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Novel Solvent-Free Reactions with Iodine: Solid–Solid and Solid–Vapor Reactions of 1-Aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes

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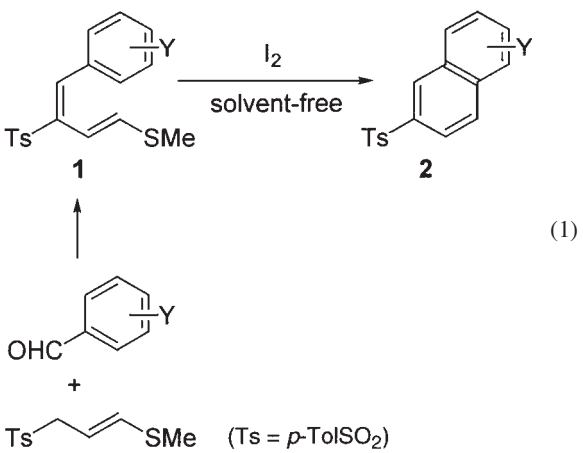
Under "solvent-free" solid–solid and solid–vapor conditions, 1-aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (**1**) react with iodine to form (*p*-tolylsulfonyl)naphthalene derivatives (**2**) in high yield. These conditions make the reaction tolerant to the kind of the aryl so that various derivatives of **2** were produced in high yield. The products (**2**) can be obtained in a nearly pure form by removing co-existing hydrogen iodide and dimethyl disulfide by evaporation. Thus, this process is environmentally benign, because no solvent and water need to get the pure product.

To date, "solvent-free" reaction conditions have been attracting much attention in the field of organic synthesis.[1–3] This is mainly because they are not only environmentally benign, but also can accelerate the reaction. Indeed, several reactions were reported to proceed more smoothly under "solvent-free" conditions than those in a solution. According to the reaction conditions employed therein, the "solvent-free" reactions are classified into three types: (i) simple mixing of a solid-substrate with a solid-reagent [Type Ⅰ];[4] (ii) exposure of a solid reactant to a vapor reagent [Type Ⅱ];[4c,4f,5] and (iii) irradiation of a solid reactant with ultraviolet light [Type Ⅲ].[6] Since iodine can be handled as a solid at room temperature, but sublimates easily, it seems to be a suitable reagent for Type Ⅰ and Type Ⅱ processes. Here, we wish to report the solvent-free iodine-mediated reaction of 1-aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (**1**) that, without any solvent, proceeds much more smoothly than in a solution.

Recently, we reported the reaction of **1** with iodine in acetonitrile that occurs at an elevated temperature (in refluxing acetonitrile) to form (*p*-tolylsulfonyl)naphthalene derivatives (**2**).[7]



(1)

These conditions cannot be applied to the reaction of the compound (**1**) having an electron-withdrawing substituent on the aryl ring. Hence, we had searched for conditions that would foster the reaction of **1** (the aryl = the phenyl having an electron-withdrawing group). After much effort, it was found that, when crystalline **1** comes into contact with solid or vaporous iodine, a reaction occurs even at room temperature and, to our surprise, the reaction tolerates the substituents on the aryl group, that is, the compounds having an electron-withdrawing or electron-donating group afford the expected products (**2**). It is worthy noting that the product can be obtained in a nearly pure form by evaporation of the reaction mixture to remove volatile by-products such as dimethyl disulfide and hydrogen iodide.

Results and Discussion

The starting materials (**1**) were prepared from (*E*)-1-(methylthio)-3-(*p*-tolylsulfonyl)propene[8] with benzaldehyde derivatives according to the method described previously.[7] In order to investigate whether the sublimation ability of iodine can be utilized for the reaction of solid **1**, the following procedures were examined: (i) Crystalline **1** was mechanically mixed with solid iodine ["mixing" method]; (ii) crystalline **1** and solid iodine were separately placed in the same vessel. The internal pressure of the vessel was maintained at atmospheric pressure ["vapor" method]; and (iii) after the vessel containing crystalline **1** and solid iodine was evacuated in vacuo for a few minutes, the evacuation was then stopped to increase the partial pressure of iodine ["reduced vapor" method] (Scheme 1). The results employing **1** (Y = H) as a reactant are summarized in Table 1.

As reported previously, the reaction in acetonitrile did not occur at room temperature even after 4 d (entry 9). To our surprise, the reaction under the "solvent-free" conditions ("mixing" method) occurred smoothly even at room temperature. The reaction using 1.0 mol-equiv. of iodine completed within 1 d to form the corresponding **2** (Y = H) in 97% yield (entry 2). As shown in entry 1 of Table 1, the reaction did not occur even after 3.5 h, suggesting that this reaction has an induction period. This is in accordance with the mechanism reported for the corresponding reaction in a solution, in which hydrogen (poly)iodide derived from iodine works as an actual reactive species.[7]

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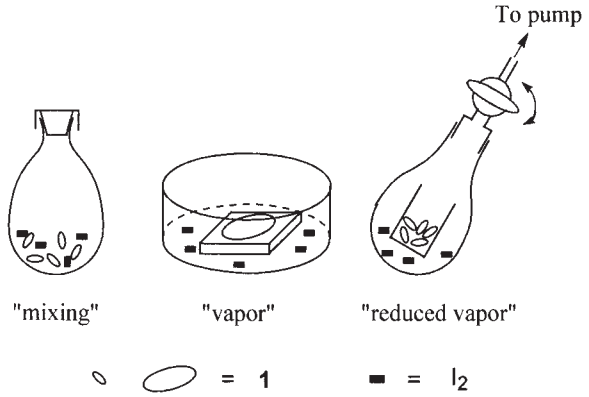


Scheme 1. Schematic description of the experimental procedure for the "solvent-free" reactions.

Table 1. "Solvent-Free" Reaction of **1** (Y = H) with Iodine

Entry	Method	Mol-equiv. of I_2	Time	Yield of **2**/%
1	"mixing"	1.0	3.5 h	n. r.[a]
2			15 h	97
3		0.5	21 h	96
4		0.1	14 d	11[b]
5	"vapor"	0.5	5 d	94
6		excess	45 h	98
7	"reduced vapor"	1.0	3.5 h	95
8	CH_3CN/reflux	0.5	2 d	89
9	CH_3CN/rt		4 d	n. r.[a]

a) n. r. = no reaction. b) Starting material was recovered in 89% yield.

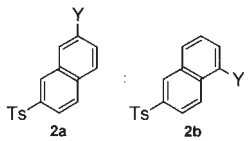
The amount of iodine could be reduced to 0.5 mol-equiv., though the reaction required somewhat longer reaction time. The "vapor" method also worked effectively. As shown in Table 1 (entry 5), the reaction in the presence of 0.5 mol-equiv. of iodine proceeded at room temperature to finish within 5 d. An excess amount of iodine accelerated the reaction to complete within a short period of time (entry 6). When the internal pressure of the reaction vessel was reduced (the "reduced vapor" method), **2** (Y = H) was quickly formed (entry 7). It is noteworthy that the mixture color turned from reddish-brown to black in every method. Hence, the reaction progress could be visually followed.

Next, the "solvent-free" reaction with iodine was applied to the transformation of various derivatives of **1** into the corresponding **2**. Among the three methods, the "mixing" one is recommendable because its procedure is convenient. In Table 2, the results are summarized. All of the compounds (**1**) examined here gave **2** in high to excellent yields. Interestingly, the "solvent-free" reaction was effectively applicable to the compound (**1**) having an electron-withdrawing group such as –COOMe or –F, which, in refluxing acetonitrile, was shown either to remain unchanged or to give the corresponding **2** in a low yield (entries 2 vs 3 and 6 vs 8).[7] A higher temperature promoted the reaction to complete in a shorter period of time (entries 5 and 7).

Table 2. "Solvent-Free" Reaction of Various Substituted Compounds **1** with Iodine[a]

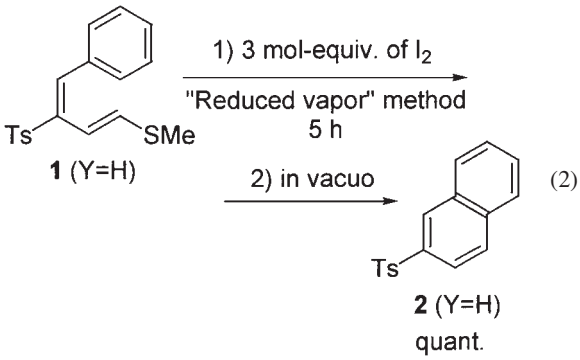
Entry	Y	Time	Yield of **2**/%
1	*p*-OMe	5 d	99
2	*p*-F	9 d	90
3[b]		3 d	7
4	*p*-Br	8 d	80
5[c]		14 h	84
6	*p*-COOMe	8 d	78
7[c]		14 h	73
8[b]		2 d	n. r.[d]
9	*m*-OMe	4 d	96 (67:33)[e]
10	*m*-Cl	27 h	82 (74:26)[e]
11	*m*-Br	4 d	86 (65:35)[e]

a) "Mixing" method was used. Amount of I_2 was 1.0 mol-equiv. b) Reacted in refluxing acetonitrile. c) Reacted at 80 °C. d) n. r. = no reaction. e) Value in parenthesis shows the ratio of **2a**:**2b**.



In the case of a *meta*-substituted **1**, two regioisomers of **2** would be formed. Indeed, **1** (Y = *m*-OMe, *m*-Cl, and *m*-Br) gave the regioisomers **2a** and **2b** (entries 9–11). The ratios are in the range of from 2:1 to 3:1; such ratios are nearly the same as those of the reaction in solution (the product ratios of **2a**:**2b** are 67:33 (Y = *m*-OMe), 67:33 (Y = *m*-Cl), and 59:41 (Y = *m*-Br) in the reaction in a refluxing acetonitrile). As mentioned in the preceding paper,[7] the reaction is initiated by the action of iodine to the vinyl sulfide moiety of **1** that forms **2** and methanethiol.[9] The formed methanethiol is converted to dimethyl disulfide by oxidation with iodine that leads to hydrogen iodide. The formed products such as dimethyl disulfide and hydrogen iodide destroy the crystal structure of **1**. In fact, the powder X-ray diffraction pattern of the crystals gradually collapsed as the reaction proceeded. This seems to be the reason why the product ratios are nearly the same irrespective of the reaction conditions, the "solvent-free" reaction or the reaction in a solution.

It should be noted that the present procedure is fully benign to the environment. This is because the co-existing compounds can be removed simply by evaporation and the remaining product is actually pure. **1** (Y = H) was treated with 3 mol-equiv. of iodine in the "reduced vapor" method. After that, the vessel containing the mixture was evaporated in vacuo to remove the unreacted iodine, the formed hydrogen iodide, and dimethyl disulfide. The product (**2**; Y = H) was shown by ^{1}H NMR to be entirely pure. This was also confirmed by elemental analysis: the found data (C, 71.57; H, 4.99%) were within the tolerance level close enough to the calculated values (Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00%). Thus, no organic solvent or water is needed to obtain the pure product according to this procedure.



(2)

In summary, the reaction of 1-aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (**1**) with iodine leading to the naphthalene derivatives (**2**) occurred at room temperature under the "solvent-free" conditions, namely either by simple mixing of crystalline **1** and solid iodine or by exposure of iodine vapor to crystalline **1**. The reaction under these conditions has several advantages over that in a solution: (i) It does not need any solvent; (ii) the reaction rate becomes faster; (iii) it is tolerant of the substituent of **1** so that the derivatives of **1** having an electron-donating and electron-withdrawing substituent gives the corresponding **2** in high yields. These findings promise that the reaction with iodine will open new forms of synthetic chemistry that are environmentally benign.[10]

Experimental

General. Melting points were determined with Yanaco MP-J3 and are uncorrected. ^{1}H NMR measurements were performed on a Varian GEMINI 300 (300 MHz) spectrometer. Chemical shifts (δ) of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). Multiplicities were indicated as br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and coupling constants (J) are reported (Hz). Infrared (IR) spectra were recorded on a JASCO FT/IR-350 spectrometer. Elemental analyses (EA) were carried out by the Chemical Analysis Center of Chiba University. Analytical thin-layer chromatography (TLC) was performed on a glass plate pre-coated with silica gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). The silica gel for chromatography was Merck Silica Gel 60 (70–230 mesh). All chemicals were obtained from commercial suppliers (Aldrich Chemical Co., Tokyo Kasei Chemical Industry Co., Wako Pure Chemical Co., Kanto Chemical Co., and Nacalai Tesque Inc.) and were used without further purification.

Physical Data for New 1-Aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (1). 1-Aryl-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadienes (**1**) were prepared according to the procedure reported previously.[7]

1-(*p*-Bromophenyl)-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadiene (1; Y = *p*-Br): 81% yield; pale yellow plate crystals; mp 120.3–121.1 °C (hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.43 (s, 3H), 5.86 (dd, 1H, J = 1.0, 16.0 Hz), 7.14 (d, 1H, J = 16.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.37 (d, 2H, J = 8.5 Hz), 7.52 (d, 2H, J = 8.7 Hz), 7.60 (s, 1H), 7.75 (d, 2H, J = 8.2 Hz); IR (KBr) 3037, 3009, 2924, 1577, 1487, 1298, 1142, 1089, 816, 671, 568 cm^{-1}; Anal. Found: C, 52.97; H, 4.36%. Calcd for $C_{18}H_{17}BrO_2S$: C, 52.81; H, 4.19%.

1-(*m*-Chlorophenyl)-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadiene (1; Y = *m*-Cl): 81% yield; pale yellow needle crystals; mp 87.8–88.2 °C (ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.43 (s, 3H), 5.88 (dd, 1H, J = 0.96, 15.7 Hz), 7.18 (d, 1H, J = 15.7 Hz), 7.30–7.39 (m, 5H), 7.44 (d, 1H, J = 0.96 Hz), 7.60 (s, 1H), 7.75 (d, 2H, J = 8.2 Hz); IR (KBr) 3052, 2986, 2902, 1596, 1552, 1419, 1289, 1213, 1105, 944, 900, 848, 708, 569 cm^{-1}; Anal. Found: C, 59.27; H, 4.79%. Calcd for $C_{18}H_{17}ClO_2S$: C, 59.25; H, 4.70%.

1-(*m*-Bromophenyl)-4-(methylthio)-2-(*p*-tolylsulfonyl)-1,3-butadiene (1; Y = *m*-Br): 76% yield; white plate crystals; mp 94.3–95.0 °C (hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.43 (s, 3H), 5.88 (d, 1H, J = 16.0 Hz), 7.18 (d, 1H, J = 16.0 Hz), 7.26 (t, 1H, J = 7.9 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.42 (d, 1H, J = 7.8 Hz), 7.48 (d, 1H, J = 8.0 Hz), 7.59 (s, 1H), 7.65 (s, 1H), 7.75 (d, 2H, J = 8.2 Hz); IR (KBr) 3568, 3053, 2981, 2918, 1934, 1819, 1290, 1151, 1105, 1076, 752, 663 cm^{-1}; Anal. Found: C, 52.71; H, 4.23%. Calcd for $C_{18}H_{17}BrO_2S$: C, 52.81; H, 4.19%.

Procedure for Solvent-Free Reaction. "Mixing" Method: To a 30-mL round-bottom flask capped with a septum were added 0.5 mmol of the substrate (**1**) and the described amount of iodine molecule. The mixture was mechanically mixed for 10 min. After being allowed to stand at room temperature, the mixture was dissolved in ethyl acetate (20 mL) and washed with $Na_2S_2O_3$ aq (20 mL × 2). After the organic layer was dried over $MgSO_4$ and concentrated in vacuo, the residue was purified by recrystallization or silica-gel column chromatography to give the corresponding naphthalene derivative (**2**).

"Vapor" Method: In a Petri dish were placed 0.5 mmol of the substrate (**1**) and the described amount of iodine molecule separately. After being allowed to stand at room temperature, the usual workup was done to afford **2**.

"Reduced Vapor" Method: In a 50-mL round-bottom flask, with a two-way stop-cock, were placed 0.5 mmol of the substrate (**1**) within a vial tube and the described amount of iodine separately. The pressure in this flask was sporadically reduced to ~1.3 kPa. After the mixture was allowed to stand at room temperature, the usual workup was done to give **2**.

The products previously synthesized were found to be identical to authentic samples.[7]

2-Bromo-6-(*p*-tolylsulfonyl)naphthalene (2; Y = Br): Pale yellow powder; mp 176.7–177.9 °C (hexane–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.31 (d, 2H, J = 8.0 Hz), 7.68 (dd, 1H, J = 1.9, 8.8 Hz), 7.82 (d, 1H, J = 8.8 Hz), 7.84 (d, 1H, J = 8.2 Hz), 7.87 (d, 1H, J = 8.9 Hz), 7.88 (d, 2H, J = 8.2 Hz), 8.04 (d, 1H, J = 1.5 Hz), 8.52 (s, 1H); IR (KBr) 3063, 2920, 1619, 1594, 1315, 1153, 1133, 1093, 813, 689, 571 cm^{-1}; Anal. Found: C, 56.53; H, 3.70%. Calcd for $C_{17}H_{13}BrO_2S$: C, 56.52; H, 3.63%.

2-Chloro-7-(*p*-tolylsulfonyl)naphthalene (2a; Y = Cl): Colorless needle crystals; mp 187.2–188.5 °C (hexane–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.31 (d(br), 2H, J = 8.5 Hz), 7.56 (dd, 1H, J = 2.1, 8.7 Hz), 7.81 (d, 1H, J = 9.2 Hz), 7.87 (d, 1H, J = 8.2 Hz), 7.88 (d, 1H, J = 8.2 Hz), 7.90 (diffused d, 2H, J = 8.5 Hz), 7.95 (d, 1H, J = 2.0 Hz), 8.46 (s, 1H); IR (KBr) 3032, 2976, 1654, 1591, 1508, 1492, 1438, 1096, 1077, 905, 817, 709, 619 cm^{-1}; Anal. Found: C, 64.25; H, 4.19%. Calcd for $C_{17}H_{13}ClO_2S$: C, 64.45; H, 4.14%.

1-Chloro-6-(*p*-tolylsulfonyl)naphthalene (2b; Y = Cl): Pale yellow plate crystals; mp 169.8–170.5 °C (hexane–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.31 (d(br), 2H, J = 8.0 Hz), 7.52 (t, 1H, J = 8.0 Hz), 7.71 (dd, 1H, J = 1.0, 7.6 Hz), 7.89 (diffused d, 2H, J = 8.4 Hz), 7.91 (d, 1H, J = 8.2 Hz), 7.95 (dd, 1H, J = 1.9, 9.0 Hz), 8.36 (d, 1H, J = 9.0 Hz), 8.68 (d, 1H, J = 1.9 Hz); IR (KBr) 3060, 2930, 1654, 1594, 1457, 1069, 1019, 972,

878, 826, 817, 750, 631, 619 cm^{-1}; Anal. Found: C, 64.31; H, 4.20%. Calcd for $C_{17}H_{13}ClO_2S$: C, 64.45; H, 4.14%.

2-Bromo-7-(*p*-tolylsulfonyl)naphthalene (2a; Y = Br): Pale brown needle crystals; mp 197.2–198.5 °C (hexane–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.31 (d(br), 2H, $J = 8.5$ Hz), 7.68 (dd, 1H, $J = 1.8$, 8.8 Hz), 7.73 (d, 1H, $J = 8.8$ Hz), 7.85 (dd, 1H, $J = 1.6$, 8.7 Hz), 7.88 (diffused d, 2H, $J = 8.5$ Hz), 7.89 (d, 1H, $J = 8.7$ Hz), 8.12 (d, 1H, $J = 1.6$ Hz), 8.45 (s, 1H); IR (KBr) 3053, 1579, 1315, 1155, 1138, 1095, 845, 708, 683, 648, 552 cm^{-1}; Anal. Found: C, 56.38; H, 3.75%. Calcd for $C_{17}H_{13}BrO_2S$: C, 56.52; H, 3.63%.

1-Bromo-6-(*p*-tolylsulfonyl)naphthalene (2b; Y = Br): Colorless plate crystals; mp 159.7–160.7 °C (hexane–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 7.31 (d(br), 2H, $J = 8.0$ Hz), 7.45 (dd, 1H, $J = 7.8$, 8.0 Hz), 7.88 (diffused d, 2H, $J = 8.2$ Hz), 7.92 (dd, 1H, $J = 1.0$, 7.6 Hz), 7.94 (dd, 1H, $J = 1.9$, 8.2 Hz), 7.95 (d(br), 1H, $J = 8.2$ Hz), 8.33 (d, 1H, $J = 8.9$ Hz), 8.55 (d, 1H, $J = 1.9$ Hz); IR (KBr) 3059, 2924, 1593, 1493, 1315, 1300, 1151, 1138, 1093, 957, 814, 787, 754, 706, 681, 663, 552, 532 cm^{-1}; Anal. Found: C, 56.58; H, 3.80%. Calcd for $C_{17}H_{13}BrO_2S$: C, 56.52; H, 3.63%.

Entirely "Solvent-Free" Procedure. In a 50-mL round bottom flask, with a two-way stop-cock, were placed 380 mg (1.50 mmol) of iodine and a 8 mL vial tube (18 mm diameter × 42 mm height) containing 165 mg (0.50 mmol) of **1** (Y = H). The pressure in this flask was sporadically reduced to ~1.3 kPa. After the mixture was allowed to stand at room temperature for 5 h, the vial tube was removed from the 50-mL round bottom flask and kept under reduced pressure (<0.1 kPa) for 9 h to obtain 142 mg (0.50 mmol) of **2** (Y = H). (mp 165.8–166.5 °C; Anal. Found: C, 71.57; H, 4.99%. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00%). 47 mg (0.19 mmol) of iodine was consumed in the 50-mL round bottom flask.

References

1 G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).

2 a) B. S. Green, M. Lahav, and D. Rabinovich, *Acc. Chem. Res.*, **12**, 191 (1979). b) M. Hasegawa, *Chem. Rev.*, **83**, 507 (1983). c) G. Kaupp and D. Matthies, *Mol. Cryst. Liq. Cryst.*, **161**, 119 (1988). d) F. Toda, *Synlett*, **1993**, 303. e) F. Toda, *Acc. Chem. Res.*, **28**, 480 (1995). f) K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000). g) G. W. V. Cave, C. L. Raston, and J. L. Scott, *Chem. Commun.*, **2001**, 2159.

3 M. Sakamoto, *Chem.—Eur. J.*, **3**, 648 (1997).

4 a) C. N. Sukenik, J. A. P. Bonapace, N. S. Mandel, P. Y. Lau, G. Wood, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 851 (1977). b) F. Toda, M. Yagi, and K. Kiyoshige, *J. Chem. Soc., Chem. Commun.*, **1988**, 958. c) F. Toda and T. Shigemasa, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 209. d) F. Toda and K. Mori, *J. Chem. Soc., Chem. Commun.*, **1989**, 1245. e) F. Toda, K. Tanaka, and S. Iwata, *J. Org. Chem.*, **54**, 3007 (1989). f) F. Toda, H. Takumi, and M. Akehi, *J. Chem. Soc., Chem. Commun.*, **1990**, 1270. g) F. Toda, K. Tanaka, and K. Hamai, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 3207. h) M. Dessolin, O. Eisenstein, M. Golfier, T. Prangé, and P. Sautet, *J. Chem. Soc., Chem. Commun.*, **1992**, 132. i) M. Smrčina, Š. Vyskočil, V. Hanuš, M. Polášek, V. Langer, B. G. M. Chew, D. B. Zax, H. Verrier, K. Harper, T. A. Claxton, and P. Kočovský, *J. Am. Chem. Soc.*, **118**, 487 (1996). j) G. Kaupp, J. Schmeyers, A. Kuse, and A. Atfeh, *Angew. Chem., Int. Ed.*, **38**, 2896 (1999).

5 a) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **96**, 6329 (1974); **96**, 6340 (1974); R. S. Miller, I. C. Paul, and D. Y. Curtin, *J. Am. Chem. Soc.*, **96**, 6334 (1974). b) I. C. Paul and D. Y. Curtin, *Science*, **187**, 19 (1975). c) C. C. Chiang, C.-T. Lin, A. H.-J. Wang, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **99**, 6303 (1977).

6 a) F. Toda and K. Tanaka, *Tetrahedron Lett.*, **29**, 4299 (1988). b) G. R. Desiraju and C. V. K. M. Sharma, *J. Chem. Soc., Chem. Commun.*, **1991**, 1239. c) C.-M. Chung and M. Hasegawa, *J. Am. Chem. Soc.*, **113**, 7311 (1991). d) V. Enkelmann, G. Wegner, K. Novak, and K. B. Wagener, *J. Am. Chem. Soc.*, **115**, 10390 (1993). e) H. Koshima, K. Ding, and T. Matsuura, *J. Chem. Soc., Chem. Commun.*, **1994**, 2053. f) M. Sakamoto, M. Takahashi, K. Kamiya, K. Yamaguchi, T. Fujita, and S. Watanabe, *J. Am. Chem. Soc.*, **118**, 10664 (1996). g) G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky, and R. H. Grubbs, *J. Am. Chem. Soc.*, **120**, 3641 (1998). h) A. Matsumoto, T. Odani, M. Chikada, K. Sada, and M. Miyata, *J. Am. Chem. Soc.*, **121**, 11122 (1999). i) M. Sakamoto, N. Sekine, H. Miyoshi, T. Mino, and T. Fujita, *J. Am. Chem. Soc.*, **122**, 10210 (2000).

7 S. Matsumoto, S. Takahashi, and K. Ogura, *Heteroat. Chem.*, **12**, 385 (2001).

8 a) K. Ogura, T. Iihama, K. Takahashi, and H. Iida, *Tetrahedron Lett.*, **25**, 2671 (1984). b) K. Ogura, T. Iihama, K. Takahashi, and H. Iida, *Bull. Chem. Soc. Jpn.*, **57**, 3347 (1984).

9 G. Cardillo and M. Orena, *Tetrahedron*, **46**, 3321 (1990).

10 D. Kano, S. Minakata, and M. Komatsu, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 3186.