found: C, 58.01; H, 5.91.

Amalgam Reduction of 7. (a) In Acetonitrile/Methanol (2/1). The usual method was employed, but in an ice bath for 6 h. NMR analysis indicated the formation of **3** (30%) and 2-*exo*-methoxy-7-oxabicyclo[2.2.1]heptane, **8** (47%). Preparative VPC (SE-30 column) was used to obtain a sample of pure **8**: ^{1}H NMR δ 1.30 (m, 2 H), 1.80 (m, 2 H), 3.30 (s, 3 H, methoxy), 3.47 (m, 1 H, endo methine), 4.55 (d, 1 H, J = 5 Hz, bridgehead adjacent to methoxy), and 4.61 (dd, apparent t, 1 H, J = 4.5 Hz, other bridgehead). The exo methoxy stereochemistry is based on the multiplicity (a simple d) of the absorption at δ 4.55.

(b) In DMF. Normal conditions with 2.51 g of **7** in 55 mL of DMF were used, with ether extraction, giving **3** and **8** in yields of 48% and 25%, respectively.

2-(Phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene (4). To a solution of **2** (12.2 g, 32.2 mmol) in 350 mL of DMF was added 1 equiv of potassium *tert*-butoxide, with stirring continued for 1 h at ambient temperature. The mixture was poured into saturated Na_2SO_4 (400 mL) and extracted with ether (4 × 40 mL). The organic phase was washed with water, dried, and evaporated to give a residue which was chromatographed on 60 g of silica gel (ether/pentane, 1/1). The vinyl sulfone was obtained in 27% yield; recrystallization from ether gave pure **4**, mp 83–84 °C: ^{1}H NMR δ 1.2–2.1 (m, 4 H), 5.15 (m, 2 H, bridgeheads), 7.10 (d, 1 H, J = 2 Hz, vinyl), and 7.5–8.1 (m, 5 H); MS-CI; calcd for (P + H) 237.0584, found 237.0601. Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 60.73; H, 5.12.

The amalgam reduction of **4** was attempted twice, in DMF solvent, and both times gave 20% of **3** (by NMR).

2-(Phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-5-ene (5). A stirred, ice-bath cooled solution of **1** (2.26 g, 6.02 mmol) and $NaBH_4$ (1.5 g) in 150 mL of acetonitrile was treated with 1 equiv of potassium *tert*-butoxide. After 4 h, water was added, and the majority of the solvent was removed by rotary evaporation. The residue was taken up in CH_2Cl_2, washed with water, dried, and evaporated to give 1.27 g (91%) of a colorless oil. Chromatography (silica gel, ether) gave pure **5** (oil): ^{1}H NMR δ 1.5–2.4 (m, 2 H), 3.15 (dd, 1 H, J = 5, 4 Hz, endo methine), 5.10 (d, 1 H, J = 5 Hz, bridgehead), 5.35 (broadened s, 1 H, bridgehead adjacent to exo sulfone), 6.40 (m, 2 H, vinyl), and 7.4–8.1 (m, 5 H).

Amalgam Reactions of 5. Two reactions were carried out in methanol at 0 °C, differing only in scale. When 450 mg of **5** was used, NMR analysis indicated the formation of **3** in 65% yield, with 8% benzene as the only distinguishable side product. Scaled up to 1.94 g of **5**, this otherwise identical procedure gave only 30% of **3**, 4% of benzene, and at least 40% (pentane extraction used) of 3-cyclopentenylmethanol (**9**). Preparative VPC was used to obtain a sample of pure **9**, which was identified by its exact correspondence to a published NMR spectrum.[8] Examination of the NMR spectra of the crude reaction mixtures indicated that the double bond isomer, 2-cyclopentenylmethanol,[9] was not present in detectable amounts. The exact cause of the difference in outcome of these two runs is not known and may be associated with localized exotherms. Repetition of the reaction at −20 °C (1.11 g of **5**) gave **3** in 48% yield, along with a trace of benzene. No indication of formation of **9** was found in the pentane extract nor in ether when the aqueous phase was further extracted with this solvent.

Amalgam Reactions of 1 (Formation of 10). (a) In Methanol. This reaction was carried out with 1.25 g of **1** in refluxing solvent for 1 h. NMR analysis indicated the formation of **10** (30%), identified by comparison with published spectral data,[10] **3** (16%), and a trace of benzene.

(b) In DMF. At room temperature, 516 mg of **1** afforded 25% of **10**, which was free of **3** as shown by both NMR and VPC analysis.

2-*exo*-Methoxy-3-*endo*-(phenylsulfonyl)-7-oxabicyclo-[2.2.1]hept-5-ene (11). To a solution of 3.0 g of KOH in 60 mL of methanol was added 2.99 g of **1** dissolved in 100 mL of acetonitrile, and the mixture was stirred for 18 h. Workup as described for **7** gave colorless solid, 2.01 g (95%), which was recrystallized from $CHCl_3$/hexane to give pure **11**, mp 127–128 °C: ^{1}H NMR δ 3.30 (s, 3 H, methoxy), 3.55 (dd, 1 H, J = 4 and 3 Hz, exo methine), 3.90 (d, 1 H, J = 3 Hz, endo methine), 5.0 (m, 2 H, bridgeheads), 6.65 (m, 2 H, vinyl), and 7.6–8.1 (m, 5 H). Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.43; H, 5.31.

Amalgam Reaction of 11 (Formation of 12). The general procedure was applied to 1.07 g of **11** in methanol for 6 h. Very small amounts of **10** and benzene were detected (NMR) in the product mixture; the major component was 2-*exo*-methoxy-7-oxabicyclo[2.2.1]hept-5-ene (**12**), formed in 48% yield. An analytical sample was obtained by preparative VPC (Carbowax column). **12**: ^{1}H NMR δ 1.55 (ddd, 1 H, J = 12, 5, and 2 Hz, exo methylene), 1.73 (dd, 1 H, J = 12 and 6 Hz, endo methylene), 3.39 (s, 3 H, methoxy), 3.56 (dd, 1 H, J = 6 and 2 Hz, $CHOCH_3$), 4.94 (d, 1 H, J = 1.5 Hz, bridgehead adjacent to methoxy), 5.00 (br, d, J = 6 Hz, other bridgehead), 6.22 (dd, 1 H, J = 6 and 2 Hz, vinyl), and 6.42 (dd, 1 H, J = 6 and 1.5 Hz, vinyl proximal to methoxy).

2-*endo*,3-*exo*-Bis(phenylsulfonyl)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (14). A solution of **13** (2.29 g, 13.9 mmol), (*E*)-1,2-bis(phenylsulfonyl)ethylene (3.89 g, 12.6 mmol), and 163 mg of mesitoic acid in 30 mL of toluene was refluxed for 24 h, after which the solvent was removed under reduced pressure. The crude product was taken up in CH_2Cl_2, washed with bicarbonate solution, dried, and evaporated to give 5.30 g (99%) of essentially pure product. Recrystallization from $CHCl_3$/hexane gave pure **14**, mp 191–192 °C: ^{1}H NMR δ 3.65 (d, 1 H, J = 5 Hz, endo methine), 4.45 (dd, apparent t, 1 H, J = 5 Hz, exo methine), 5.72 (d, 1 H, J = 5 Hz, bridgehead), 5.83 (s, 1 H, bridgehead adjacent to exo sulfone), and 7.1–7.9 (m, 14 H); MS, calcd for P − H_2O 409.0566, found 409.0571. Anal. Calcd for $C_{22}H_{18}O_5S_2$: C, 61.95; H, 4.25. Found: C, 61.83; H, 4.24.

Amalgam Reaction of 14. (a) In Methanol. The standard conditions were used with 529 mg of **14** in refluxing solvent for 6 h. Silica gel chromatography gave 46 mg (29%) of naphthalene, 27 mg (15%) of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**16**), and 84 mg (47%) of 1,4-epoxy-1,4-dihydronaphthalene (**15**); these products had NMR spectra identical with those of commercial samples.

(b) In DMF/Methanol (No Buffer). A 700-mg sample of **14** was subjected to the amalgam in DMF/methanol (80/20) at room temperature for 5 h. The mixture was poured into water and extracted with ether. After the usual workup, silica gel chromatography (graded elution, pentane to ether) gave four products in overall 92% yield; in order of elution these are naphthalene (10 mg, 5%), **15** (46 mg, 20%), **17** (150 mg, 55%), and **18** (32 mg, 12%).

17 (oil): ^{1}H NMR δ 1.90 (m, 2 H, methylene), 3.45 (s, 3 H, methoxy), 3.65 (dd, apparent, 1 H, J = 4.5 Hz, C*H*OCH_3), 5.40 (m, 2 H, bridgeheads), and 7.25 (br s, 4 H); MS-CI, m/z (relative intensity) 177 (P + H, 7), 160 (12), 159 (100), 147 (17), 145 (54), 119 (32), 118 (63), and 117 (44).

18: mp 54–55 °C (recrystallized from $CHCl_3$/hexane); ^{1}H NMR δ 2.6 (d, 1 H, J = 8 Hz, hydroxyl; disappears with D_2O), 3.45 (s, 3 H, methoxy), 4.0 (dd, apparent t, J = ca. 5 and 4 Hz, C*H*OCH_3), 4.78 (dd, 1 H, J = 8 and 5 Hz, C*H*OH; with D_2O, d, J = 5 Hz), 6.08 (dd, 1 H, J = 10 and 4 Hz, vinyl proximal to methoxy), 6.59 (d, 1 H, J = 10 Hz, benzylic vinyl), and 7.1–7.5 (m, 4 H).

1,4-Dihydro-1,4-epoxy-2-*exo*-methoxy-3-*endo*-(phenylsulfonyl)naphthalene (19). To a suspension of **14** (1.22 g) in 20 mL of methanol was added 0.4 g of KOH in 12 mL of methanol, and the mixture was stirred for 24 h. Most of the solvent was then removed by rotary evaporation, and the residue was taken up in CH_2Cl_2; washing with brine, drying, and evaporation gave 820 mg (99%) of colorless solid. Recrystallization from $CHCl_3$ gave pure **19**, mp 160–161 °C: ^{1}H NMR δ 3.20 (s, 3 H, methoxy), 3.85 (m, 2 H), 5.35 (s, 1 H, benzylic adjacent to methoxy), 5.52 (d, 1 H, J = 4.5 Hz, other benzylic), and 7.2–7.9 (m, 9 H). Anal. Calcd for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10. Found: C, 64.32; H, 5.20.

Amalgam Reactions of 19. (a) In Methanol. The usual conditions applied to 177 mg of **19** with CH_2Cl_2 extraction gave, after evaporation, a mixture (91%) consisting of **17** (75%) and **15** (16%).

(b) In DMF. The general procedure was used (6 h) with ether extraction. The crude product was chromatographed on silica gel (graded elution, pentane/ether to ether) to provide naphthalene (20%), **15** (22%), and 300 mg (54%) of **20**, which after recrystallization ($CHCl_3$/hexane) had mp 167–168 °C: ^{1}H NMR ($CDCl_3$/acetone-d_6) δ (7.2, 1 H, OH, shift varies with concentration and dissappears upon addition of D_2O), 7.45–7.65 (m, 6 H), 7.9–8.0

(m, 3 H), 8.12 (s, 1 H), and 8.25 (m, 1 H); MS, m/z (relative intensity) 286 (8.7), 285 (20.8), 284 (parent and base), 191 (14), 143 (17), 131 (59), 115 (29); IR (KBr) 3360 cm^{-1}. **20** is freely soluble in dilute hydroxide and precipitates upon acidification.

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Synthesis of Optically Active 2,2′-Dihalo-1,1′-binaphthyls via Stable Diazonium Salts

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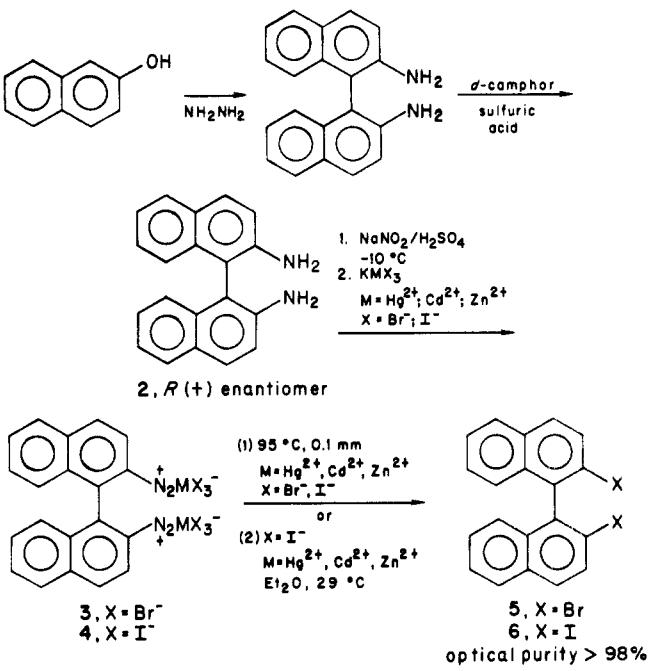
Optically pure 2,2′-dibromo-1,1′-binaphthyl (DBBN) (**5**) and optically pure 2,2′-diiodo-1,1′-binaphthyl (DIBN) (**6**) are synthesized in preparative quantities starting from 2-naphthol. These compounds are useful for the preparation of chiral, bidentate ligands based on the 1,1′-binaphthyl system. The synthesis proceeds through a common optically active precursor, 2,2′-diamino-1,1′-binaphthyl ((*R*)-(+)-DABN) (**2**), and involves the preparation and subsequent decomposition of stable diazonium metal complexes (**3** and **4**). The effect of several variables, including the nature of the metal M, on these reactions is discussed, and comparison to related procedures reported in the literature is made.

Previous reports[1,2] have described the preparation of 2-lithio-2′-halo-1,1′-binaphthyl and 2,2′-dilithio-1,1′-binaphthyl intermediates and their reaction with electrophiles such as $ClPPh_2$, MeOH, or H_2O and aromatic aldehydes to form optically active 2- and/or 2′-substituted 1,1′-binaphthyl derivatives. The usefulness of this synthetic method lies in its ability to produce a wide variety of symmetrical *or* unsymmetrical chiral, bidentate ligands which all derive from a common optically active precursor (2,2′-diamino-1,1′-binaphthyl) and thus do not require the development of separate, specialized resolution methods. The value of the product ligands and of the lithiated intermediates from these reactions in the study of asymmetric synthesis has been discussed.[1,2]

Success of this method depends on the ability to obtain samples of optically active 2,2′-dibromo-1,1′-binaphthyl (DBBN) and 2,2′-diiodo-1,1′-binaphthyl (DIBN). Racemic DBBN has been synthesized in 45% yield by treating 2,2′-dihydroxy-1,1′-binaphthyl with Br_2/PPh_3 at 320 °C[3] and in 55% yield by treating 2-bromonaphthalene with $Pb(O_2CCH_3)_4$.[4] Another preparation of racemic DBBN by a method which is similar to the one reported in the present work (vide infra) resulted in yields of 80%.[5] A synthesis of racemic DIBN has also been reported in the literature,[6] and yields are on the order of 18%. However, none of these methods[3-6] has been shown to be applicable to the direct synthesis of optically active biaryls. We now describe detailed procedures for obtaining optically pure DBBN and DIBN via two novel modifications to the classical Sandmeyer reaction.

It should also be noted that while this is the first reported synthesis of optically pure 2,2′-dihalo-1,1′-binaphthyls, there have been reports of the partial resolution of small quantities of DBBN by HPLC[7a] and by fractional crystallization.[7b]

Scheme I[a]



[a] For 3 and 4: (a) M = Hg^{2+}; (b) M = Cd^{2+}; (c) M = Zn^{2+}.

The synthesis proceeds via 2,2′-diamino-1,1′-binaphthyl (DABN), which is efficiently resolved with *d*-camphorsulfonic acid, (*d*-CSA) and then converted to the bis(diazonium) salts **3** and **4** (Scheme I). The dry salts, when mixed with a large excess of KX, can be pyrolyzed under vacuum to yield DBBN or DIBN. Although the isolation

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