was also carried out in a solvent: ^{1}H NMR δ_A 7.35 (J_{AB} = 8.2 Hz), δ_B 6.8 (J_{AB} = 8.2 Hz, J_2 = 1.96 Hz), 7.00 (d, J = 19.6 Hz), 2.27 (superimposed, s, t, q, J = 2 Hz), 2.2 (s), 2.19 (t, J = 2 Hz); ^{13}C NMR δ 137.19 (s), 136.81 (s), 131.89 (s), 131.49 (s), 127.96 (s), 121.42 (s), 21.91 (superimposed s, t, q), 20.50 (superimposed s, t, J = 19.3 Hz).

Reaction of 1-Bromo-2,4,6-trimethylbenzene (2-Bromomesitylene, 3). A mixture of 0.769 g (3.86 mmol) of **3**, 0.525 g (1.54 mmol, 40 mol %) of (TBA)HSO_4, and 3.370 g of NaOD/D_2O was stirred magnetically in the standard vial for 23 h at room temperature. The standard workup procedure was applied. The same reaction was also carried out in a solvent: ^{1}H NMR δ 6.76 (s), 2.29 (s), 2.15 (s); ^{13}C NMR δ 137.57 (s), 135.93 (s), 128.85 (s), 124.06 (s), 23.08 (superimposed s, t, J = 19.3 Hz), 20.38 (s).

Reaction of 1-Iodo-2,3,5,6-tetramethylbenzene (1-Iododurene, 4). A mixture of 0.515 g (1.98 mmol) of **4**, 0.28 g (0.82 mmol, 41 mol %) of (TBA)HSO_4 and 2.54 g of NaOD/D_2O in 3 mL of hexane was magnetically stirred for 23 h at room temperature. The reaction mixture was worked up in diethyl ether: ^{1}H NMR δ 6.86 (s), 2.42 (s), 2.28 (s).

Mass Spectroscopy. Electron-impact mass spectra of the following deuterated compounds were recorded on a Finnigan GC MS.

o-Bromotoluene: *m/e* 170 (M), 171 (M + 1), 172 (M + 2), 173 (M + 3), 174 (M + 4), 175 (M + 5).

o-Chlorotoluene: *m/e* 126 (M), 127 (M + 1), 128 (M + 2), 129 (M + 3), 130 (M + 4).

m-Iodotoluene: *m/e* 218 (M), 219 (M + 1), 220 (M + 2), 221 (M + 3), 222 (M + 4).

m-Bromotoluene: *m/e* 170 (M), 171 (M + 1), 172 (M + 2), 173 (M + 3), 174 (M + 4), 175 (M + 5).

p-Chlorotoluene: *m/e* 126 (M), 127 (M + 1), 128 (M + 2).

p-Bromotoluene: *m/e* 170 (M), 171 (M + 1), 172 (M + 2), 173 (M + 3).

2-Bromo-1,3-dimethylbenzene: *m/e* 107, 184 (M), 185 (M + 1), 186 (M + 2), 187 (M + 3), 188 (M + 4), 189 (M + 5), 190 (M + 6).

1-Bromo-2,4-dimethylbenzene: *m/e* 107, 184 (M), 185 (M + 1), 186 (M + 2), 187 (M + 3), 188 (M + 4), 189 (M + 5).

1-Bromo-2,4,6-trimethylbenzene: *m/e* 119, 198 (M), 199 (M + 1), 200 (M + 2), 201 (M + 3), 202 (M + 4), 203 (M + 5).

Acknowledgment. We thank Dr. S. Zitrin and Mrs. Z. Tamiri from the laboratories of the Israel Police Headquarters for mass spectroscopic determinations.

Registry No. 1, 576-22-7; 2, 583-70-0; 3, 576-83-0; 4, 2100-25-6; (TBA)HSO_4, 32503-27-8; *o*-fluorotoluene, 95-52-3; *o*-chlorotoluene, 95-49-8; *o*-bromotoluene, 95-46-5; *o*-nitrotoluene, 88-72-2; *m*-fluorotoluene, 352-70-5; *m*-chlorotoluene, 108-41-8; *m*-bromotoluene, 591-17-3; *m*-iodotoluene, 625-95-6; *p*-chlorotoluene, 106-43-4; *p*-bromotoluene, 106-38-7; *p*-iodotoluene, 624-31-7; *p*-nitrotoluene, 99-99-0.

Magnesium in Methanol: Substitute for Sodium Amalgam in Desulfonylation Reactions

Alan C. Brown and Louis A. Carpino*

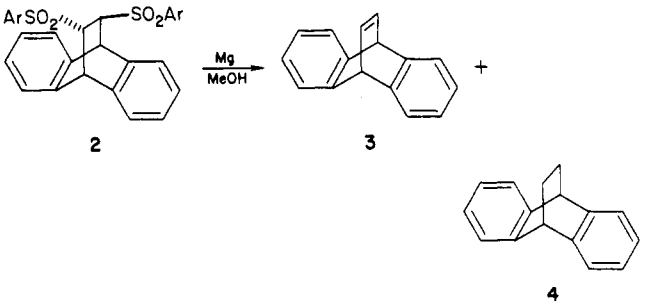
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received September 6, 1984

Synthetic equivalents of acetylene in the Diels–Alder reaction are of special utility in view of the low reactivity of acetylene itself toward most dienes. Recently[1] *cis*- and *trans*-1,2-bis(phenylsulfonyl)ethylenes (1, Ar = C_6H_5) have

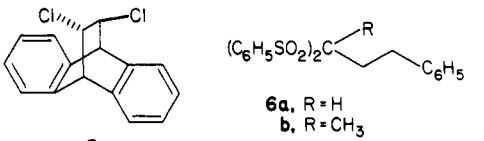
$$ArSO_2CH{=}CHSO_2Ar$$
1

been recommended for this purpose, with eventual reductive elimination of the activating sulfone functions by treatment with sodium amalgam. In connection with a study of some general routes to substituted derivatives of ethenoanthracene **3**, we examined the utility of *cis*- and



2 **3** **4**

trans-**1** (Ar = *p*-$CH_3C_6H_4$) in this system. In the initial Diels–Alder reaction *trans*-**1** proved far more reactive than the corresponding cis isomer[2] and was therefore used exclusively in this study. Not wishing to be faced, in expectation of eventual large-scale work, with the tedious handling of massive quantities of toxic metallic mercury, we devised a simple method of desulfonylation involving treatment of the appropriate bis(sulfone) with an excess of magnesium in methanol at 50 °C for several hours. Under these conditions adduct **2** gave **3** in 62% yield accompanied by 21% of the corresponding dihydro derivative **4**. For comparison, under the same conditions the analogous dichloro compound **5** gave only 27% of **3**.



5 **6a**, R = H; **b**, R = CH_3

The simplicity of this technique encouraged us to extend it to 1,1-bis(sulfones) as well as simple monosulfones. Application to **6a** and **6b** gave the expected hydrocarbons *n*-propylbenzene and *n*-butylbenzene in yields of 84% and 81%, respectively. Phenyl β-phenethyl sulfone gave ethylbenzene in 68% yield. The fate of the sulfonyl residues was not determined in any of these conversions. The magnesium turnings used in this study were activated by treatment with dilute hydrochloric acid. Turnings activated in this way were especially reactive in the Grignard reaction as well as these desulfonylation processes.

Experimental Section[3]

(*Z*)-1,2-Bis[(4-methylphenyl)sulfonyl]ethene. Obtained by oxidation of the corresponding bis(thio ether) by the method of Truce and McManimie.[4] The precursor was most simply prepared from vinylidene chloride by the technique of Truce and Boudakian[5] except that refluxing the *p*-toluenethiol for a 4-day period with lithium isopropoxide in isopropyl alcohol took the place of the sealed tube reaction. The sulfone was obtained in an overall yield of 40%: mp 152–153 °C (lit.[4] mp 149 °C); ^{1}H

(1) For recent references and citations to earlier examples, see: (a) DeLucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596. (b) DeLucci, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585.

(2) The greater reactivity of *trans*-**1** over *cis*-**1** has been previously noted. See: Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.

(3) Melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 237B instrument and NMR spectra on Varian A-60 and Perkin-Elmer R12 instruments with Me_4Si as internal standard. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory under the direction of Greg Dabkowski. Thin-layer chromatography was performed on aluminum-backed Merck silica gel 60 F254 plates using the solvents specified.

(4) Truce, W. E.; McManimie, R. J. *J. Am. Chem. Soc.* **1953**, *75*, 1672.

(5) Truce, W. E.; Boudakian, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 2750.

0022-3263/85/1950-1749$01.50/0

NMR ($CDCl_3$) δ 2.42 (s, 6, CH_3), 6.83 (s, 2, vinyl), 7.72 (q, AA'BB', 8, aryl).

(*E*)-1,2-Bis[(4-methylphenyl)sulfonyl]ethene. A mixture of 100 mL of dry xylene, 6.0 g of the *Z* isomer, and 300 mg of I_2 was refluxed for 24 h under N_2. Upon cooling, an off-white solid (5.5 g, 92%) was isolated by filtration, washing with ethanol, and drying. The solid obtained at this stage was pure enough (TLC analysis gave a single spot) for further reactions: mp 223–225 °C (lit.[6] mp 227–229 °C); ^1H NMR ($CDCl_3$) δ 2.48 (s, 6, CH_3), 7.35 (s, 2, vinyl), 7.65 (q, AA'BB', 8, aryl).

(*E*)-11,12-Bis[(4-methylphenyl)sulfonyl]-9,10-dihydroethanoanthracene (2). A mixture of 25 mL of degassed mesitylene, 1.1 g of bis(sulfonyl)ethene ((*E*)-1, Ar = *p*-$CH_3C_6H_4$) and 0.56 g of anthracene (Eastman) was heated to reflux under N_2 for 24 h. After cooling, filtration followed by washing with two 5-mL portions of ethanol gave an off-white solid (1.5 g, 93%). The crude solid was dissolved in 25 mL of warm (60 °C) benzene, the hot solution was filtered, and the filtrate was treated with 75 mL of hot ethanol with stirring. Slow cooling to 0 °C gave the white crystalline adduct (1.35 g, 85%): mp 234–235 °C; ^1H NMR ($CDCl_3$) δ 2.40 (s, 6, CH_3), 4.0 (bs, 2, -HCR_2SO_2R'), 4.85 (bs, 2, bridgehead), 7.1–7.6 (m, 16, aryl); IR (KBr) 1320, 1140 cm^{-1}.

Anal. Calcd for $C_{30}H_{28}O_4S_2$: C, 70.03; H, 5.09. Found: C, 70.19; H, 5.08.

1,1-Bis(phenylsulfonyl)-3-phenylpropane (6a). Into 200 mL of dry THF was placed 6.0 g of bis(phenylsulfonyl)methane[7] under N_2 at 0 °C. To the solution was added over a period of 15 min to control foaming 1.25 g of 50% sodium hydride in mineral oil. The mixture was allowed to warm to room temperature over a 1-h period, and to the stirred solution was added 4.1 g of 2-bromo-1-phenylethane dropwise over a 20-min period. After being stirred at room temperature for 3 h, the mixture was poured into 400 mL of ice water and extracted once with 40 mL of pentane (discarded) and twice with 70-mL portions of ether. The extracts were washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo, yielding 7.8 g (94%) of an off-white oily solid. Recrystallization from toluene gave 6.5 g (78%) of the sulfone as fluffy white needles: TLC (CH_2Cl_2/silica gel, R_f 0.7), mp 146–148 °C; ^1H NMR ($CDCl_3$) δ 2.25–2.65 (m, 2, $CH_2CH_2C_6H_5$), 2.9 (t, 2, $CH_2CH_2C_6H_5$), 4.35 (t, 1, $CH(SO_2C_6H_5)_2$), 6.95–8.10 (m, 15, aromatic), IR (KBr) 2850, 1320, 1130 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}O_4S_2$: C, 62.99; H, 5.03. Found: C, 63.01; H, 5.14.

1-Phenyl-3,3-bis(phenylsulfonyl)butane (6b). Using the same procedure as described for the synthesis of **6a**, 6.0 g of bis(sulfonyl)propane **6a**, 800 mg of 50% NaH in mineral oil, 150 mL of dry THF, and 2.5 mL of methyl iodide gave 5.5 g (89%) of an oily solid. After two recrystallizations (with carbon) from toluene, 4.2 g (68%) of the sulfone was obtained as white needles: mp 127–129 °C; ^1H NMR ($CDCl_3$) δ 1.8 (s, 3, CH_3), 2.15–2.55 (m, 2, $CH_2CH_2C_6H_5$), 2.70–3.05 (m, 2, $CH_2CH_2C_6H_5$), 7.0–8.15 (m, 15, aryl); IR (KBr) 2870, 1310, 1140 cm^{-1}.

Anal. Calcd for $C_{22}H_{22}O_4S_2$: C, 63.74; H, 5.35. Found: C, 63.40; H, 5.45.

Activation of Magnesium Metal. Into a 125-mL Erlenmeyer flask was placed 10 g of Mg turnings.[8] Repeated washings with 0.5% aqueous HCl were carried out by covering the turnings with the acidic solution, swirling and decanting the liquid. Normally, after five washings, the metal brightened noticeably. After ten rinses, the turnings were washed five times with fresh portions of distilled water, dry ethanol, and finally dry ether. The metal was then heated in an oven (100 °C) overnight.

General Procedure for Magnesium Reduction of Sulfonyl Compounds. Into 100 mL of dry methanol was placed 1.0 g of cleaned magnesium turnings with stirring. The mixture was heated to 50 °C to initiate continuous hydrogen generation. Hydrogen continued to be evolved when the heating source was removed and the substrate (5 mmol) was added at this time. The reaction mixture was normally stirred without heating for the rest of the time (temperature remained near 50 °C) and 1.0 g of magnesium was added intermittently to maintain the reaction. After 2.5–3.5 g of magnesium had been added, reduction was normally complete (TLC). If not, more Mg was added. Upon completion, the cloudy mixture was poured into 250 mL of dilute hydrochloric acid and ice and extracted with an appropriate solvent, the extracts were washed well with dilute KOH and brine and dried over $MgSO_4$, and the solvent was removed. The crude product was purified as appropriate.

Reductive Elimination of (*E*)-11,12-Bis[(4-methylphenyl)sulfonyl]-9,10-dihydro-9,10-ethanoanthracene (2). Into 150 mL of dry methanol was placed 2.00 g of activated Mg turnings. The mixture was heated to 45–50 °C with stirring until gas evolution started (10 min) and 2.1 g of the bis(sulfonyl) compound **2** added in one portion. The mixture was stirred without additional heat for **4–5** h or until TLC analysis showed no starting material (CH_2Cl_2/silica gel, R_f (**2**) 0.4). After aqueous workup as described previously and extraction with ethyl ether, 760 mg (91%) of a light tan solid was obtained. TLC analysis (hexane/alumina) showed two components, R_f 0.35 and 0.45. These were separated on a short (3 × 30 cm) basic alumina column (Merck) after two elutions with hexane. Eluting first was 165 mg (21%) of 9,10-dihydroethanoanthracene (**4**): mp 145.5–146.5 °C (lit.[9] mp 142–143 °C); ^1H NMR ($CDCl_3$) δ 1.7 (bs, 4, CH_2CH_2), 4.3 (bs, 2, bridgehead), 7.0–7.4 (m, 8, aryl). Eluting second was 510 mg (62%) of 9,10-dihydroethenoanthracene (**3**): mp 118–119 °C (lit.[10] mp 119 °C); ^1H NMR ($CDCl_3$) δ 5.15 (t, 2, bridgehead), 6.87–7.47 (m, 10, vinylic and aromatic). The physical constants and spectral data matched those previously described in the literature.[10,11] Hydrogenation of **3** in ethanol using Pd/C at atmospheric pressure gave a material whose properties matched those of 9,10-ethanothracene (**4**) described directly above.

Reduction of 3,3-Bis(phenylsulfonyl)-1-phenylbutane (6b). According to the general procedure described above, 2.0 g of substrate was added to 2.3 g of Mg in 120 mL of methanol. After 4 h, the reaction appeared complete by TLC and the mixture was subjected to the above aqueous workup. After removal of solvent, the colorless oil was distilled in vacuo to give 520 mg (81%) of *n*-butylbenzene as a colorless oil: bp 55–60 °C (9 mm); ^1H NMR ($CDCl_3$) δ 0.9 (t, 3, CH_3), 1.05–1.80 (m, 4, $CH_2CH_2CH_2C_6H_5$), 2.55 (t, 2 -$CH_2C_6H_5$), 7.05–7.35 (m, 5, aryl).

Reductive Elimination of (*E*)-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (5). With the procedure previously described for analogous sulfonyl compounds, 275 mg of (dichloro compound) **5** and 480 mg of activated Mg was stirred at 50 °C for 5 h in 50 mL of dry methanol. After aqueous workup, 250 mg of an off-white solid was isolated which showed two spots by TLC analysis (CH_2Cl_2/hexane, 1:1/silica gel, R_f 0.5 and 0.9). The ^1H NMR spectrum showed incomplete reaction, with dibenzobarrelene **3** being formed in a yield of 27%. The yield was determined by integration of the barrelene bridgehead proton (δ 5.1, t) relative to either the starting material bridgehead proton (δ 4.15, m) or the proton (δ 4.35, m) α to chlorine.

Reduction of Phenyl 2-Phenylethyl Sulfone. Into 70 mL of dry methanol was placed 2.00 g of activated Mg. After warming to 50 °C, 1.5 g of phenyl 2-phenylethyl sulfone was added in one portion with stirring. After all of the Mg had reacted, the mixture was subjected to the usual aqueous workup yielding 460 mg (68%) of pure ethylbenzene: bp 134–136 °C; ^1H NMR ($CDCl_3$) δ 1.2 (t, 3, CH_3), 2.65 (q, 2, CH_2), 7.25 (bs, 5, aryl).

Acknowledgment. We thank the National Science Foundation (Grant CHE-79-23622) for support of this work. We also thank George (Tony) Truran for checking some of the preparations.

Registry No. (*E*)-1 (Ar = *p*-$CH_3C_6H_4$), 15717-50-7; (*Z*)-1 (Ar = *p*-$CH_3C_6H_4$), 15645-75-7; **2**, 95274-96-7; **3**, 2734-13-6; **4**, 5675-64-9; **5**, 6476-15-9; **6a**, 95274-97-8; **6b**, 95274-98-9; phenyl β-phenethyl sulfone, 27846-25-9; 2-bromo-1-phenylethane, 103-63-9; *n*-propylbenzene, 103-65-1; *n*-butylbenzene, 104-51-8; ethylbenzene, 100-41-4; anthracene, 120-12-7; bis(phenylsulfonyl)methane, 3406-02-8; methyl iodide, 74-88-4; magnesium, 7439-95-4.

(6) Truce, W. E.; McManimie, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 5745.
(7) Kohler, E. P.; Tishler, M. *J. Am. Chem. Soc.* **1935**, *57*, 217.
(8) Magnesium obtained from different suppliers gave somewhat varying results, possibly because of the presence of differing amounts of trace metals. The magnesium turnings used in this study were obtained from Fisher Scientific, Medford, MA.
(9) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193.
(10) Figeys, H. P.; Dralants, A. *Tetrahedron* **1972**, *28*, 3031.
(11) Tori, K.; Takano, Y.; Kitahonoki, K. *Chem. Ber.* **1964**, *97*, 2798.