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New Construction of *p*-Tolylsulfonyl-Substituted Naphthalenes by Thermal and Photochemical Cyclization of 1-Aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes

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ABSTRACT: *Transformation of 4-(methylthio)-1-phenyl-2-(p-tolylsulfonyl)-1,3-butadiene* **1a** *was found to give 2-(p-tolylsulfonyl)naphthalene* **3a** *either by the action of I_2 in refluxing acetonitrile or by irradiation with a high-pressure Hg lamp. An electron-withdrawing group (p-F or p-CO_2Me) on the phenyl ring retarded the thermal reaction, but the corresponding naphthalene derivative was efficiently produced by the photolysis in the presence of I_2. The substituent effect of an electron-donating methoxyl group is also reported.*
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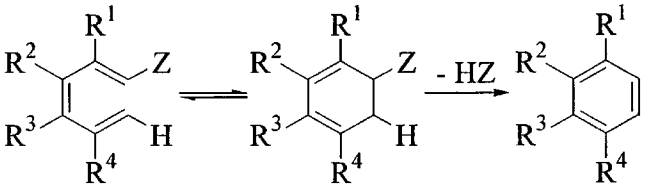
INTRODUCTION

Efficient methods for the construction of a benzene ring are very important for developing a new type of biologically active compounds and functional materials with a π-electron system. Hitherto, the benzene ring has been made mainly by the following methods: (i) an aromatic substitution reaction [1]; (ii) coupling reaction [2]; (iii) cycloaddition [3]; (iv) electrocyclization [4,5]. Among them, our attention was focused on the electrocyclization of a 1,3,5-alkatriene accompanied by elimination of an appropriate moiety to give the benzene ring (Equation 1) because it can fix the position of the substituent(s) on the newly formed benzene ring unambiguously, and various ways are employed for the preparation of the starting 1,3,5-alkatriene.



(1)

In this reaction sequence, it is anticipated that if a good leaving group (Z) is introduced at the 1-position of the triene, the irreversible elimination step would take place so smoothly and drive the cyclization step forward. However, we had to solve the problem of how to prepare the 1,3,5-alkatrienes bearing the central double bond with the geometry appropriate to the cyclization. These considerations prompted us to investigate the ring-closure of 1-aryl-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadienes (**1**) because the methylthio group is thought to be a good, versatile leaving group because it is removable

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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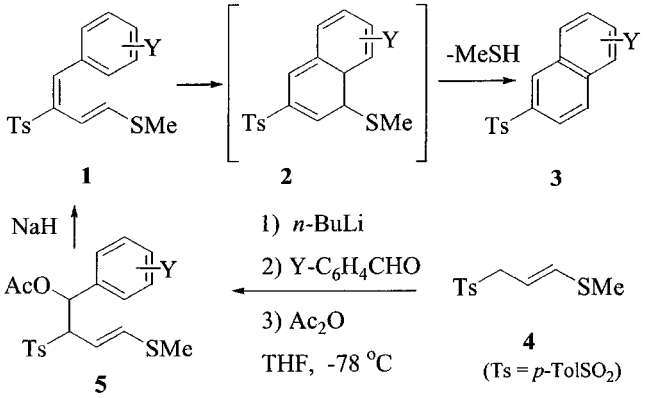
as the corresponding methylsulfenyl cation, methylthio radical, or methanethiolate ion.

Since **1** can be prepared from 1-(methylthio)-3-(*p*-tolylsulfonyl)-1-propene (**4**) as summarized in Scheme 1, the presence of a *p*-tolylsulfonyl group is expected to force the *E* geometry of the central double bond that is favorable for the cyclization. Now, we wish to report the convenient preparation of **1** and its thermal and photochemical conversion into the naphthalene derivatives (**3**) having an electron-withdrawing sulfonyl group at a specific position.

RESULTS AND DISCUSSION

The starting compound **1** could be prepared according to Scheme 1. Successive treatment of (*E*)-**4** [6] with n-butyllithium, followed by the addition of an aromatic aldehyde and the subsequent acetylation with acetic anhydride, gave, in a one-pot manner, 4-acetoxy-4-aryl-1-(methylthio)-3-(*p*-tolylsulfonyl)-1-butene **5**. Furthermore, **5** was treated with sodium hydride in THF at room temperature to afford **1**. The overall yields of **1a, 1b, 1c, 1d**, and **1e** were 96%, 87%, 90%, 90%, and 85%, respectively. It should be noted that the obtained **1** has the *E* geometry at the central double bond. Since the allylic carbanion of **5** is stabilized by the adjacent sulfonyl group, the E1cb mechanism is likely for the transformation of **5** into **1** to produce (1*E*,3*E*)-**1** by the repulsive interaction between the *p*-tolylsulfonyl group and the aryl (Y-C_6H_4) group.

First, we examined the thermal reaction of **1a** (Y = H). When a solution of **1a** in acetonitrile was refluxed for 4 days, no reaction occurred, and **1a** remained unchanged. However, the addition of I_2 (0.5 mol equiv.) was found to initiate the reaction to form the expected **3a** in refluxing acetonitrile and, after 2 days, we obtained **3a** in 89% yield (run 2 in Table 1). The structure of **3a** was confirmed by its spectral data and elemental analysis. On irradiation with a high-pressure Hg lamp under a N_2 atmosphere, the electrocyclization of **1a** took place in acetonitrile. It was followed by elimination of the methanethiol moiety to give **3a** in 89% yield (run 3). Thus, the transformation of **1a** into **3a** can be attained either by an I_2-assisted thermal reaction or by photolysis.



[**a** Y=H, **b** Y=*p*-F, **c** Y=*p*-CO_2Me, **d** Y=*p*-MeO, **e** Y=*m*-MeO]

SCHEME 1

In these reactions, a significant effect of the substituent on the phenyl ring was observed, as summarized in Table 1. Introduction of an electron-withdrawing group on the phenyl ring of **1** retarded the thermal reaction of **1** with I_2: **1b** (Y = *p*-F) and **1c** (Y = *p*-CO_2Me) did not react efficiently (runs 4 and 7 of Table 1). In contrast, a *p*-methoxyl substituent did not retard the reaction to transform **1d** into the corresponding **3d** (Run 10). It is noteworthy that **1e** (Y = *m*-MeO) reacted more smoothly than **1d** (Y = *p*-MeO). The reaction of **1e** finished within 3 hours in refluxing acetonitrile to produce two regioisomers (**3e** and **3e′**) in a ratio of 67:33. This tendency is identical to that observed in the usual electrophilic aromatic substitution of anisole, in which the methoxyl group acts as an ortho, para-directing and activating substituent. Thus, it was suggested that this reaction might involve an electrophilic (of the Friedel-Crafts type) reaction on the phenyl ring [7].

The reaction of **1a** and iodine in CD_3CN at 95°C was examined by ^{1}H NMR (300 MHz) spectroscopy, showing that the reaction has an induction period in the formation of **3a**, as depicted in Figure 1. At the initial stage of the reaction, a small amount of the (1*E*, 3*Z*)-geometric isomer of **1a** appeared. After 8

TABLE 1 Transformation of **1** into **3**

Run		*Method*[a]	*I_2 (equiv.)*	*Time*	*Yield (%)*
1	**1a**	A	—	4 days	No reaction
2		A	0.5	2 days	89
3		B	—	24 hours	89
4	**1b**	A	0.5	3 days	7
5		B	—	41 hours	Trace
6		B	0.5	41 hours	93
7	**1c**	A	0.5	2 days	0[b]
8		B	—	10 hours	33 (45)[b]
9		B	1.0	10 hours	98
10	**1d**	A	0.5	3 days	86
11		B	—	45 hours	8 (19)[c]
12		B	1.0	45 hours	44 (96)[c]

[a]Method A: Refluxing a solution of **1** in acetonitrile. Method B: Irradiation of **1** in acetonitrile with a 100 W high-pressure Hg lamp.
[b]The starting material (**1a**) was recovered in 99% yield.
[c]The value in parenthesis is the yield based on the unrecovered **1**.

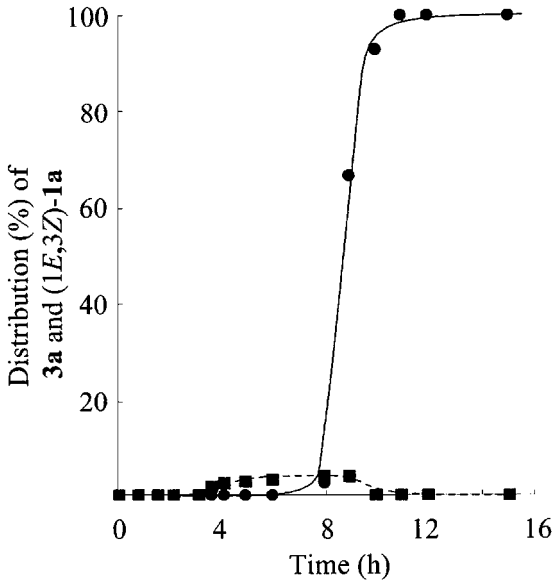
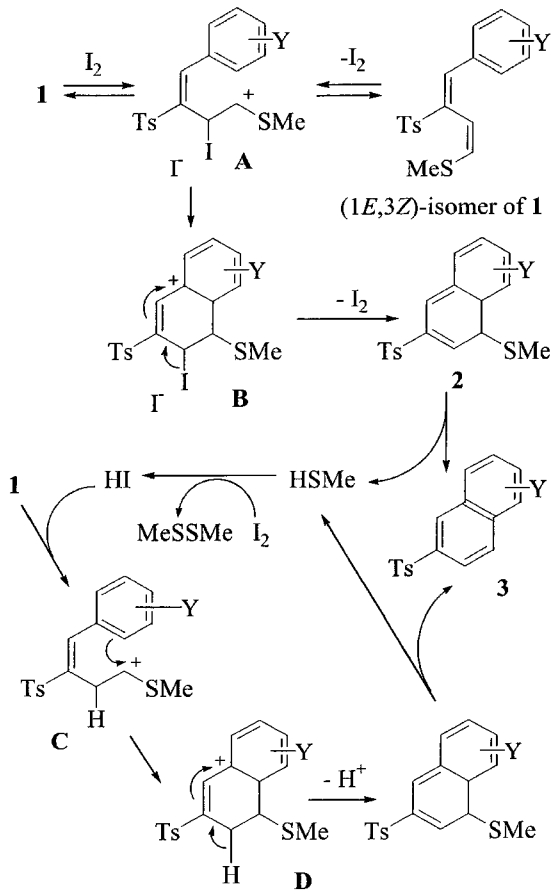


FIGURE 1 The time dependence of the distributions of **3a** (solid line) and (1*E*, 3*Z*)-**1a** (dashed line) in the I_2-assisted thermal reaction of **1a** in CD_3CN at 95°C (bath temperature).

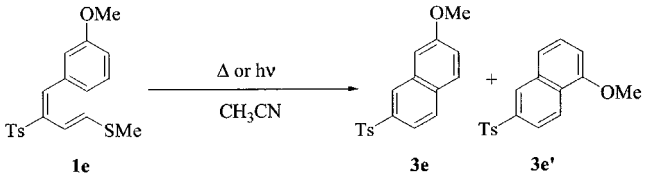


SCHEME 3

hours, the formation of **3a** occurred and then there was a sharp increase in the amount of **3a**.

It is noteworthy that the I_2-assisted reaction was almost inhibited by the addition of aqueous $NaHCO_3$ [8]. This indicates that any acidic component plays an important role in the initiation of the present reaction. In fact, *p*-toluenesulfonic acid was effective for the present reaction of **1e** to give **3e** and **3e′** quantitatively in a ratio of 67:33, though a longer reaction time was necessitated (3 days). From these results, it is supposed that, during the induction period, an acidic substance is produced in the reaction of **1** with I_2. Hence, one possible mechanism, depicted in Scheme 3, can be proposed for the I_2-assisted formation of **3** from **1**: (1) The iodine attacks the Δ^3 double bond of **1** to form a cationic intermediate (**A**), which is stabilized by the adjacent methylthio group. It is likely that olefinic isomerization proceeds via this intermediate. (2) The intermediate **A** undergoes an intramolecular cyclization to form an intermediate (**B**), though the rate is very slow. (3) The subsequent removal of iodine forms a cyclized product (**2**), which is easily aromatized to give **3** along with methanethiol. (4) The methanethiol is easily oxidized with coexisting I_2 to form dimethyl disulfide and HI. (5) The thus-obtained HI (or its complex with I_2) acts as an acid to catalyze the transformation of **1** into **3**. In this process, the methanethiol is generated and, as a result, HI is formed again to amplify the reaction rate.

In order to investigate the substituent effect on the photochemical electrocyclization, we irradiated various 1-aryl-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadienes **1** having *p*-F, *p*-CO_2Me, *p*-MeO, and *m*-MeO on the phenyl ring. The para-substituent of the phenyl ring (runs 5 and 8) made the yield of the corresponding **3** lower. When a methoxyl group was substituted at the meta-position of the phenyl ring, the reaction took place to form one isomer (**3e′**) predominantly between two possible products (**3e:3e′** = 7:93). This seems to reflect the conservation of orbital symmetry (the Woodward-Hoffmann rule) [9]. Again, I_2 accelerates the reaction to form the corresponding **3** in good yields (runs 6, 9, and 12). In the photochemical reaction of **1e** in the presence of I_2 (2.0 mol equiv. or 0.1 mol equiv.), the product distribution changed to **3e:3e′** = 50:50 or 55:45, respectively (Scheme 2). Since even a small amount of iodine was effective, this effect does not seem to be attributable to the oxidative property of iodine. The UV spectrum of **1e** was not changed by the addition of iodine, but its photoluminescence (PL) spectrum (Figure 2) exhibited a dramatic effect: the addition of I_2 (1 mol equiv.) quenched the strong PL peak at



Reflux with I_2 (0.5 mol-equiv), 3 h	98% (67:33)
hν without I_2, 10 h	100% (7:93)
hν with I_2 (2.0 mol-equiv), 10 h	72% (50:50)
hν with I_2(0.1 mol-equiv), 10 h	95% (55:45)

SCHEME 2

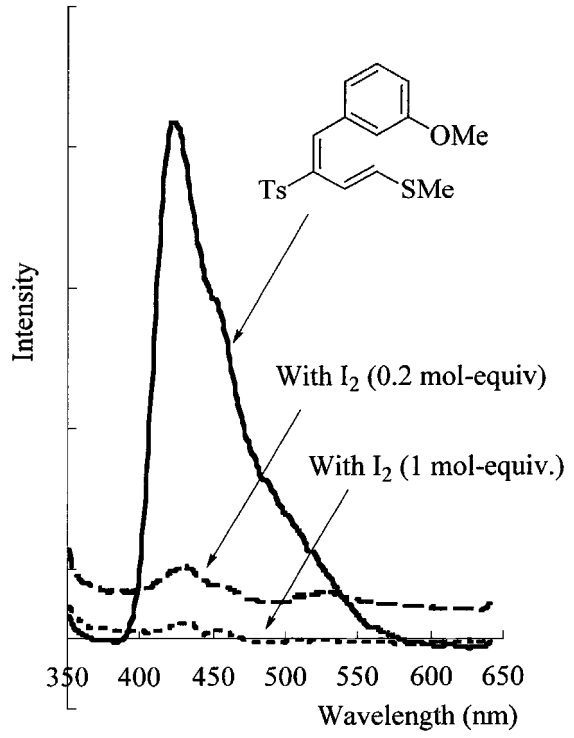


FIGURE 2 PL spectrum of **1e** (10^{-2} M in CH_3CN) in the absence and presence of I_2 (excitation at 332 nm).

420 nm. Even in the presence of 0.2 mol equiv. of I_2, the PL peak diminished drastically. Although we do not have sufficient evidence at the present time, it is presumed that the heavy atom effect [10] of iodine works so as to accelerate the intersystem crossing to a triplet excited state that brings about rate enhancement in the cyclization of **1** and poor regioselectivity in the formation of **3e** and **3e′**.

In conclusion, 1-aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (**1**) underwent the cyclization, followed by the removal of the methanethiol moiety, to give the naphthalene derivatives (**3**), which was achieved either by the I_2-assisted thermal reaction or by photolysis. The iodine was shown to promote the photochemical reaction. The present procedures provide a synthetic route leading to the naphthalenes with an electron-withdrawing sulfonyl group, which can be utilized in the development of useful functional materials with a π-electron system.

EXPERIMENTAL

General

Melting points were determined with a Yanaco MP-J3 instrument, and values were uncorrected. ^{1}H NMR measurements were performed on JEOL JNM-GSX 270 (270 MHz) or Varian GEMINI 300 (300 MHz) spectrometers. Chemical shifts (δ) of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). Multiplicities are indicated as br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and coupling constants (J) are reported in Hz. IR spectra were recorded on JASCO A-202 or JASCO FT/IR-350 spectrometers. Elemental analyses (EA) were carried out in the Analytical Chemical Center of Chiba University using a Perkin-Elmer 240B or 2400CHN instrument. Fluorescence spectra were recorded with JASCO FP-750 spectrophotometer. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. Acetonitrile (CH_3CN) was freshly distilled over CaH_2.

*Preparation of (1E,3E)-1-(m-Methoxyphenyl)-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadiene (**1e**): A Typical Procedure*

To a solution of (*E*)-1-(methylthio)-3-(*p*-tolylsulfonyl)-1-propene (469 mg, 1.9 mmol) in THF (15 mL) was added n-butyllithium (1.63 M in hexane, 1.31 mL, 2.1 mmol) and 3-methoxybenzaldehyde (0.283 mL, 2.3 mmol) at −78°C, and the resulting mixture was stirred at the same temperature for 30 minutes under an atmosphere of N_2. Then, acetic anhydride (0.220 mL, 2.3 mmol) was added at the same temperature, and the resulting mixture was stirred for 30 minutes. The usual workup (quenching with aqueous NH_4Cl, extraction with diethyl ether, and evaporation) gave yellow crystals (891 mg), which were subjected to column chromatography on SiO_2 (hexane:ethyl acetate = 2:1) to give yellow crystals (742 mg). To a solution of the crystals (684 mg) in THF (20 mL) was added NaH (60% content, 153 mg, 3.8 mmol) at 0°C, and the resulting mixture was stirred at room temperature for 5 days under an atmosphere of N_2. Quenching with H_2O (20 mL), extraction with diethyl ether, and column chromatography on SiO_2 (hexane:ethyl acetate = 2:1) gave **1e** (500 mg, 1.4 mmol, 85%) as light yellow crystals:

m.p. 106.0–107.0°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 2.42 (s, 3H), 3.81 (s, 3H), 5.95 (d, 1H, J = 15.6 Hz), 6.91 (ddd, 1H, J = 0.9, 2.7, 8.1 Hz), 7.05 (m, 1H), 7.09 (diffused d, 1H, J = 7.5 Hz), 7.13 (d, 1H, J = 15.6 Hz), 7.30 (t, 1H, J = 7.8 Hz), 7.31 (d(br), 2H, J = 8.3 Hz), 7.66 (s, 1H), 7.76 (diffused d, 2H, J = 8.3 Hz); IR (KBr) 3044, 2958, 2345, 1654, 1596, 1297, 1174, 1085, 950, 934, 903, 881, 811, 778, 617 cm^{-1}; Anal. calcd for $C_{19}H_{20}O_3S_2$: C, 63.30; H, 5.59; Found: C, 63.32; H, 5.53.

*(1E,3E)-4-(Methylthio)-1-phenyl-2-(p-tolylsulfonyl)-1,3-butadiene (***1a***)*

Similarly, this compound was prepared in 96% yield (two steps): colorless crystals; m.p. 111.0–112.0°C;^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.23 (s, 3H), 2.42 (s, 3H), 5.94 (d, 1H, J = 15.6 Hz), 7.14 (d, 1H, J = 15.6 Hz), 7.31 (d(br), 2H, J = 7.8 Hz), 7.34–7.42 (m, 3H), 7.50 (dd, 2H, J = 2.0, 7.8 Hz), 7.70 (s, 1H), 7.76 (diffused d, 2H, J = 8.4 Hz); IR (KBr) 1596, 1556, 1309, 1298, 1146, 1102, 1074, 929, 850, 819, 768, 740, 697, 666, 607 cm^{-1}; Anal. calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49; Found: C, 65.24; H, 5.68.

*(1E,3E)-1-(p-Fluorophenyl)-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadiene (***1b***)*

The overall yield was 87%: colorless crystals; m.p. 112.5–113.0°C;^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 2.43 (s, 3H), 5.86 (d, 1H, J = 15.6 Hz), 7.08 (tm, 2H, J = 8.5 Hz), 7.12 (d, 1H, J = 15.6 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.51 (diffused dd, 2H, J = 9 Hz, $J_{H\text{-}C2\text{-}F}$ = 5.4 Hz), 7.65 (s, 1H), 7.75 (d, 2H, J = 8.1 Hz); IR (KBr) 1599, 1504, 1299, 1218, 1149, 1092, 930, 845, 824, 810, 743, 660, 594 cm^{-1}; Anal. calcd for $C_{18}H_{17}FO_2S_2$: C, 62.04; H, 4.92; Found: C, 62.00; H, 4.67.

*(1E,3E)-1-(p-Methoxycarbonylphenyl)-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadiene (***1c***)*

The overall yield was 90%: light yellow crystals; m.p. 132.5–133.0°C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.23 (s, 3H), 2.43 (s, 3H), 3.93 (s, 3H), 5.90 (d, 1H, J = 15.5 Hz), 7.17 (d, 1H, J = 15.5 Hz), 7.32 (d(br), 2H, J = 7.9 Hz), 7.54 (d, 2H, J = 8.6 Hz), 7.67 (s, 1H), 7.75 (diffused d, 2H, J = 8.6 Hz), 8.04 (d, 2H, J = 8.6 Hz); IR (KBr) 1710, 1310, 1280, 1140, 1100, 740, 670, 580 cm^{-1}; Anal. calcd for $C_{20}H_{20}O_4S_2$: C, 61.83; H, 5.19; Found: C, 61.66; H, 5.05.

*(1E,3E)-1-(p-Methoxyphenyl)-4-(methylthio)-2-(p-tolylsulfonyl)-1,3-butadiene (***1d***)*

Compound **1d** was prepared in 90% yield (two steps): colorless crystals; m.p. 87.0–88.0°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.42 (s, 3H), 3.83 (s, 3H), 5.91 (d, 1H, J = 15.7 Hz), 6.91 (dm, 2H, J = 8.8 Hz), 7.08 (d, 1H, J = 15.7 Hz), 7.30 (d, 2H, J = 8.5 Hz), 7.49 (dm, 2H, J = 8.8 Hz), 7.65 (s, 1H), 7.75 (diffused d, 2H, J = 8.5 Hz); IR (KBr) 1594, 1573, 1508, 1468, 1300, 1261, 1177, 1147, 1101, 1074, 1019, 932, 846, 825, 742, 661, 594 cm^{-1}; Anal. calcd for $C_{19}H_{20}O_3S_2$: C, 63.30; H, 5.59; Found: C, 63.27; H, 5.79.

I_2-Assisted Reaction of **1a***: A Typical Procedure*

To a solution of (1*E*,3*E*)-**1a** (49.2 mg, 0.15 mmol) in dry CH_3CN (15 mL) was added iodine (17.3 mg, 0.07 mmol), and the resulting mixture was refluxed for 2 days. Then, the reaction mixture was poured into aqueous $Na_2S_2O_3$ solution and extracted with ethyl acetate (20 mL × 3). The extracts were combined, dried with $MgSO_4$, evaporated, and subjected to column chromatography on SiO_2 (hexane:ethyl acetate = 4:1) to give 2-(*p*-tolylsulfonyl)naphthalene **3a** (37.6 mg: 89% yield) as white powder: m.p. 158.5–159.5°C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.39 (s, 3H), 7.29 (d, 2H, J = 8.6 Hz), 7.56–7.66 (m, 2H), 7.83 (dd, 1H, J = 1.6, 8.6 Hz), 7.88 (d, 2H, J = 8.6 Hz), 7.88 (d, 1H, J = 8.6 Hz), 7.87–7.99 (m, 2H), 8.58 (d, 1H, J = 1.7 Hz); IR (KBr) 3061, 2958, 1595, 1347, 1318, 1152, 1094, 1065, 909, 815, 750 cm^{-1}; Anal. calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; Found: C, 72.02; H, 5.18.

*2-Fluoro-6-(p-tolylsulfonyl)naphthalene (***3b***)*

Colorless crystals; m.p. 137.5–138.5°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 7.30 (dm, 2H, J = 8.4 Hz), 7.37 (ddd, 1H, J = 2, 7, 8.8 Hz, $J_{H\text{-}C2\text{-}F}$ = 8.8 Hz), 7.47 (dd, 1H, J = 2.7 Hz, $J_{H\text{-}C2\text{-}F}$ = 9.6 Hz), 7.86 (br, 2H), 7.89 (diffused d, 2H, J = 8.4 Hz), 7.97 (dd, 1H, J = 8.8 Hz, $J_{H\text{-}C3\text{-}F}$ = 5.4 Hz), 8.55 (s, 1H); IR (KBr) 1626, 1595, 1506, 1401, 1319, 1305, 1256, 1153, 1121, 1095, 886, 815, 745, 679, 652, 588 cm^{-1}; Anal. calcd for $C_{17}H_{13}FO_2S$: C, 67.98; H, 4.36; Found: C, 67.79; H, 4.53.

2-Methoxycarbonyl-6-(p-tolylsulfonyl)-naphthalene (3c)

White powder; m.p. 180.1–180.6°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 3.99 (s, 3H), 7.32 (d, 2H, J = 8.2 Hz), 7.90 (d, 2H, J = 8.2 Hz), 7.94 (d, 1H, J = 8.5 Hz), 8.02 (d, 1H, J = 8.4 Hz), 8.03 (d, 1H, J = 8.5 Hz), 8.17 (dd, 1H, J = 1.6, 8.4 Hz), 8.59 (s(br), 1H), 8.61 (s, 1H); IR (KBr) 1724, 1433, 1315, 1287, 1232, 1184, 1160, 1135, 1097, 750, 710, 693, 658, 576 cm^{-1}; Anal. calcd for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; Found: C, 66.59; H, 4.69.

*2-Methoxy-6-(p-tolylsulfonyl)naphthalene (***3d***)*

Yellow crystals; m.p. 146.0–147.5°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H), 3.93 (s, 3H), 7.12 (d, 1H, J = 1.3 Hz), 7.24 (dd, 1H, J = 1.3, 7.6 Hz), 7.28 (d, 2H, J = 8.2 Hz), 7.79 (d, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 6.6 Hz), 7.85 (d, 1H, J = 6.6 Hz), 7.86 (diffused d, 2H, J = 8.5 Hz), 8.46 (s, 1H); IR (KBr) 1620, 1300, 1260, 1140, 1090, 1020, 810, 740, 680, 580, 520 cm^{-1}; Anal. calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; Found: C, 69.48; H, 5.09.

*2-Methoxy-7-(p-tolylsulfonyl)naphthalene (***3e***)*

Colorless crystals; m.p. 139.5–140.0°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H), 3.93 (s, 3H), 7.24 (d, 1H, J = 2.4 Hz), 7.27 (d, 1H, J = 8.7 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.70 (dd, 1H, J = 1.8, 8.7 Hz), 7.75 (d, 1H, J = 8.7 Hz), 7.83 (dm, 1H, J = 8.7 Hz), 7.88 (dm, 2H, J = 8.4 Hz), 8.44 (d, 1H, J = 1.8 Hz); IR (KBr) 1627, 1597, 1508, 1464, 1442, 1390, 1308, 1256, 1222, 1177, 1153, 1092, 1028, 847, 813, 706, 674, 635, 553, 529 cm^{-1}; Anal. calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; Found: C, 69.06; H, 5.08.

*1-Methoxy-6-(p-tolylsulfonyl)naphthalene (***3e′***)*

Colorless crystals; m.p. 161.8–162.4°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 3.99 (s, 3H), 6.94 (dd, 1H, J = 1.8, 6.9 Hz), 7.28 (dm, 2H, J = 8.2 Hz), 7.49 (t, 1H, J = 8.7 Hz), 7.53 (dd, 1H, J = 1.8, 8.7 Hz), 7.82 (dd, 1H, J = 1.8, 8.9 Hz), 7.87 (diffused d, 2H, J = 8.2 Hz), 8.33 (d, 1H, J = 8.9 Hz), 8.49 (d, 1H, J = 1.8 Hz); IR (KBr) 2937, 1579, 1503, 1467, 1426, 1389, 1364, 1309, 1290, 1268, 1240, 1146, 1112, 1092, 815, 783, 754, 708, 681, 648, 591 cm^{-1}; Anal. calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; Found: C, 69.21; H, 5.11.

The Follow-Up Experiment Monitored by ^{1}H NMR Spectroscopy for the I_2-Assisted Reaction of **1a**

A solution of **1a** (5.0 mg, 0.015 mmol) in CD_3CN (0.5 mL), which was dried on MS 4Å, was placed in an NMR tube. After a 0.2 M solution of iodine in CD_3CN (38 μL, 0.0076 mmol) had been added and N_2 gas had been bubbled through the solution for 5 minutes, the NMR tube was sealed. After being heated at 95°C (bath temperature), the reaction mixture was cooled to room temperature and its ^{1}H NMR spectrum (300 MHz) was measured. This procedure was repeated. The NMR spectrum was measured when the mixture was heated for 45, 90, and 130 minutes and 3, 4, 5, 6, 8, 9, 10, 11, 12, 15, 21, and 32 hours. The ratio was determined by the integration of the corresponding peaks [**1a**: 5.96 ppm (d, 1H, J = 15.6 Hz), (1*E*,3*Z*)-**1a**: 6.39 ppm (d, 1H, J = 8.5 Hz), **3a**: 8.59 ppm (d, 1H, J = 1.8 Hz)].

Photochemical Reaction of **1e***: A Typical Procedure*

A solution of **1e** (36.1 mg, 0.10 mmol) in dry CH_3CN (10 mL) was bubbled with N_2 for 20 minutes and was irradiated for 10 hours with a 100-W high-pressure mercury lamp (Shigemi AHH-100S) through a Pyrex filter under a N_2 atmosphere. The reaction mixture was evaporated and subjected to column chromatography on SiO_2 (hexane: ethyl acetate = 4:1) to give a 7:93 mixture of **3e** and **3e′** (31.3 mg: 100%).

Photochemical Reaction of **1e** *in the Presence of Iodine: A Typical Procedure*

(1*E*,3*E*)-1-(*m*-Methoxyphenyl)-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadiene (**1e**, 53.5 mg, 0.15 mmol) and iodine (75.8 mg, 0.30 mmol) in dry CH_3CN (15 mL) was bubbled by N_2 for 20 minutes, and then irradiated for 10 hours. The workup mentioned in the I_2-assisted thermal reaction of **1a** gave a 50:50 mixture of **3e** and **3e′** (33.1 mg: 72% yield).

REFERENCES

[1] (a) Olah, G., Ed. Friedel-Crafts and Related Reactions; Wiley-Interscience; New York, 1964; (b)] Miller, J. Aromatic Nucleophilic Substitution; Elsvier: Amsterdam, 1968; (c) Bunnett, J. F. Acc Chem Res 1978, 11, 413–420; (d) Rossi, R. H.; de Rossi, R. H. Aromatic Substitution by the $S_{RN}1$ Mechanism; American Chemical Society: Washington, D. C., 1983.

[2] (a) Knight, D. W. Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon:: Oxford, 1991; Vol. 3, pp 481–520; (b) Sonogashira, K. Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon:: Oxford, 1991; Vol. 3, pp 521–549; (c) Bachmann, W. E.; Hoffman, R. A. Org React 1944, 2, 224–261; (d) Sainsbury, M. Tetrahedron, 1980, 36, 3327–3359; (e) Ames, D. E.; Opalko, A. Tetrahedron 1984, 40, 1919–1925; (f) Miyaura, N.; Suzuki, A. Chem Rev 1995, 95, 2457–2483.

[3] (a) Schore, N. E. Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp. 1129–1162; (b) Negishi, E.; Ay, M.; Sugihara, T. Tetrahedron 1993, 49, 5471–5482; (c) Lautens, M.; Klute, W.; Tam, W. Chem Rev 1996, 96, 49–92.

[4] Okamura, W.; De Lera, A. R. Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Ed.; Pergamon: Oxford, 1991; Vol. 5, pp 699–750.

[5] (a) Mallory, F. B.; Mallory, C. W. Org React 1984, 30, 1–456; (b) Liu, L.; Yang, B.; Katz, T. J.; Poindextev, M. K. J Org Chem 1991, 56, 3769–3775.

[6] Ogura, K.; Iihama, T.; Takahashi, K.; Iida, H. Bull Chem Soc Jpn 1984, 57, 3347–3348.

[7] (a) Harding, K. E.; Tiner, T. H. Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 363–421; (b) Dowle, M. D.; Davis, D. I. Chem Soc Rev 1979, 8, 171–197; (c) Cardillo, G.; Orena, M. Tetrahedron 1990, 46, 3321–3408.

[8] (a) Woodward, R. B.; Hoffmann, R. J Am Chem Soc 1965, 87, 395–397; Angew Chem Int Engl 1969, 8, 781–853; (b) Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry; Verlag Chemie GmbH/Academic Press: Weinheim, 1970.

[9] (a) Rychnovsky, S. D.; Bartlett, P. A. J Am Chem Soc 1981, 103, 3963–3964; (b) Mahn, K.; Ryu, E. K. Tetrahedron Lett 1990, 37, 1441–1444.

[10] (a) Cowan, D. O.; Koziar, J. C. J Am Chem Soc 1975, 97, 249–254; (b) Samanta, A.; Fessenden, R. W. J Phys Chem 1989, 93, 5823–5827.