Regio- and Stereoselective Hydrosulfonylation of Conjugated Dienes via a (π-Allyl)palladium Complex[1a,b]

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Received June 1, 1983

The combination of a sulfonylpalladation of acyclic dienes **1** (with 2 equiv of $NaSO_2R$ and 1 equiv of $PdCl_2$ in acetic acid or acetic acid–H_2O at 50–80 °C under air) and a protiodepalladation of the thus obtained [1-(sulfonylmethyl)-π-allyl]palladium complexes **3** with dimethylglyoxime (in a protic solvent at room temperature) provides di- and trisubstituted (*Z*)-Δ^3-sulfones **12** selectively, irrespective of the stereochemistry of the starting dienes. Similar treatment of 1-vinylcycloalkenes **5** ($n \leq 6$) provides the stereochemically defined (2-sulfonylethylidene)cycloalkanes **19**, the formal 1,4-addition products of a sulfinic acid to *s-cis*-**5**, in high selectivity. The dienes **5** ($n = 8$ and 10) are transformed to a mixture of **19** and **20**. These regio- and stereoselectivities are rationalized uniformly by assuming a hydrolytic cleavage of the (σ-allyl)palladium intermediate activated by an $A^{(1,3)}$ strain between Pd and the substituent on the allylic position.

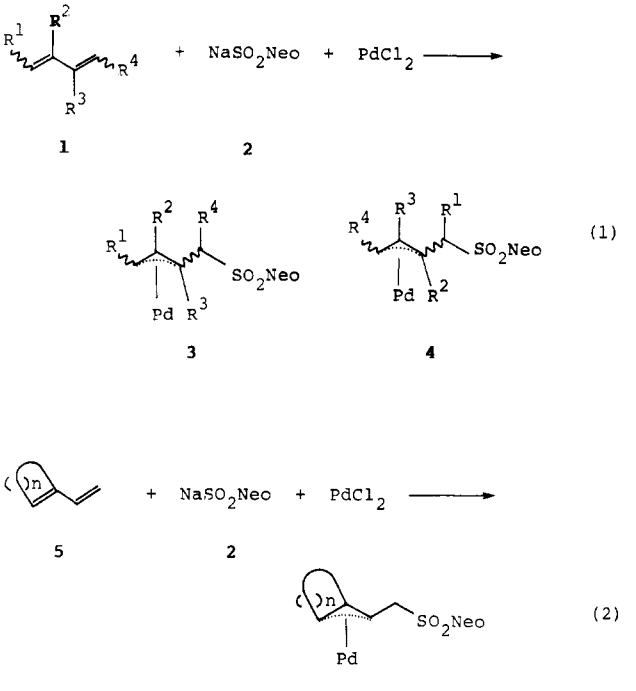
The sulfonyl group has played important roles in organic reactions especially in C–C bond-forming reactions due to its ability to stabilize an adjacent carbanion[2] and to lower the frontier orbitals of conjugated olefins.[3] The ease with which sulfonyl group can be prepared and removed[4] makes these reactions very feasible.

In organo-transition-metal chemistry, however, little attention has been paid to the utilization of this functional group.[5]

In this paper we describe a full scope of the regio- and stereoselective hydrosulfonylations of 1,3-dienes which consist of the formation of [1-(sulfonylmethyl)-π-allyl]-palladium complexes **3** and **6** by the reaction of sodium alkyl- or arylsulfinate with 1,3-dienes in the presence of a stoichiometric amount of $PdCl_2$ and a protiodepalladation of the thus-formed **3** and **6** by treatment with dimethylglyoxime (DMG). Through these transformations (*Z*)-Δ^3-alkenyl sulfones (from acyclic dienes **1**) and (2-sulfonylethylidene)cycloalkanes (from 1-vinylcycloalkenes **5**) were obtained regio- and stereoselectively.

Results and Discussion

Sulfonylpalladation of 1,3-Dienes: Synthesis of (π-Allyl)palladium Complexes 3 and 6. Sulfonylpalladations of 1,3-dienes were performed most successfully by heating a mixture of sodium alkylsulfinate (2 mol), $PdCl_2$ (1 mol), and 1,3-diene (1.5–3 mol) in acetic acid at 70–80 °C under air (eq 1 and 2). Among sulfinates examined, sodium neophylsulfinate was most satisfactory from view points of its good crystallinity, a high yield formation of [1-(sulfonylmethyl)-π-allyl]palladium complex (**3** and **6**) and a good solubility of **3** and **6** in common organic solvents. Sodium *n*-butylsulfinate and *tert*-butylsulfinate were rather unreactive and provided **3** and **6** (*n*-Bu or *t*-Bu in place of Neo) in low yields. Some of these complexes showed very poor solubility in common organic solvents.



The reaction behavior of the sulfinate quite depends on the reaction media, and acetic acid was found to be the

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Table I. Regio- and Stereoselective 1,2-Hydrosulfonylation of Acyclic 1,3-Dienes 1 via (π-Allyl)palladium Complex 3[a]

entry	dienes 1[b] no.	R^1	R^2	R^3	R^4	reaction conditions[c]	Pd complex 3, (isolated yield,[d] %)	sulfones 12-15, (isolated yield,[e] %)
1	1a	H	H	H	H	A, AcOH-H_2O, 50 °C, 1 h; B, MeOH, rt, 20 h	**3a** (40)	**12a, 13a** (63, 80:20)
2	1b	H	Me	H	H	A, AcOH, 75 °C, 1.5 h; B, MeOH, rt, 20 h	*f*	**12b** (89)
3	1c	H	Me	Me	H	A, AcOH, 75 °C, 5 h; B, MeOH, rt, 20 h	**3c** (80)	**12c** (72)
4	1d	H	$(CH_2)_2CH=CMe_2$	H	H	A, AcOH, 75 °C, 3 h; B, MeOH, rt, 20 h	*f*	**12d** (43)
5	1e	Me	H	H	H	A, AcOH, 50 °C, 4 h; B, MeOH, rt, 20 h	**3e** (45)[g]	**12e, 14e** (43, 55:45)
6	1e	Me	H	H	H	A, AcOH-H_2O, 40 °C, 4 h; B, MeOH-CH_2Cl_2, rt, 20 h		**12e, 14e** (60, 73:27)
7	1f	Et	H	H	H	A, AcOH, 75 °C, 2 h; B, MeOH, rt, 20 h	**3f** (91)[g]	**12f, 14f** (82, 88:12)
8	1f	Et	H	H	H	A, AcOH-H_2O, 75%, 4 h; B, MeOH-CH_2Cl_2, rt, 20 h		**12f, 14f** (70, 91:9)
9	1g	$CHMe_2$	H	H	H	A, AcOH-H_2O, 70 °C, 4 h; B, MeOH, rt, 20 h	**3g** (57)	**12g** (55)
10	1h	CHMePh	H	H	H	A, AcOH, 70 °C, 4 h; B, MeOH, rt, 20 h	**3h** (45)	**12h** (55)
11	1i	Me	H	H	Me	A, AcOH-H_2O, 70 °C, 4 h; B, MeOH, rt, 20 h	**3i** (34)	**12i** (64)
12	1j	Me	Me	H	H	A, AcOH, 80 °C, 1.5 h; B, MeOH-Py, rt, 20 h	**3j** (79)[g]	**12j, 15j** (73, 87:13)
13	1j	Me	Me	H	H	A, AcOH-H_2O, 90 °C, 2.5 2.5 h; B, MeOH-Py, rt, 20 h		**12j, 15j** (71, 98:2)
14	1j	Me	Me	H	H	A, AcOH-H_2O, 90 °C, 2.5 h; B, AcOH-H_2O, rt, 20 h		**12j, 15j** (85, 97:3)
15	1k	Me	Ph	H	H	A, AcOH-H_2O, 90 °C, 2.5 h; B, MeOH, rt, 20 h	**3k** (91)	**12k, 13k** (65, 83:17)

[a] For the structures of 1, 3, and 4, see eq 1. For the structures of **12-15**, see eq 6 and 7. [b] Stereoisomeric mixture of dienes was used. [c] The conditions A and B refer to those for the sulfonylpalladation and degradation, respectively; rt = room temperature. [d] The isolated yield of 3 after column chromatography on silica gel with a benzene-ethyl acetate gradient. In this table the regioisomer 4 was neglected for entries 5-8 and 12-14. [e] Overall yield for the isolated sulfone(s), based on $PdCl_2$. All reactions were carried out without purification of (π-allyl)palladium complex(es) 3 (and 4). Separation of sulfones **12-15** was carried out by HPLC (μ-Porasil; hexane-EtOAc, 95:5). The ratio of sulfones was determined on the basis of area intensity on VPC (SiDC 550 or PEG, 250 °C, He). [f] (π-Allyl)palladium complex 3 was not isolated. [g] The isolated (π-allyl)palladium complex 3 was contaminated with a trace amount of regioisomer 4 (<5%).

choice of the solvents. For example, in acetic acid, neophylsulfinate **2** reacted with butadiene as a S nucleophile to provide di-μ-chloro-bis[1-[(neophylsulfonyl)methyl]-π-allyl]palladium **3a** in 40% yield (entry 1, Table I), while in ethanol, **2** served as an efficient cocatalyst for the palladium catalyzed dimerization of butadiene to produce 2,7-octadienyl ethyl ether **7**.[6] In ethanol, 2,3-dimethyl-1,3-butadiene **1c** (2 equiv) reacted with **2** (2 equiv) and $PdCl_2$ (1 equiv) to provide di-μ-chloro-bis[1-[(neophylsulfonyl)methyl]-2,3-dimethyl-π-allyl]palladium **3c** in a low yield (3%, 65° for 15 h), while the same reaction in acetic acid (75 °C, 5 h) provided **3c** in as high as 80% yield. The same reaction in acetonitrile was completely unsuccessful.

Nucleophilic substitution of readily available di-μ-chloro-bis[1-(chloromethyl)-π-allyl]palladium[7] with **2** seems to be another method viable for the synthesis of **3**, but to our surprise, no trace amount of **3** was yielded: Into a solution of **2** (2 equiv) in acetic acid or ethanol was added di-μ-chloro-bis[1-(chloromethyl)-π-allyl]palladium in one portion. During the reaction, the color of the mixture turned from yellow to deep red (75 °C, 5 h). The reaction mixture was completely free from **3a**, as judged from TLC.

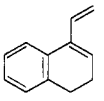
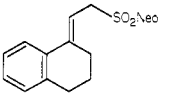
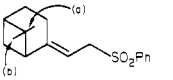
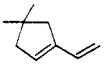
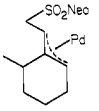
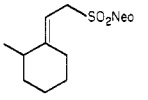
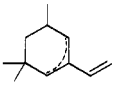
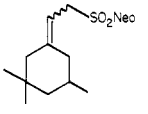
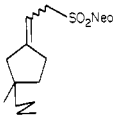
The sulfonylpalladation of 1,3-dienes with a wide structural variety was undertaken in acetic acid or in acetic acid–H_2O (5:1 by volume), and the results with acyclic dienes **1** and 1-vinylcycloalkenes **5** were summarized in Tables I and II, respectively. Among 1,3-dienes examined, the highly substituted dienes, e.g., 2,5-dimethyl-2,4-hexadiene, bicyclohexenyl, isopropenylcyclohexene, and 1,3-cyclooctadiene, were either unreactive or provided intractable mixture of products under the conditions shown in Table I.

For some 1-substituted and 1,2-disubstituted acyclic dienes, the regioisomer **4** was produced in addition to **3** (entries 5–8 and 14, Table I). The population of **4**, as judged from the ratios of protiodepalladation products **12** and **14** (vide infra), largely depends on the steric bulk of substituent(s) and decreases from piperylene (55:45 **3e**/**4e**, entry 5) to 1,3-hexadiene (88:12 **3f**/**4f**, entry 7) and finally becomes negligibly small as in the case of 5-methyl-1,3-hexadiene (99:1 **3g**/**4g**, entry 9, Table I). As is apparent by the comparisons of entries 5 with 6, 7 with 8, and 12 with 13, the regioselectivity in favor of **3** was greatly improved by changing the solvent from acetic acid to acetic

(6) (a) Tamaru, Y.; Kagotani, M. Suzuki, R.; Yoshida, Z. *Chem. Lett.* **1978**, 1329. For the action of sulfinate as a cocatalyst of palladium-catalyzed dimerization of butadiene, see: (b) Tamaru, Y.; Suzuki, R.; Kagotani, M.; Yoshida, Z. *Tetrahedron Lett.* **1980**, *21*, 3787. (c) *Ibid.* **1980**, *21*, 3791.

(7) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1963**, 4806.

Table II. Regio- and Stereoselective 1,4-Hydrosulfonylation of 1-Vinylcycloalkenes 5 via (π-Allyl)palladium Complexes 6[a]

entry	dienes 5	reaction conditions[b]	Pd complex 6[c] (isolated yield, %)	sulfones 19-22[d] (isolated yield, %)
1	5 (n = 3)	A, AcOH-H_2O, 70 °C, 2 h; B, AcOH-$CHCl_3$, rt, 36 h	6 (n = 3; 61)	19 (n = 3; 100)
2	5 (n = 4)	A, AcOH-H_2O, 80 °C, 3 h; B, AcOH-$CHCl_3$, rt, 63 h	6 (n = 4; 88)	19 (n = 4; 75)
3	5 (n = 6)	A, AcOH-H_2O, 60 °C, 6 h; B, MeOH-Py, rt, 34 h	6 (n = 6; 88)	19, 21 (n = 6; 57, 1:2)
4	5 (n = 6)	A, AcOH-H_2O, 60 °C, 6 h; B, AcOH, rt, 37 h		19 (n = 6; 55)
5	5 (n = 8)	A, AcOH-H_2O, 60 °C, 9 h; B, AcOH-$CHCl_3$, rt, 67 h	6 (n = 8; 85)	19, 20, 21 (n = 8; 69, 4:2:1)
6	5 (n = 10)	A, AcOH-H_2O, 80 °C, 9 h; B, MeOH-Py, rt, 34 h	6 (n = 10; 79)	19, 20, 21 (n = 10; 56, 3:1:2)
7	5 (n = 10)	B, AcOH-$CHCl_3$-PhH, rt, 91 h		19, 20 (n = 10; 77, 1:1)
8	 5a	A, AcOH-H_2O, 70 °C, 7 h; B, AcOH-$CHCl_3$, rt, 16 h	6a (78)	 19a (93)
9	 5b	A, AcOH-H_2O, rt, 50 h; B, MeOH-$CHCl_3$, rt, 17 h	6b (77)	 19b (77)
10	 5c	A, AcOH, 75 °C, 4 h; B, MeOH-$CHCl_3$, rt, 30 h	6c (80)	19c, 22 (59%, 33:67)
11	5c	B, AcOH-PhH, rt, 21 h		19c, 22 (61, 57:43)
12	5c	B, AcOH-PhH, rt, 40 h (under argon)		19c (59)
13	 5d	A, AcOH-H_2O, 62 °C, 9 h; B, AcOH-PhH, rt, 48 h	6d (96)	19d (92)
14	 5e	A, AcOH-H_2O, 80 °C, 5 h; B, AcOH-PhH, rt, 168 h	 6e (91)	 19e (59)
15	 5f	A, AcOH-H_2O, 80 °C, 3 h; B, AcOH-PhH, rt, 58 h	6f (69)	 19f (100)
16		A, AcOH-H_2O, 80 °C, 7 h; B, MeOH, rt, 17 h	6g (70)	 19g (50)

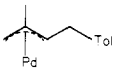
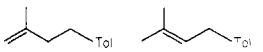
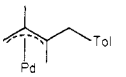
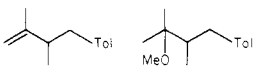
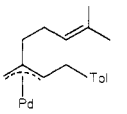
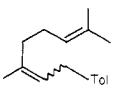
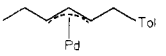
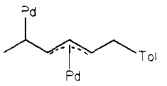
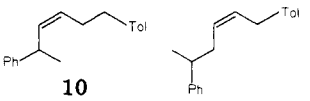
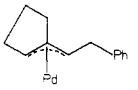
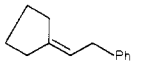
[a] For the structures of 5 and 6, see eq 2. For the structures of 19, 20, and 21, see eq 8. For the structures of 19c and 22, see eq 9. For the structure of 19d, see eq 10. [b] The conditions A and B refer to those conditions for sulfonylation and degradation, respectively. [c] The isolated yield of 6 after column chromatography on silica gel with a benzene-EtOAc gradient. The (π-allyl)palladium complexes 6f and 6g were obtained as a mixture of regioisomers. [d] Isolated yield for sulfone(s), based on 6. The ratio of sulfones was determined by means of VPC and ^1H and/or ^{13}C NMR. The ratio of 19c to 22 was calculated from the isolated yields of these sulfones.

acid-H_2O (5:1 by volume). This solvent system (AcOH-H_2O) was also found to effect the high-yield formation of 3, possessing a newly created SO_2-C (secondary) bond. For example the complex 3i, which was not obtainable by the reaction in acetic acid, could be obtained in 34% isolated yield by the application of this mixed reaction medium (entry 11, Table I). The low yield of 3i may be attributed to its partial decomposition during purification by column chromatography upon silica gel, as judged from the doubled overall yield of sulfone 12i (based on $PdCl_2$, vide infra). The decomposition of such complexes as 3i and 4, which possess the SO_2-C (secondary) bonds, over silica gel seems to be general and this propensity rendered the purification of 3 from a mixture of 3 and 4 possible.

In sharp contrast to acyclic 1,3-dienes 1, only single regioisomers 6 were produced in the sulfonylpalladation of 1-vinylcycloalkenes 5, irrespective of their ring sizes or substitution patterns (eq 2, Table II).

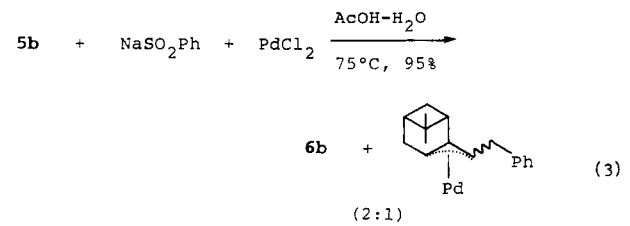
Compared with alkylsulfinates, arylsulfinates generally show a reduced S nucleophilicity, and they have been

Table III. Arylpalladation of 1,3-Dienes and Degradation of 8 or 9 with DMG[a]

entry	diene[b]	π-allyl complex 8 or 9[c] (isolated yield, %)	degradation product[d] (isolated yield, %)
1	1b	 **8b** (59)	 (43, 66:34)
2	1c	 **8c** (56)	 (43, 22:78)
3	1d	 **8d** (51)	 (35)
4	1f	 **8f** (74)	*e*
5	1h	 **8h** (41)	 **10** **11** (97, 33:67)
6	5 (n = 3)	 **9** (68)	 (54)

[a] The (π-allyl)palladium complexes 8 or 9 were prepared by refluxing a mixture of $PdCl_2$ (3 mmol), sodium arenesulfinate (6 mmol), and a diene (4–5 mmol) in 20 mL of CH_3OH for 4–6 h. Degradation of 8 (in CH_3OH) and 9 (in AcOH–$CHCl_3$) was undertaken by treatment with 2 equiv of DMG (room temperature, 1–20 h). [b] For the structures of dienes 1 and 5, see Tables I and II, respectively. [c] Isolated yield of 8 or 9, based on $PdCl_2$. [d] Yields refer to overall yields based on $PdCl_2$, except for entries 5 and 6. The yields in entries 5 and 6 are based on 8h and 9, respectively. Product ratio was determined on the basis of area intensities on VPC. [e] At least seven peaks with similar area intensities were observed on VPC.

mostly employed as precursors for the formation of arylpalladium intermediates via an extrusion of sulfur dioxide.[5] Indeed, sodium benzenesulfinate was unreactive toward the sulfonylpalladation of acyclic dienes (e.g., 1,2-dimethyl-1,3-butadiene, **1j**). However, 1-vinylcycloalkenes were found to react with arylsulfinates to provide the sulfonylpalladation products in reasonable yields. For example, 6,6-dimethyl-2-vinyl-bicyclo[3.1.1]hept-2-ene (**5b**, 2 equiv) reacted with sodium benzenesulfinate (2 equiv) and $PdCl_2$ (1 equiv) in AcOH–H_2O (5:1 by volume) to give rise to **6b** in 77% yield (at an ambient temperature, overnight; entry 9, Table II). The course of the reaction was highly dependent upon the reaction conditions and reaction media as well as the structures of dienes. The same reaction, when being conducted at 72–78 °C for 1.5 h, provided a mixture of **6b** and phenylpalladated product in a ratio of 2:1 (95% combined isolated yield, eq 3).



(3)

Interestingly in the reaction with 1-vinylcyclooctene, no arylpalladation took place, and sulfonylpalladated product **6** (n = 6) was obtained in 67% yield even when the reaction was conducted at an elevated temperature (80 °C for 5 h; cf. entry 3, Table II).

In marked contrast to these, in methanol arylsulfinates completely lost their nucleophilic ability and provided arylpalladated products irrespective of the structures of the dienes. The results of arylpalladation of 1,3-dienes are summarized in Table III. The present arylsulfinate-mediated arylpalladation is apparently a nice substitute for the method using arylmercuric compounds (Heck reaction).[8]

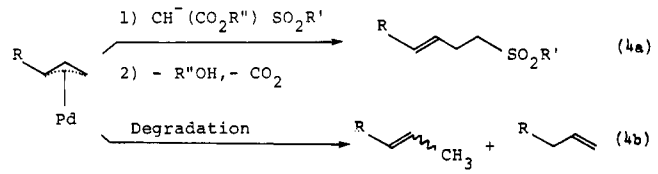
Protiodepalladation of (π-Allyl)palladium Complexes 3 and 6: Stereoselective Syntheses of (*Z*)-Δ³-Alkenyl Sulfones 12 and (2-Sulfonylethylidene)cycloalkanes 19. Stereocontrolled di- and trisubstituted olefin synthesis is still a problem of pressing concern in organic synthesis. Palladium chemistry has made a pivotal role in C–C bond-forming reactions;[9] however, the reactions via (π-allyl)palladium intermediates are generally limited to the synthesis of *E* olefins, reflecting the thermodynamically favored syn geometry of these intermediates.[10] A

(8) Kasahara, A.; Izumi, T.; Endo, K.; Takeda, T.; Ookita, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1967.

(9) (a) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (b) Trost, B. M.; Klum, T. P. *Ibid.* **1981**, *103*, 1864. (c) Grieco, P. A.; Tuthill, P. A.; Sham, H. L. *J. Org. Chem.* **1981**, *46*, 5005. (d) Trost, B. M.; Runge, T. A.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 2840. (e) Trost, B. M.; Fortunack, J. M. *Ibid.* **1980**, *102*, 2841. (f) Trost, B. M.; Curran, D. P. *Ibid.* **1980**, *102*, 5699. (g) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *Ibid.* **1980**, *102*, 5979. (h) Overman, L. E.; Knoll, F. M. *Ibid.* **1980**, *102*, 865. (i) Negishi, E.; Valente, L. F.; Kobayashi, M. *Ibid.* **1980**, *102*, 3298. For a review, see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

(10) In some instances, *Z* olefins are produced by kinetically controlled reactions with (*Z*)-allylic acetates as starting materials: Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215.

typical examples is illustrated in eq 4a. An alkylation of



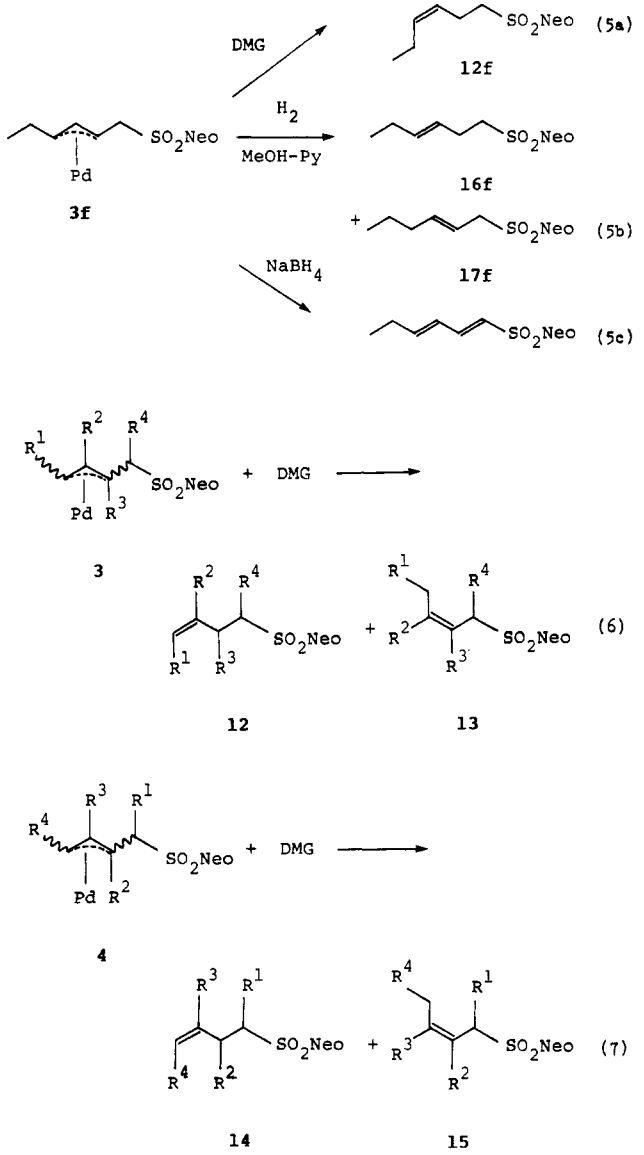
(π-allyl)palladium complex with sulfonylacetate anion provides (E)-Δ^3-sulfone derivatives. Degradation with CH_3ONa–CH_3OH,[11] NaCN–CH_3OH,[12] or reducing agents ($NaBH_4$,[13] $LiAlH_4$,[14] HCO_2H–pyridine[15]) also gives rise to E olefins predominantly together with small amounts of Z isomers. Moreover, in these cases, comparable amounts of regioisomers are produced, generally more predominant than the more substituted ones (eq 4b).

In sharp contrast to these precedents, we have found that treatment of **8h** with 2 equiv of dimethylglyoxime (DMG; in CH_3OH in the presence of an appropriate amount of pyridine to dissolve **8h** at ambient temperature overnight) provided Z olefins exclusively, although a mixture of regioisomers **10** and **11** was obtained (entry 5, Table III).

On the other hand, acyclic [1-(sulfonylmethyl)-π-allyl]palladium complexes **3** were degradated regio- and stereoselectively to give rise to (Z)-Δ^3-sulfones **12** (eq 6), the stereoisomer of the sulfone shown in eq 4a. For example, DMG treatment of **3f** (**3**: R^1 = Et, R^2 = R^3 = R^4 = H) containing a small amount of **4f** (**4**: R^1 = Et, R^2 = R^3 = R^4 = H) in CH_3OH–CH_2Cl_2 at an ambient temperature for 20 h provided exclusively (Z)-3-hexenyl neophyl sulfone [**12f** (from **3f**), together with a small amount of **14f** (from **4f**), eq 5a, 6, and 7]. Partial hydrogenation of **3f** (1 atm of H_2 for 10 min at ambient temperature in CH_3OH in the presence of 3 equiv of pyridine)[16] funished a 1:1 mixture of regioisomers of E sulfones **16f** and **17f** in 63% yield (eq 5b). Unexpectedly, an attempted reduction of **3f** with $NaBH_4$ (0.33 molar equiv at 0 °C in CH_3OH) failed and gave 1,3-hexadienyl neophyl sulfone in 64% yield (eq 5c). The reaction with *O,O'*-dimethylglyoxime (4 equiv in AcOH–$CHCl_3$) or *N,N'*-dimethylethylenediamine (4 equiv in MeOH–$CHCl_3$) resulted either in no reaction or in production of 1,3-dienyl sulfones in low yield, respectively.

The present degradation of (π-allyl)palladium complexes with DMG was usually undertaken under air in an appropriate protic solvent at an ambient temperature. Acetic acid or methanol was mostly employed as a solvent. Special caution should be paid to add DMG to a completely homogeneous solution of **3**, otherwise the reaction may result in an intractable mixture of products. For this purpose we usually employed dichloromethane, chloroform, or benzene as a cosolvent or an appropriate amount of pyridine as an additive. Results together with the reaction conditions (conditions B) are summarized in Table I, which indicates that the protiodepalladation generally provides (Z)-Δ^3-sulfones in high regio- and stereoselectivity.

Among the reactions examined, we encountered three exceptions with respect to the regioselectivity (entries 1, 12, and 15), where (Z)-Δ^2-sulfones **13a** and **13k** (from **3a** and **3k**, respectively) and **15j** (from **4j**)[17] were produced as minor products. The Z structure of **13a** is apparent by the comparison of the ^1H NMR and IR spectra with those of an authentic E isomer prepared from *trans*-crotyl bromide and **2** in CH_3OH [J(vinylic protons) = 10.5 Hz for **13a** and 16.0 Hz for the trans isomer; IR (neat film) 970 cm^{-1}]. The Z structure of **13k** was determined similarly by the comparison of spectral data with those of an authentic sample.[18]



The results in entries 12–15 are especially rewarding, because in these cases the trisubstituted Z olefins **12j** (**12**: R^1 = R^2 = CH_3, R^3 = R^4 = H) and **12k** (**12**: R^1 = CH_3, R^2 = Ph, R^3 = R^4 = H) were obtained stereoselectively together with small amounts of **15j** and **13k**, respectively. The absence of other regio- and stereoisomers was concluded from a thorough examination of the reaction mixtures by means of ^1H NMR, VPC, and/or HPLC.[19]

The results obtained above may be summarized as follows: the protiodepalladation of [1-(arylmethyl)-π-allyl]palladium complexes **8** yields Z olefins selectively but

(11) (a) Faller, J. W.; Laffey, K. *J. Organomet. Chem. Synth.* **1972**, *1*, 471. (b) Christ, D.-C. H.; Huttel, R. *Angew. Chem.* **1963**, *75*, 921. (c) Schenach, T. A.; Caserio, F. F., Jr. *J. Organomet. Chem.* **1969**, 17. (d) Huttel, R. Kochs, P. *Chem. Ber.* **1968**, *101*, 1043.

(12) Dunne, K.; McQuillin, F. J. *J. Chem. Soc. C* **1970**, 2196.

(13) (a) Bullpitt, M. L.; Kiching, W. *J. Organomet. Chem.* **1972**, *46*, 21. (b) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* **1980**, *21*, 27.

(14) Jones, D. N.; Knox, S. D. *J. Chem. Soc., Chem. Commun.* **1975**, 165.

(15) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613.

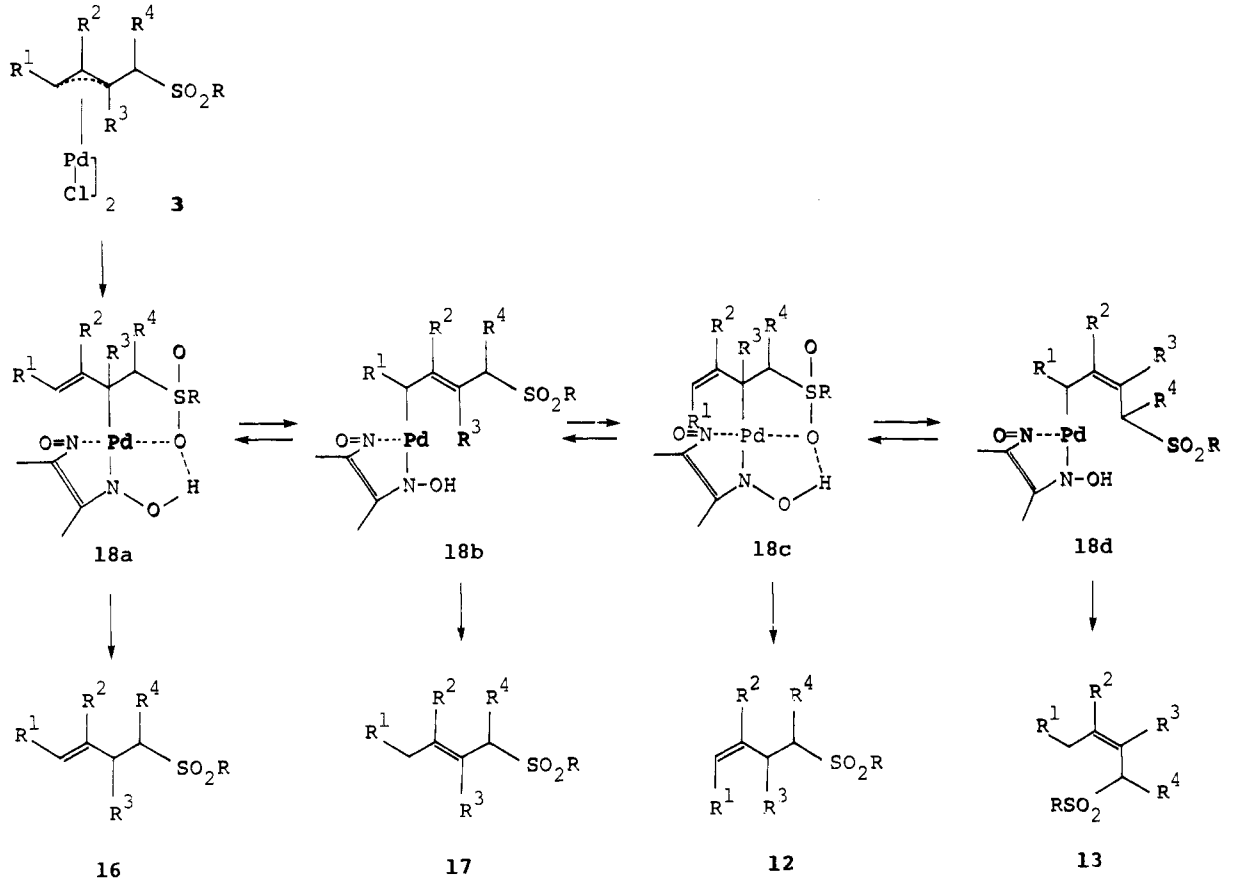
(16) Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1979**, *44*, 1188.

(17) The stereochemistry of **15j** was not determined.

(18) For detail of the stereochemical determination of trisubstituted olefinic sulfones, see the section on Structural Determination of Sulfones.

(19) Conditions for VPC analyses: SiDC 550 or PEG at 220–250 °C, He. Conditions for HPLC analyses: μ-Porasil, hexane or hexane–ethyl acetate (95:5), 2 mL/min.

Scheme I



as a mixture of regioisomers (e.g., entry 5, Table III). [1-(Sulfonylmethyl)-π-allyl]palladium complexes **3** are, on the other hand, degradated regio- and stereoselectively to give rise to (*Z*)-Δ^3-alkenyl sulfones **12**. Mechanistically, the present degradation seems to involve a hydrolytic cleavage of the Pd–C bond, which is indicated by the regioselective degradation of [1-[(neophylsulfonyl)-methyl]-2,3-dimethyl-π-allyl]palladium **3c** in CH_3OD to provide 2-deuterio-2,3-dimethyl-3-butenyl neophyl sulfone selectively.

A reaction mechanism, which accommodates all these results, might be expressed as in Scheme I. Owing to a strong coordination of DMG to Pd(II), the di-μ-chloro-bis(π-allyl)palladium complexes **3** or **8** might be dissociated to a monomer with a σ-allyl structure.[20] Among the possible four kinds of regio- and stereoisomers of σ-allyl intermediates **18a–d**, the Pd–C bond in **18c** and **18d** seems to be weakened and becomes susceptible to a hydrolytic cleavage owing to a severe $A^{(1,3)}$ strain[21] between Pd–C and the olefinic substituent (R^1 in **18c** and CHR^4SO_2R in **18d**). Hydrolytic Pd–C bond cleavage of intermediates **18** c and **18d**, with allylic retention, might produce *Z* sulfones **12** and **13**, respectively. Taking into consideration the lack of regiocontrol in the degradation of **8**, one might explain the regiocontrol in **3** by invoking some kind of participation of sulfonyl group, which involves a coordination of the sulfonyl oxygen and the hydroxyl group of DMG to form a tricyclic structure as depicted in **18c** (Scheme I). Another rationale for the regio- and stereoselectivity may be based on a kinetic protonation of the thermodynamically more stable (*Z*)-allylic anion[22] liberated from **3**. In this case, the regioselective formation of **12** may be attributed to the higher electron density of the allylic terminus closer to a highly electron-withdrawing sulfonyl substituent.

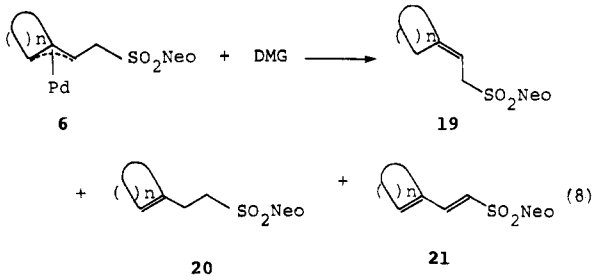
In order to shed more light on a mechanistic aspects and also to demonstrate the synthetic flexibility of the present procedure, we next examined the protiodepalladation of [1-(sulfonylmethyl)-π-allyl]palladium complexes **6**, where the C-2 and C-3 of an allylic moiety of (π-allyl)palladium complex **3** were connected with an appropriate number of methylene units.

According to the proposed mechanism (Scheme I), the complexes **6** ($n \leq 6$) are expected to furnish (2-sulfonylethylidene)cycloalkanes **13** selectively via intermediate **18d** ($R^1,R^2 = (CH_2)_n$, $n \leq 6$), because **6** might hardly take configuration **18c** owing to a steric constraint in the ring system. Indeed, this proved to be the case, and only the type of compound **19** (or **13** according to the numbering of the compound in Scheme I) was obtained exclusively (eq 8; entries 1–4 and 8–16, Table II). Naturally the complexes **6** with the larger numbers of methylene units (n = 8 and 10) were degradated to give rise to a mixture of **19** and endo olefin products **20** (or **12** according to the numbering of the compound in Scheme I, via **18c**), the latter in an increased proportion with an increase of the number of methylene units (entries 5–7, Table II). Compared with that of **3**, the degradation of **6** was rather re-

(20) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1, Chapter V.

(21) (a) Johnson, F. *Chem. Rev.* **1968**, *68*, 375. (b) Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397. See also his extensive current works. (c) Wilsen, S. R.; Missa, R. N. *J. Org. Chem.* **1980**, *45*, 5079. (d) Overman, L. E.; Yokomitsu, T. *Ibid.* **1980**, *45*, 5229.

(22) (a) Hoffmann, R.; Olofson, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 943. (b) Schlosser, J.; Hartmann, J. *Ibid.* **1976**, *98*, 4674. (c) Bartmess, J. E.; Hehre, W. J.; McIver, R. T., Jr.; Overman, L. E. *Ibid.* **1977**, *99*, 1976. (d) Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497. (e) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459. (f) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1982**, *23*, 1982.



luctant. When being conducted in methanol, the degradation of **6** (n = 6, 8, and 10) provided dienyl sulfones **21** in substantial amounts. The formation of **21** could be minimized by undertaking the reaction in acetic acid (cf. entries 3 with 4 and 6 with 7, Table II).

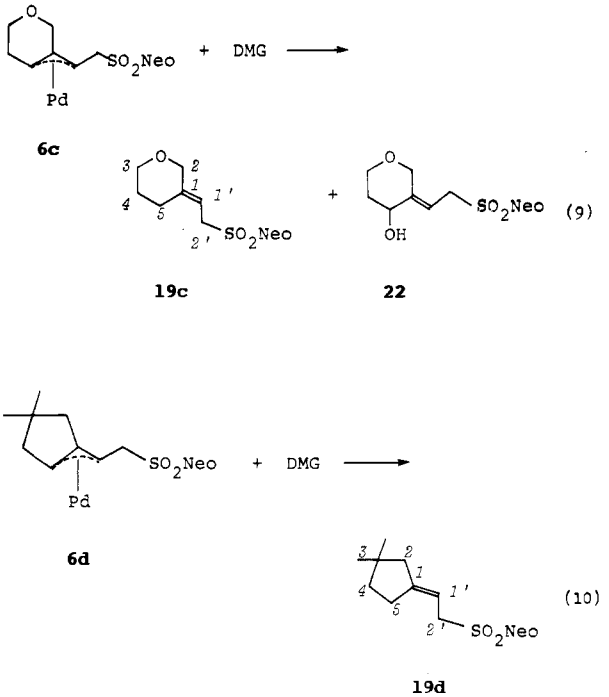
The selective formation of **19** through an intermediate **18d** does not seem to require the sulfonyl group participation any more, and hence the selective formation of *exo*-alkylidene products might be expected even in the degradation of a type of compound like **6** without a sulfonyl substituent. This was verified by the selective formation of an *exo*-alkylidene product, (2-phenylethylidene)cyclopentane, from di-μ-chloro-bis(1-benzyl-2,3-trimethylene-π-allyl)palladium **9** (entry 6, Table III). This is in marked contrast to the selective endo olefin formation as in the degradation of di-μ-chloro-bis(1,2-pentamethylene-π-allyl)palladium with CH_3ONa–CH_3OH.[11b]

Another interesting feature which might be deduced from Scheme I is that the present reaction, as a whole, should be the stereo- and regioselective 1,4-addition of sulfinic acid to *s-cis*-1-vinylcycloalkenes and hence might be applied to the regio- and stereoselective synthesis of unsymmetrically substituted (2-sulfonylethylidene)cycloalkanes. As expected, the specific 1,4-addition of sulfinic acid to *s-cis*-1-vinyl-5,6-benzocyclohexene (**5a**) and *s-cis*-2-vinyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene (**5b**) took place to provide (*E*)-2-sulfonylethylidene products **19a** and **19b**, respectively (entries 8 and 9, Table II). In these cases, however, the products are thermodynamically much more stable than the corresponding *Z* isomers, and hence these results seem to be hardly acceptable as supporting evidence for the mechanism shown in Scheme I. In this context, the *E* specificity in the reactions of 1-vinyl-3-oxacyclohexene (**5c**) and 1-vinyl-4,4-dimethylcyclopentene (**5d**) seems much more convincing (eq 9 and 10, entries 10–13 in Table II). No traces of regio- and stereoisomers were detected in these runs.

On the basis of these high stereo- and regioselectivities, the mechanism involving the protonation of allylic anion seems to be unlikely (vide supra), especially because of the completely reversed regioselectivity in the protiodepalladation of **3** and **6**. The regioselective monodeuteriation of **6a**, providing (*E*)-1-[2-(neophylsulfonyl)ethylidene]-2-deuteriotetraline either in MeOD–$CHCl_3$ or in CD_3CO_2D–$CHCl_3$, suggests that the protiodepalladation of **3** and **6** proceeds according to the same reaction mechanism.

Although all the other reactions could be conducted under air, the degradation of **6c** required the anaerobic conditions. Under the aerobic conditions **6c** was degradated to provide a mixture of an almost equal amount of the expected sulfone **19c** and its oxidized analogue **22**[23] (eq 9, cf. entries 10–12).

Interestingly from a mixture of 1-vinyl-2-methylcyclohexene and 1-vinyl-6-methylcyclohexene (**5e**) was produced



(*E*)-1-[2-(neophylsulfonyl)ethylidene]-2-methylcyclohexane (**19e**) selectively, the selectivity of which originates from a selective sulfonylpalladation of the latter isomer. Unfortunately such a selective sulfonylpalladation was not observed for **5f** and **5g**, and stereoisomeric mixtures of sulfones **19f** and **19g** were obtained nonselectively (entries 15 and 16, Table II).

In conclusion, it is demonstrated in this paper that the combination of the sulfonylpalladation of acyclic dienes followed by the protiodepalladation with DMG provided di- and trisubstituted (*Z*)-Δ^3-sulfones selectively, irrespective of the stereochemistry of the starting dienes. Similar treatment of 1-vinylcycloalkenes provides the stereochemically defined (2-sulfonylethylidene)cycloalkanes; the stereoselection in these sulfones is formally based on the 1,4-addition of sulfinic acid to a *s*-cis conformer of dienes. The efficiency of the present procedure may be augmented by the ease with which it can be performed and will find wide application in organic synthesis.

Structural Determination of Sulfones. In appropriate places in this paper, the structural determination of the disubstituted olefinic sulfones **12–14** was already mentioned. In this section is discussed the structural determination of the trisubstituted olefinic sulfones.

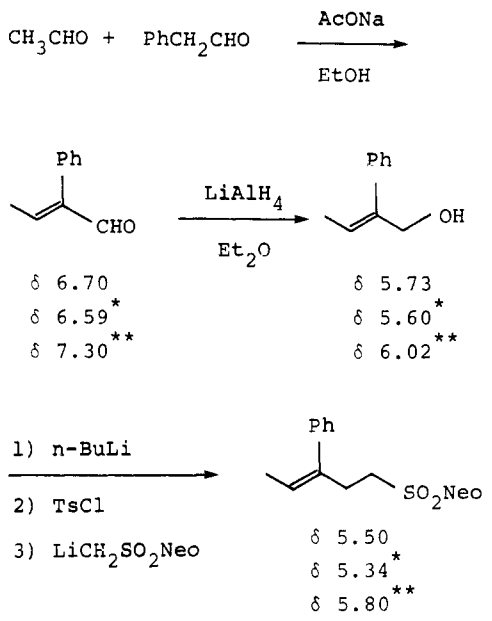
The relative stereochemistry of **12j** and its *E* isomer, the latter being prepared by an alkylation of (*E*)-2-methyl-2-butenyl bromide with (neophylsulfonyl)methyllithium, was determined on the basis of a nuclear Overhauser effect.[24] Irradiation of the allylic methylene protons of the *E* isomer enhanced the area intensity of the olefinic proton by 15%, whereas in **12j**, an irradiation of the analogous protons showed no effect on the intensity of the olefinic proton signal.

The authentic *Z* isomer of **12k** was prepared similarly by an alkylation of (*E*)-2-phenyl-2-propenyl tosylate, generated in situ from the corresponding alcohol, with (neophylsulfonyl)methyllithium (Scheme II). In these cases, the comparison of chemical shifts of the olefinic

(23) Due to inseparable impuriti(es), no satisfactory analysis was obtained for this compound.

(24) For the nuclear Overhauser effect and LIS in ^1H NMR spectra, see: (a) Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, England, 1969. (b) Gaudemer, A. In "Stereochemistry"; Kagan, H. B., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 1.

Scheme II[a]



[a] The values given under the compounds refer to olefinic protons. The asterisked and double asterisked values are meant to refer to the calculated chemical shifts for the compounds shown in this scheme and those for another stereoisomers, respectively.

protons in both isomers was most diagnostic due to a large anisotropy of the phenyl substituent [**12k**, δ(olefinic proton) 5.77 (calcd 5.80);[25] *Z* isomer of **12k**, δ 5.50 (calcd 5.34);[25] in CCl_4].

The structure of **13k** was confirmed by the complete coincidence of its IR and ^1H NMR spectra and the retention times on VPC (SiDC 550 and PEG) with those of an authentic sample prepared by the sulfonylation of (*E*)-3-phenyl-2-pentenyl tosylate with sodium neophylsulfinate.

The structure of **19a** was based on the characteristic low-field resonance of the olefinic proton (δ 5.87 in CCl_4) as observed in (*E*)-1-ethylidene-1,2,3,4-tetrahydronaphthalene (δ 5.90; *Z* isomer, δ 5.39; in CCl_4).[26]

The structural confirmation of **19b** was obtained by a LIS experiment: by gradual dopings of $Eu(fod)_3$, large paramagnetic shifts were observed for the CH_3(a) protons, while the CH_3(b) protons shifted downfield very slightly, implying a closer proximal relationship of the CH_3(a) protons to the sulfonyl group (for the structure of **19b**, see entry 9, Table II).

The NOE experiments clearly indicate the structure of **19c** as shown in eq 9. On irradiation at the signal of the C(2)H protons, the area intensity of the C(1′)H proton increased by 20%. The structure of oxidized product **22** was assigned tentatively[23] as shown in eq 9, on the basis of the upfield shift of resonance of C(2) by ca. 10 ppm compared with that of the corresponding carbon C(2) in **19c** in the ^{13}C NMR spectra.[27]

The long-range coupling (^4J = 1.5 Hz) between C(1′)H and C(5)H and a large NOE effect (ca. 30% increase of the area intensity of the C(1′)H proton upon irradiation of the C(2)H protons) clearly indicate the structure of **19d** as *E*. Further confirmation was obtained by the very large downfield shifts of the resonance of the C(5)H protons obtained by gradual dopings with $Eu(fod)_3$, where only very slight downfield shifts were observed for the signals of the C(2)H protons.

The authentic sample of **19c** was prepared from (*E*)-(2-hydroxyethylidene)-2-methylcyclohexane via a tosylation followed by a sulfonylation with sodium neophylsulfinate. This alcohol was prepared by a hydrolysis of the corresponding acetate, which was obtained as a single product by a Pd(II)-catalyzed rearrangement of 1-acetoxy-1-vinyl-2-methylcyclohexane.[28]

Experimental Section

Melting points were determined in capillary tubes with a Büchi apparatus and were not corrected. Microanalyses were performed by the Microanalysis Center of Kyoto University. Analyses agreed with calculated values within ±0.3%. Infrared spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer. Proton magnetic resonance (^1H NMR) spectra were determined either at 60 MHz on a JEOL JNM-PMX60 instrument or at 100 MHz on a Varian HA-100 instrument with tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined at 90 MHz on a JEOL FX90Q instrument with tetramethylsilane as an internal standard. Mass spectra were recorded either on a Hitachi Model RMU 6C instrument or on a JEOL D-300 instrument (high-resolution mass spectrophotometer).

Solvents and Reagents. Commercially available solvents (acetic acid, methanol, ethanol, dichloromethane, etc) were used without further purification for the preparation and degradation of (π-allyl)palladium complexes. Tetrahydrofuran and ether were distilled over sodium–benzophenone under argon. Sodium benzenesulfinate and sodium toluenesulfinate were purchased from Nakarai Chemical Co. Sodium neophylsulfinate was prepared according to the method described previously.[6a] Dimethylglyoxime (DMG) was obtained from a commercial source. *n*-Butyllithium (*n*-hexane solution) was purchased from Aldrich Chemical Co.

1,3-Dienes. Acyclic 1,3-dienes **1a–f,i** were obtained from commercial sources and distilled prior to use in the presence of a small amount of hydroquinone monomethyl ether. 5-Methyl-1,3-hexadiene (**1g**) and 5-phenyl-1,3-hexadiene (**1h**) were prepared by the Wittig reaction[29] of allyltriphenylphosphonium bromide with isobutyraldehyde and 2-phenylpropionaldehyde, respectively (*n*-BuLi, Et_2O, 0 °C). 3-Methyl-1,3-pentadiene (**1j**) was synthesized according to the reported method.[30] 3-Phenyl-1,3-pentadiene (**1k**) was prepared by a continuous distillation from 2-hydroxy-3-phenyl-3-pentene, small amounts of $KHSO_4$, and hydroquinone [93–96 °C (45 mmHg), bath temperature 160 °C, 77% yield]. The alcohol was obtained quantitatively by the reaction of 2-phenylcrotonaldehyde with MeMgI (ether, 0 °C).

1-Vinylcycloalkenes **5** (*n* = 3–10) and **5a,e–g** were obtained by the reaction of the corresponding cycloalkanones and vinylmagnesium bromide, followed by the dehydration of the thus-obtained vinyl carbinols through a continuous distillation from each carbinol in the presence of small amounts of $KHSO_4$ and hydroquinone (bath temperatures 160–190 °C). 6,6-Dimethyl-2-vinylbicyclo[3.1.1]hept-2-ene (**5b**) was prepared by the reaction of myrtenal and MeMgI in ether, followed by the usual dehydration ($KHSO_4$, hydroquinone, 66 °C (14–15 mmHg), bath temperature 140 °C, 45% yield). 1-Vinyl-3-oxa-cyclohexene (**5c**) and 1-vinyl-4,4-dimethylcyclopentene (**5d**) were prepared by the

(25) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164.
(26) A mixture of (*E*)- and (*Z*)-1-ethyliene-1,2,3,4-tetrahydronaphthalenes (69:31) was obtained by the reaction of α-tetralone with ethylenetriphenylphosphorane, generated by treatment of ethyltriphenylphosphonium bromide with potassium *tert*-butoxide in THF (−78 °C for 30 min, room temperature for 30 min, and then THF reflux for 30 min).
(27) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 NMR Spectroscopy", 2nd ed.; Wiley: New York, 1980. (c) Uskokovic, M. R.; Lewis, R. L.; Partridge, J. J.; Despreaux, C. W.; Pruess, D. L. *J. Am. Chem. Soc.* **1979**, *103*, 6742.
(28) Detail of this stereoselective rearrangement will be reported in due course.
(29) Maercker, A. *Org. React.* **1965**, *14*, 270.
(30) Kerides, L. P. *J. Am. Chem. Soc.* **1933**, *55*, 3434.

Wittig reaction of the corresponding aldehyde[31] and methyltriphenylphosphonium iodide (*n*-BuLi in ether and KO-*t*-Bu in THF, respectively).

General Procedure for Sulfonylpalladation. Into a homogeneous solution of $PdCl_2$ (1 mmol) and sodium neophylsulfinate (1.1–2 mmol) in the solvent (10–15 mL) shown in Table I or II was added the 1,3-diene (1.2–3 mmol). The mixture was stirred and heated under air at the temperatures and for the intervals indicated in Tables I and II. After being cooled to ambient temperature, the reaction mixture was poured into EtOAc (40–50 mL) and water (40 mL). This yellow mixture was stirred and neutralized by a careful addition of $NaHCO_3$. The aqueous layer was separated and extracted with EtOAc (30 mL). The combined organic layers were washed with saturated NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The sticky yellow residue was subjected to column purification (silica gel, benzene–EtOAc gradient) to provide an air-stable (in most cases), spectroscopically pure di-μ-chloro-bis[1-(sulfonylmethyl)-π-allyl]palladium complex.

3a: mp 170 °C dec (EtOH–$CHCl_3$); IR (KBr disk) 2980 (m), 1450 (m), 1319 (s), 1320 (sh), 1295 (sh), 1125 (s), 844 (m), 775 (m), 705 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 3 H), 1.67 (s, 3 H), 2.34 (dd, J = 14.0, 10.5 Hz, 1 H), 2.92 (dd, J = 14, 4 Hz, 1 H), 3.04 (d, J = 11.5 Hz, 1 H), 3.33 (s, 2 H), 3.50 (dt, J = 10.5, 4 Hz, 1 H), 4.06 (d, J = 7 Hz, 1 H), 5.32 (ddd, J = 11.5, 10.5, 7 Hz, 1 H). Anal. Calcd for $C_{14}H_{19}SO_2ClPd$: C, 42.76; H, 4.87; O, 8.14; Cl, 9.02. Found: C, 42.58; H, 5.19, O, 8.32; Cl, 9.45.

3c: heavy yellow oil; IR (neat film) 2960 (s) 1440 (m), 1310 (s), 1280 (m), 1140 (s), 910 (m), 760 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.60 (s, 6 H), 2.12 (s, 3 H), 2.58 (d, J = 13 Hz, 1 H), 2.78 (s, 1 H), 3.02 (d, J = 13 Hz, 1 H), 3.20 (s, 1 H), 3.80 (s, 1 H), 7.37 (m, 5 H). The neophylsulfonyl derivatives of **3c,e,f** did not give the satisfactory analytical data, and hence analyses of these complexes were performed on the *tert*-butylsulfonyl derivatives. Anal. (*tert*-butylsulfonyl derivative) Calcd for $C_{10}H_{19}SO_2ClPd$: C, 34.80; H, 5.55; O, 9.27; Cl, 10.27. Found: C, 34.84; H, 5.72; O, 9.55; Cl, 10.26.

3e: heavy yellow oil; IR (neat film) 2960 (m), 1420 (s), 1310 (s), 1120 (s), 755 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, J = 6 Hz, 3 H), 1.64 (s, 6 H), 2.5–3.1 (m, 2 H), 3.32 (s, 2 H), 3.2–3.4 (m, 1 H), 3.8–4.1 (m, 1 H), 5.24 (t, J = 10 Hz, 1 H), 7.4 (m, 5 H). Anal. (*tert*-butylsulfonyl derivative) Calcd for $C_9H_{17}SO_2ClPd$: C, 32.64; H, 5.35; O, 9.66; Cl, 10.71. Found: C, 32.71; H, 5.17; O, 9.49; Cl, 10.67.

3f: heavy yellow oil; IR (neat film) 3000 (s), 1530 (m), 1380 (m), 1320 (s), 1145 (s), 1130 (s), 780 (s), 745 (s), 705 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, J = 7 Hz, 3 H), 1.62 (m, 2 H), 1.67 (s, 6 H), 2.58 (dd, J = 14, 11 Hz, 1 H), 3.32 (s, 2 H), 3.91 (dt, J = 11, 6 Hz, 1 H), 5.19 (t, J = 11 Hz, 1 H), 7.4 (m, 5 H). Anal. (*tert*-Butylsulfonyl derivative) Calcd for $C_{10}H_{19}SO_2ClPd$: C, 34.80; H, 5.55; O, 9.27; Cl, 10.27. Found: C, 34.53; H, 5.65; O, 9.33; Cl, 10.24.

3g: mp 99–101 °C (EtOAc); IR (KBr) 2950 (m), 1460 (m), 1310 (s), 1280 (sh), 1130 (m), 1118 (m), 818 (m), 765 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 6 Hz, 6 H), 1.65 (s, 6 H), 1.94 (m, 1 H), 2.56 (dd, J = 13, 10 Hz, 1 H), 2.92 (dd, J = 13, 4 Hz, 1 H), 3.32 (s, 2 H), 3.30 (td, J = 10, 4 Hz, 1 H), 3.90 (dd, J = 12, 4 Hz, 1 H), 5.18 (t, J = 11 Hz, 1 H), 7.4 (m, 5 H). Anal. Calcd for $C_{17}H_{25}SO_2ClPd$: C, 46.90; H, 5.79; O, 7.35; S, 7.37; Cl, 8.19. Found: C, 47.09; H, 5.99; O, 7.10; S, 7.18; Cl, 8.03.

3h: heavy yellow oil; IR (neat film) 2950 (m), 1490 (m), 1450 (m), 1310 (s), 1240 (s), 1130 (m), 1045 (m), 765 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42–1.64 (m, 9 H), 2.24–3.48 (m containing two singlets at 3.22 and 3.30, 4 H), 4.0–4.16 (m, 1 H), 4.90–5.22 (t, J = 11 Hz, 1 H), 7.3–7.4 (m, 10 H). Anal. Calcd for $C_{22}H_{27}O_2SClPd$: C, 53.35; H, 5.47; O, 6.43; S, 6.45. Found: C, 52.83; H, 5.71; O, 6.22; S, 6.29.

3i: mp 150 °C dec ($CHCl_3$); IR (KBr) 2950 (m), 1440 (m), 1290 (s), 1110 (s), 1025 (m), 760 (m), 670 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, J = 7 Hz, 3 H), 1.44 and 1.58 (d, J = 8 Hz, 3 H), 1.63 and 1.68 (s, 3 H each), 2.71 (dd, J = 9, 7 Hz, 1 H), 3.09 (t, J = 10 Hz, 1 H), 3.24 (m, 2 H), 3.88 (qd, J = 11, 7 Hz, 1 H), 5.28–5.40 (t, J = 11 Hz, 1 H), 7.4 (m, 5 H). Anal. Calcd for $C_{16}H_{23}SO_2ClPd$: C, 45.61; H, 5.50; O, 7.60; Cl, 8.42. Found: C, 45.13; H, 5.51; O, 7.34; Cl, 8.67.

3j: mp 170 °C dec (EtOH–CH_2Cl_2); IR (KBr) 2960 (m), 1545 (m), 1310 (s), 1285 (m), 1135 (m), 1120 (m), 760 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (d, J = 7 Hz, 3 H), 1.61 (s, 3 H), 1.68 (s, 3 H), 1.96 (s, 3 H), 2.8–2.96 (m, 2 H), 3.16–3.37 (m, 3 H), 3.68 (q, J = 7 Hz, 1 H), 7.4 (m, 5 H). Anal. Calcd for $C_{16}H_{23}SO_2ClPd$: C, 45.62; H, 5.50; O, 7.60; S, 7.61; Cl, 8.42. Found: C, 45.42; H, 5.49; O, 7.72; S, 7.58; Cl, 8.39.

6 (n = 3): mp 176–177 °C dec (CH_2Cl_2–EtOH); IR (KBr) 1308 (vs), 1108 (vs), 762 (m), 698 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42–2.20 (m, 4 H), 1.62 (s, 6 H), 2.20–2.57 (m, 2 H), 2.76–3.03 (m, 1 H), 3.22–3.80 (m, 2 H), 3.36 (br s, 2 H), 3.97–4.23 (m, 1 H), 7.43 (br s, 5 H). Anal. Calcd for $C_{17}H_{23}SO_2ClPd$: C, 47.13; H, 5.35; Cl, 8.18; S, 7.40. Found: C, 46.85; H, 5.40; Cl, 7.97; S, 7.56.

6 (n = 4): mp 171–172 °C dec (benzene); IR (KBr) 1315 (vs), 1120 (vs), 965 (s), 765 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30–2.20 (m, 4 H), 1.66 (s, 6 H), 2.40–2.73 (m, 4 H), 2.78–3.03 (m, 1 H), 3.25 (d, J = 8.0 Hz, 2 H), 3.40 (s, 2 H), 4.15 (br s, 1 H), 7.20–7.64 (m, 5 H). Anal. Calcd for $C_{18}H_{25}ClO_2SPd$: C, 48.33; H, 5.63; Cl, 7.93; S, 7.17. Found: C, 48.86; H, 5.75; Cl, 7.86; S, 7.34.

6 (n = 6): mp 112–114 °C (CH_2Cl_2–EtOH); IR (KBr) 2920 (s), 1310 (m), 1115 (m), 695 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.20 (m, 8 H), 1.70 (s, 6 H), 1.90–2.90 (m, 5 H), 3.26–3.43 (br s, 2 H), 3.43 (s, 2 H), 3.66–3.93 (br s, 1 H), 7.20–7.76 (m, 5 H). Anal. Calcd for $C_{20}H_{29}ClO_2SPd$: C, 50.53; H, 6.15; Cl, 7.46; S, 6.74. Found: C, 50.39; H, 6.08; Cl, 7.64; S, 6.75.

6 (n = 6; *p*-toluenesulfonyl derivative): mp 184–186 °C dec (CH_2Cl_2–EtOH); IR (KBr) 1315 (m), 1150 (s), 815 (m), 735 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34–2.18 (m, 12 H), 2.46 (s, 3 H), 2.26–4.48 (m, 4 H), 7.21–7.53, 7.65–7.93 (AA'BB', 4 H). Anal. Calcd for $C_{17}H_{23}ClO_2SPd$: C, 47.13; H, 5.35; Cl, 8.18; O, 6.73; S, 7.40. Found: C, 46.85; H, 5.24; Cl, 8.48; O, 6.56; S, 7.12.

6 (n = 8): mp 107–109 °C (CH_2Cl_2–EtOH); IR (KBr) 2920 (s), 1314 (s), 1118 (s), 689 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–2.20 (m, 12 H), 1.63 (s, 6 H), 1.90–2.90 (m, 5 H), 3.31 (br s, 2 H), 3.43 (s, 2 H), 3.95–4.40 (br s, 1 H), 7.20–7.76 (m, 5 H). Anal. Calcd for $C_{22}H_{33}ClO_2SPd$: C, 52.49; H, 6.61; Cl, 7.04; S, 6.37. Found: C, 52.76; H, 6.95; Cl, 6.87; S, 6.19.

6 (n = 10): mp 173–175 °C dec (without recrystallization); IR (KBr) 2935 (s), 1316 (s), 1120 (m), 698 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–2.00 (m, 16 H), 1.66 (s, 6 H), 1.83–2.80 (m, 4 H), 2.88 (br s, 1 H), 3.22 (m, 2 H), 3.37 (s, 2 H), 3.30–3.73 (m, 1 H), 7.20–7.70 (m, 5 H). Anal. Calcd for $C_{24}H_{37}ClO_2SPd$: C, 54.24; H, 7.02; Cl, 6.67; O, 6.02; S, 6.03. Found: C, 53.98; H, 7.21; Cl, 6.77; O, 6.02; S, 5.78.

6a: mp 129–133 °C ($CHCl_3$–EtOH); IR (KBr) 1315 (s), 1120 (s), 765 (m), 742 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (s, 6 H), 1.87–3.17 (m, 6 H), 3.25 (s, 2 H), 4.20 (br s, 1 H), 4.50–4.90 (m, 1 H), 7.03–7.57 (m, 9 H). Anal. Calcd for $C_{22}H_{25}ClO_2SPd$: C, 53.34; H, 5.09; Cl, 7.16; S, 6.47. Found: C, 53.05; H, 5.21; Cl, 7.42; S, 6.39.

6b (phenylsulfonyl derivative): mp 100–102 °C (CH_2Cl_2–EtOH): IR (KBr) 2915 (m), 1305 (s), 1135 (vs), 1080 (m), 760 (m), 685 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.03 (s, 3 H), 1.39 (s, 3 H), 1.70–2.87 (m, 6 H), 2.87–4.33 (m, 2 H), 4.54 (br s, 1 H), 7.47–8.10 (m, 5 H). Anal. Calcd for $C_{17}H_{21}ClO_2SPd$: C, 47.35; H, 4.91; Cl, 8.22; S, 7.43. Found: C, 47.62; H, 5.15; Cl, 8.51; S, 7.18.

6c: mp 160 °C dec (benzene); IR (KBr) 2980 (w), 1602 (w), 1310 (s), 1110 (s), 835 (w), 765 (m), 695 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52–1.88 (m, 8 H), 2.22–2.88 (m, 2 H), 3.16–4.84 (m, 8 H), 7.30–7.52 (m, 5 H). Anal. Calcd for $C_{17}H_{23}ClO_3SPd$: C, 45.56; H, 4.95; Cl, 7.91; O, 10.71. Found: C, 45.84; H, 5.22; Cl, 7.87; O, 10.27.

6d: mp 168–170 °C dec (CH_2Cl_2–EtOH); IR (KBr) 2950 (m), 2920 (m), 1312 (s), 1138 (m), 1110 (s), 842 (m), 764 (m), 702 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.42 (s, 3 H), 1.63 (s, 3 H), 1.68 (s, 3 H), 2.11–2.55 (m, 2 H), 2.61–3.16 (m, 3 H), 3.33 (s, 2 H), 3.39–3.79 (m, 2 H), 4.20 (br s, 1 H), 7.29–7.71 (m, 5 H). Anal. Calcd for $C_{19}H_{27}ClO_2SPd$: C, 49.47; H, 5.90; Cl, 7.68; S, 6.95. Found: C, 49.69; H, 5.84; Cl, 7.75; S, 6.90.

6e: mp 160 °C dec (benzene); IR (KBr) 2940 (m), 1605 (w), 1310 (s), 1120 (s), 965 (m), 840 (m), 765 (m), 700 (s) cm^{-1}; ^1H NMR

(31) 5,6-Dihydro-2*H*-pyran-3-carboxyaldehyde is of commercial origin. 4,4-Dimethylcyclopentene-1-carboxaldehyde was prepared according to the method reported by Magnusson: Magnusson, G.; Thôren, S. *J. Org. Chem.* **1973**, *38*, 1380.

($CDCl_3$) δ 0.98–2.63 (m, 10 H), 1.62 (br s, 6 H), 2.63–4.35 (m, 6 H), 7.35 (br s, 5 H).

6f [a mixture of di-μ-chloro-bis[1-[(neophylsulfonyl)-methyl]-2,3-(2,2,4- and 2,4,4-trimethyltetramethylene)-π-allyl]palladium]: mp 175–176 °C dec (without recrystallization); IR (KBr) 2960 (s), 1602 (w), 1310 (s), 1120 (s), 840 (m), 770 (m), 700 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.67–1.40 (m, 9 H), 1.62 (br s, 6 H), 1.40–2.20 (m, 5 H), 2.20–4.15 (m, 6 H), 7.10–7.60 (m, 5 H). Anal. Calcd for $C_{21}H_{31}ClO_2SPd$: C, 51.54; H, 6.38; Cl, 7.24; O, 6.54; S, 6.50. Found: C, 50.95; H, 6.31; Cl, 7.49; O, 6.13; S, 6.67.

6g: semisolid (decomposes slowly at ambient temperature within a few hours); IR (KBr) 3060 (w), 2960 (s), 2920 (s), 1600 (w), 1310 (s), 1135 (m), 1115 (s), 960 (br s), 835 (m), 765 (m), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75–2.68 (m, 22 H), 2.68–4.43 (m, 6 H), 7.10–7.75 (m, 5 H).

General Procedure for Arylpalladation. Sodium benzene- or toluenesulfinate (1.2–2 mmol), $PdCl_2$ (1 mmol), and the 1,3-diene were dissolved in 15 mL of methanol, and the mixture was heated with stirring at 60–65 °C for 0.5–6 h under air. During the reaction the color of the mixture turned from deep red to yellow. After evaporation of the solvent under reduced pressure, a yellow residue was extracted with EtOAc. The extract was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave a yellow solid, which was purified by means of column chromatography (silica gel, benzene as an eluent) to provide an air-stable spectroscopically pure di-μ-chloro-bis[1-(arylmethyl)-π-allyl]palladium complex.

8b: mp 175 °C dec (EtOAc); IR (KBr) 1520 (s), 1460 (m), 1030 (m), 900 (m), 810 (m), 780 (w), 750 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 2.30 (s, 3 H), 2.73 (s, 1 H), 3.02 (d, J = 9 Hz, 1 H), 3.04 (d, J = 6 Hz, 1 H), 3.76 (s, 1 H), 3.80 (dd, J = 6, 9 Hz, 1 H), 7.08 (s, 4 H). Anal. Calcd for $C_{12}H_{15}ClPd$: C, 47.87; H, 5.02; Cl, 11.77. Found: C, 47.74; H, 4.97; Cl, 11.59.

8c: mp 150 °C dec (CH_3OH); IR (KBr) 1520 (s), 1450 (m), 1030 (w), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 2.10 (s, 3 H), 2.31 (s, 3 H), 3.00 (s, 2 H), 3.43 (s, 1 H), 3.93 (s, 1 H), 7.0 (m, 4 H). Anal. Calcd for $C_{13}H_{17}ClPd$: C, 49.55; H, 5.44; Cl, 11.25. Found: C, 49.50; H, 5.47; Cl, 11.70.

8d: heavy oil; IR (neat film) 2920 (m), 1515 (m), 1480 (m), 1450 (m), 1375 (m), 805 (m), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (s, 3 H), 1.68 (s, 3 H), 2.30 (s, 3 H), 2.1–2.5 (m, 4 H), 2.66 (s, 1 H), 3.03 (d, J = 8.5 Hz, 1 H), 3.04 (d, J = 6 Hz, 1 H), 3.74 (s, 1 H), 3.81 (dd, J = 6, 8 Hz, 1 H), 5.14 (m, 1 H), 7.10 (s, 4 H).

8f: mp 149.5–151 °C dec (EtOH); IR (KBr) 2980 (m), 1520 (s), 1460 (m), 1440 (m), 810 (m), 800 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, J = 9 Hz, 3 H), 1.60 (q, J = 9 Hz, 2 H), 2.33 (s, 3 H), 3.0 (d, J = 8 Hz, 2 H), 3.80 (dt, J = 15, 8 Hz, 2 H), 5.13 (t, J = 15 Hz, 1 H), 7.17 (s, 4 H). Anal. Calcd for $C_{13}H_{17}ClPd$: C, 49.55; H, 5.44; Cl, 11.25. Found: C, 49.67; H, 5.46; Cl, 11.32.

8h: mp 170 °C dec (EtOH–CH_2Cl_2); IR (KBr) 3030 (w), 2970 (m), 2920 (m), 1600 (w), 1515 (s), 1495 (m), 1450 (m), 1425 (s), 760 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57 (d, J = 7 Hz, 3 H), 2.32 (s, 3 H), 2.8–3.25 (m, 3 H), 3.8–4.1 (m, 2 H), 4.95 (t, J = 10 Hz, 1 H), 7.17 (s, 5 H), 7.4 (s, 5 H). Anal. Calcd for $C_{19}H_{21}ClPd$: C, 58.33; H, 5.41; Cl, 9.06. Found: C, 58.51; H, 5.14; Cl, 8.72.

9: mp 164–165 °C dec (EtOAc–hexane); IR (KBr) 2955 (m), 1602 (w), 1494 (s), 1450 (m), 746 (m), 696 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–2.90 (m, 8 H), 2.90–3.30 (m, 1 H), 3.76–4.33 (m, 1 H), 7.00–7.90 (m, 5 H). Anal. Calcd for $C_{13}H_{15}ClPd$: C, 49.87; H, 4.83; Cl, 11.32. Found: C, 49.66; H, 4.92; Cl, 11.39.

General Procedure for the Protiodepalladation of [1-(Sulfonylmethyl)-π-allyl]palladium Complexes 3 and 6 with DMG. To a homogeneous solution of (π-allyl)palladium complex (0.5 mmol) in an appropriate solvent (ca. 15 mL) as indicated in Table I or II was added dimethylglyoxime(1.0–1.5 mmol) in one portion. It is necessary to dissolve the palladium complex completely before addition of DMG, otherwise an intractable mixture of sulfones might be produced. The mixture was stirred at an ambient temperature under air (except for entry 12, Table II). After completion of the reaction (TLC monitoring), the mixture was diluted with EtOAc (50 mL) and neutralized with 1 N NaOH or saturated $NaHCO_3$. The aqueous layer was extracted with EtOAc (20 mL). The combined extracts were washed with saturated NaCl and dried over $MgSO_4$. After evaporation of the solvent, the residue was directly subjected to column chromatography (silica gel, hexane–EtOAc or benzene–EtOAc gradient) to provide alkenyl sulfone(s) in the yields shown in Tables I and II. The mixture of sulfones was separated by means of HPLC (μ-Porasil; hexane–EtOAc, 95:5), and the ratio of the components was determined on the basis of area intensities on HPLC or VPC (SiDC 550 or PEG, He carrier, 220–250 °C).

12a: bp 170 °C (3 mmHg); IR (neat film) 2960 (m), 1440 (w), 1300 (s), 1290 (sh), 1270 (sh), 1120 (s), 990 (w), 910 (w), 840 (m), 765 (m), 700 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.60 (s, 6 H), 2.30 (d, J = 2 Hz, 4 H), 3.22 (s, 2 H), 4.75–6.0 (m, 3 H), 7.2–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 252 (M^+, 1), 132 (70), 119 (10), 117 (16), 90 (100), 105 (10). Anal. Calcd for $C_{14}H_{20}SO_2$: C, 66.63; H, 7.99; O, 12.68; S, 12.70. Found: C, 66.37; H, 8.12; O, 12.75; S, 12.94.

13a: IR (neat film) 2980 (m), 1645 (w), 1320 (s), 1125 (s), 845 (m), 770 (m), 705 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.60 (d, J = 7 Hz, 3 H), 1.62 (s, 6 H), 3.08 (d, J = 7 Hz, 2 H), 3.12 (s, 2 H), 5.35 (dt, J = 10.5, 7 Hz, 1 H), 5.90 (dq, J = 10.5, 7 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 5), 149 (10), 133 (100), 119 (27), 105 (24), 91 (96).

(*E*)-4-(Neophylsulfonyl)-2-butene (trans isomer of 13a) was prepared by the sulfonylation of *trans*-crotyl bromide with sodium neophylsulfinate (acetone, room temperature, overnight): bp 150 °C (0.2 mmHg); IR (neat film) 2970 (m), 1445 (m), 1310 (s), 1285 (sh), 1130 (m), 1120 (s), 965 (m), 840 (m), 770 (m), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.60 (s, 6 H), 1.72 (d, J = 7 Hz, 3 H), 2.95 (d, J = 7 Hz, 2 H), 3.12 (s, 2 H), 5.32 (dt, J = 16, 7 Hz, 1 H), 5.57 (dq, J = 16, 7 Hz, 1 H), 7.2–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 252 (M^+, 2), 187 (5), 133 (100), 91 (59). Anal. Calcd for $C_{14}H_{20}SO_2$: C, 66.63; H, 7.99; O, 12.68. Found: C, 66.81; H, 8.28; O, 12.52.

12b: bp 140 °C (0.1 mmHg); IR (neat film) 2960 (s), 1650 (m), 1440 (m), 1310 (s), 1280 (s), 1120 (s), 900 (m), 840 (m), 760 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.63 (s, 6 H), 2.32 (s, 4 H), 3.28 (s, 2 H), 4.44 (br s, 1 H), 4.68 (br s, 1 H), 7.4–7.20 (m, 5 H); mass spectrum, m/e (relative intensity) 266 (M^+, 2), 133 (47), 119 (13), 105 (10), 91 (100). Anal. Calcd for $C_{15}H_{22}SO_2$: C, 67.63; H, 8.32; O, 12.01. Found: C, 67.54; H, 8.59; O, 11.97.

12c: bp 150 °C (0.15 mmHg); IR (neat film) 2980 (s), 1640 (w), 1300 (s), 1290 (m), 1135 (m), 1120 (s), 900 (m), 840 (m), 770 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.07 (d, J = 6 Hz, 3 H), 1.56 (m, 3 H), 1.62 (s, 6 H), 2.22 (dd, J = 14, 8 Hz, 1 H), 2.46 (dd, J = 14, 5 Hz, 1 H), 2.85 (ddd, J = 8, 6, 5 Hz, 1 H), 3.25 (s, 2 H), 4.62 (m, 1 H), 4.68 (m, 1 H), 7.5–7.3 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 1), 199 (1), 133 (43), 119 (10), 105 (7), 96 (6), 91 (100). Anal. Calcd for $C_{12}H_{24}SO_2$: C, 68.53; H, 8.63; O, 11.41. Found: C, 68.73; H, 8.93; O, 11.55.

12d: bp 158 °C (0.05 mmHg); IR (neat film) 2960 (s), 1440 (m), 1310 (s), 1280 (m), 1120 (s), 840 (w), 760 (m), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.58 (br s, 3 H), 1.65 (br s, 3 H), 1.63 (s, 6 H), 1.85–2.15 (m, 4 H), 2.33 (s, 4 H), 3.28 (s, 2 H), 4.48 (br s, 1 H), 4.70 (br s, 1 H), 5.1 (m, 1 H), 7.2–7.5 (m, 5 H). Anal. Calcd for $C_{20}H_{30}SO_2$: C, 71.81; H, 9.04; O, 9.57. Found: C, 72.06; H, 9.08; O, 9.44.

12e: bp 140 °C (0.1 mmHg); IR (neat film) 2970 (m), 1610 (w), 1450 (m), 1310 (s), 1290 (sh), 1275 (sh), 1135 (sh), 1120 (s), 845 (m), 770 (m), 705 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.60 (d, J = 6 Hz, 3 H), 1.62 (s, 6 H), 2.23 (br s, 4 H), 3.12 (s, 2 H), 5.12 (td, J = 11, 6 Hz, 1 H), 5.48 (dq, J = 11, 6 Hz, 1 H), 7.2–7.45 (m, 5 H); mass spectrum, m/e (relative intensity) 266 (M^+, 12), 197 (49), 133 (100), 119 (20), 91 (80). Anal. Calcd for $C_{15}H_{22}SO_2$: C, 67.62; H, 8.33; O, 12.04. Found: C, 68.87; H, 8.45; O, 12.11.

***trans*-1-(Neophylsulfonyl)-3-pentene** (trans isomer of 12e) was prepared as follows. To a THF solution of (neophylsulfonyl)methyllithium, generated by treatment of neophyl methyl sulfone with 1.1 equiv of *n*-BuLi at 0 °C, was added *trans*-crotyl chloride with stirring at 0 °C, and then the temperature was allowed to warm to ambient temperature (4 h). The usual workup and purification by column chromatography (silica gel, benzene) provided the title compound: 86% yield; bp 160 °C (0.15 mmHg); IR (neat film) 2980 (m), 1605 (w), 1445 (m), 1310 (s), 1130 (s), 1120 (s), 970 (m), 845 (m), 770 (m), 705 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.62 (br s, 9 H), 2.22–2.41 (m, 4 H), 3.15 (s, 2 H), 5.18 (m, 1 H), 5.4 (dq, J = 15, 5 Hz, 1 H), 7.18–7.45 (m, 5 H); mass spectrum, m/e (relative intensity); 266 (M^+, 1), 199 (7), 133 (83). Anal. Calcd for $C_{15}H_{22}SO_2$: C, 67.62; H, 8.33; O, 12.01. Found: C, 67.87; H, 8.45; O, 12.11.

14e: bp 140 °C (0.1 mmHg); IR (neat film) 2980 (m), 1450 (m),

1310 (s), 1290 (sh), 1130 (s), 1120 (s), 1000 (w), 920 (m), 835 (m), 770 (m), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (d, J = 6 Hz, 3 H), 1.66 (s, 6 H), 3.08 (s, 2 H), 4.95–5.65 (m, 3 H), 7.2–7.5 (m, 5 H); mass spectrum, calcd for $C_{15}H_{22}SO_2$ m/e 226.1339, found m/e 266.1364.

12f: bp 140 °C (0.01 mmHg); IR (neat film) 2980 (s), 1320 (s), 1290 (m), 1140 (s), 1135 (s), 850 (m), 780 (m), 710 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (t, J = 7 Hz, 3 H), 1.63 (s, 6 H), 2.0 (t, J = 7 Hz, 2 H), 2.2 (br s, 4 H), 3.15 (s, 2 H), 5.18 (dt, J = 10.5, 6 Hz, 1 H), 5.27 (dt, J = 10.5, 7 Hz, 1 H), 7.15–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 100), 200 (61), 199 (96), 134 (77), 133 (96), 132 (60). Anal. Calcd for $C_{16}H_{24}SO_2$: C, 68.53; H, 8.63; O, 11.41. Found: C, 68.43; H, 8.85; O, 11.65.

14f: IR (neat film) 2970 (s), 1605 (w), 1460 (sh), 1430 (m), 1305 (s), 1285 (sh), 1130 (sh), 1120 (s), 1000 (w), 920 (m), 840 (m), 770 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (t, J = 7 Hz, 3 H), 1.5–2.5 (m, 11 H), 3.07 (s, 2 H), 4.95–5.80 (m, 3 H), 7.16–7.44 (m, 5 H); mass spectrum, calcd for $C_{16}H_{24}SO_2$ m/e 280.1496, found m/e 280.1490.

12g: bp 165 °C (0.15 mmHg); IR (neat film) 2950 (s), 1590 (w), 1460 (m), 1440 (m), 1305 (s), 1280 (sh), 1260 (s), 1115 (s), 1025 (m), 840 (m), 790 (m), 760 (m), 695 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (d, J = 6 Hz, 6 H), 1.62 (s, 6 H), 2.2 (m, 4 H), 2.56 (m, 1 H), 3.15 (s, 2 H), 4.92 (dt, J = 10, 6 Hz, 1 H), 5.20 (dd, J = 10, 9 Hz, 1 H), 7.2–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 294 (M^+, 3), 247 (2), 218 (3), 199 (9), 133 (90), 119 (31), 97 (100), 81 (78). Anal. Calcd for $C_{17}H_{26}SO_2$: C, 69.34; H, 8.90; O, 10.87. Found: C, 69.14; H, 9.01; O, 10.83.

12h: bp 205 °C (0.01 mmHg); IR (neat film) 2960 (m), 1600 (w), 1490 (m), 1450 (m), 1310 (s), 1130 (sh), 1120 (s), 1030 (w), 840 (w), 765 (m), 695 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (d, J = 7 Hz, 3 H), 1.60 (s, 3 H), 2.25 (br, 4 H), 3.10 (s, 2 H), 3.7 (m, J = 9, 7 Hz, 1 H), 5.17 (m, 1 H), 5.62 (dd, J = 10, 9 Hz, 1 H), 7.1–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 356 (M^+, 64), 267 (6), 199 (7), 143 (100), 108 (100). Anal. Calcd for $C_{22}H_{28}SO_2$: C, 74.11; H, 7.92; O, 8.98. Found: C, 74.11; H, 7.83; O, 8.71.

12i: bp 160 °C (0.3 mmHg); IR (neat film) 2960 (s), 1605 (w), 1445 (m), 1305 (s), 1285 (sh), 1130 (s), 1115 (s), 835 (m), 760 (m), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (d, J = 6 Hz, 3 H), 1.60 (d, J = 6 Hz, 3 H), 1.63 (s, 6 H), 2.0–2.6 (m, 3 H), 3.10 (s, 2 H), 5.12 (m, 1 H), 5.56 (dq, J = 11, 6 Hz, 1 H), 7.1–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 1), 199 (81), 133 (99), 91 (98), 83 (100), 55 (97). Anal. Calcd for $C_{16}H_{24}SO_2$: C, 68.53; H, 8.63; O, 11.41. Found: C, 68.26; H, 8.64; O, 11.44.

12j: bp 150 °C (0.7 mmHg); IR (neat film) 2970 (m), 1605 (w), 1145 (m), 1310 (s), 1280 (m), 1130 (sh), 1120 (s), 845 (m), 770 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.5 (br s, 6 H), 1.64 (s, 6 H), 2.33 (s, 4 H), 3.28 (s, 2 H), 5.24 (m, 1 H), 7.2–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 3), 199 (100), 133 (59). Anal. Calcd for $C_{16}H_{24}SO_2$: C, 68.53; H, 8.63; O, 11.41. Found: C, 68.68; H, 8.69; O, 11.13.

(*E*)-1-(Neophylsulfonyl)-2-methylpent-3-ene (*E* isomer of **12j**) was prepared according to the procedure mentioned for the preparation of 1-(neophylsulfonyl)-*trans*-pent-3-ene by alkylation of 2-methyl-2-butenyl bromide (E/Z ratio of 73:27) with (neophylsulfonyl)methyllithium. The mixture of *E* and *Z* isomers was separated by means of HPLC (μ-Porasil; hexane–EtOAc, 95:5): bp 160 °C (0.1 mmHg); IR (neat film) 2970 (s), 1600 (w), 1445 (m), 1310 (s), 1290 (m), 1270 (m), 1115 (s), 1030 (m), 845 (m), 770 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.43–1.60 (m, 6 H), 1.64 (s, 6 H), 2.33 (br s, 4 H), 3.26 (s, 2 H), 5.12 (m, 1 H), 7.24–7.5 (m, 5 H); mass spectrum, m/e (relative intensity) 199 (91), 135 (45), 119 (15), 82 (100). Anal. Calcd for $C_{16}H_{24}SO_2$: C, 68.53; H, 8.63; O, 11.41. Found: C, 68.77; H, 8.88; O, 11.42.

12k: bp 190 °C (0.005 mmHg); IR (neat film) 3050 (w), 2960 (s), 1600 (w), 1490 (m), 1440 (m), 1305 (s), 1280 (m), 1120 (s), 760 (s), 695 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.57 (s, 6 H), 1.76 (d, J = 7.0 Hz, 3 H), 2.0–2.45, 2.6–3.0 (m, A_2B_2, 2 H each), 3.11 (s, 2 H), 5.77 (q, J = 7.0 Hz, 1 H), 7.2 (m, 10 H). Anal. Calcd for $C_{21}H_{26}SO_2$: C, 73.64; H, 7.56; O, 9.34. Found: C, 73.60; H, 7.81; O, 9.11.

1-(Neophylsulfonyl)-3-phenyl-(*Z*)-pent-3-ene was prepared similarly to the preparation 1-(neophylsulfonyl)-*trans*-pent-3-ene by alkylation of (*E*)-2-phenyl-2-butenyl tosylate [generated in situ by treatment of the corresponding alcohol with 1.1 equiv of *n*-BuLi, followed by addition of 1.05 equiv of TsCl (at 0 °C in THF)] with (neophylsulfonyl)methyllithium (40% yield). The *E* alcohol was obtained (90%, $LiAlH_4$ in ether) by the reduction of (*E*)-2-phenylcrotonaldehye, which was prepared selectively by the cross-aldol condensation (50%, AcONa in EtOH) of phenylacetaldehyde and acetaldehyde (see Scheme II): bp 200 °C (0.01 mmHg); IR (neat film) 3070 (w), 3030 (w), 2975 (s), 1603 (w), 1490 (m), 1440 (m), 1310 (s), 1285 (m), 1265 (m), 1115 (s), 820 (m), 765 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.50 (d, J = 8 Hz, 3 H), 1.58 (s, 6 H), 2.0–2.35, 2.5–2.85 (m, A_2B_2, 2 H each), 3.11 (s, 2 H), 5.50 (q, J = 8 Hz, 1 H), 6.95–7.5 (m, 10 H). Anal. Calcd for $C_{21}H_{28}SO_2$: C, 73.64; H, 7.65; O, 9.34. Found: C, 73.60; H, 7.55; O, 9.09.

13k: bp 190 °C (0.005 mmHg); IR (neat film) 3050 (w), 2970 (s), 1600 (w), 1500 (w), 1445 (m), 1310 (s), 1285 (m), 1115 (s), 840 (m), 765 (s), 695 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (t, J = 7 Hz, 3 H), 1.65 (s, 6 H), 2.35 (q, J = 7 Hz, 2 H), 3.20 (d, J = 7 Hz, 2 H), 3.23 (s, 3 H), 5.50 (t, J = 7 Hz, 1 H), 7.3 (m, 10 H). Anal. Calcd for $C_{21}H_{26}SO_2$: C, 73.64; H, 7.65; O, 9.34. Found: C, 73.50; H, 7.70; O, 9.50. The authentic sample of **13k** was prepared as follows. A mixture of (*E*)- and (*Z*)-ethyl 3-phenyl-2-butenoates (7:3), prepared by the Wittig–Horner reaction of ethyl (dimethylphosphono)acetate with phenyl ethyl ketone (NaH in benzene–DMF, room temperature),[32] was separated easily by column chromatography (silica gel, benzene). *E* isomer: R_f 0.65 (silica gel plate, benzene); IR (neat film) 1705 (s), 1615 (m), 1440 (m), 1360 (m), 1280 (m), 1155 (s), 1030 (m), 865 (m), 760 (m), 690 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.08 (t, J = 7.0 Hz, 3 H), 1.29 (t, J = 7.0 Hz, 3 H), 3.13 (q, J = 7.0 Hz, 2 H), 4.19 (q, J = 7.0 Hz, 2 H), 6.00 (s, 1 H, calcd value 6.20),[24] 7.4 (m, 5 H). *Z* isomer: R_f 0.36 (silica gel plate, benzene); IR (neat film) 1715 (s), 1630 (m), 1435 (m), 1360 (m), 1265 (m), 1215 (s), 1150 (s), 1040 (m), 690 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.02 (t, J = 7 Hz, 3 H), 1.06 (t, J = 7 Hz, 3 H), 2.45 (q, J = 7 Hz, 2 H), 3.91 (q, J = 7 Hz, 2 H), 5.81 (t, J = 1 Hz, 1 H, calcd value 5.76),[25] 7.3 (m, 5 H). The separated *E* isomer was reduced with $LiAlH_4$ in ether, tosylated (1.1 equiv of *n*-BuLi and then 1.1 equiv of TsCl, 0 °C, in THF), and then sulfonylated with sodium neophylsulfinate (THF–Me_2SO reflux) to provide the sulfone (10% overall yield), which showed the identical retention times on VPC (SiDC 550 and PEG) and IR and ^1H NMR spectra in all respects with those of **13k**.

19 (n = 3): bp 185 °C (0.2 mmHg); IR (neat film) 2960 (s), 1312 (vs), 1135 (s), 1120 (s), 768 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.61 (s, 6 H), 1.46–1.83 (m, 4 H), 1.97–2.49 (m, 4 H), 3.05 (dt, J = 7.6, 2.0 Hz, 2 H), 3.19 (s, 2 H), 5.21 (tt, J = 7.6, 2.0 Hz, 1 H), 7.13–7.60 (m, 5 H); mass spectrum, m/e (relative intensity) 292 (M^+, 1) 199 (29), 133 (51), 119 (51), 109 (49), 95 (100), 94 (92), 91 (56). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27; O, 10.94. Found: C, 69.91; H, 8.23; O, 11.19.

19 (n = 4): bp 200 °C (0.2 mmHg); IR (KBr) 2920 (vs), 1305 (vs), 1285 (s), 1130 (vs), 1115 (vs), 760 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–1.80 (m, 6 H), 1.59 (s, 6 H), 1.90–2.27 (m, 4 H), 3.06 (d, J = 8.0 Hz, 2 H), 3.12 (s, 2 H), 5.01 (t, J = 7.0 Hz, 1 H), 7.05–7.48 (m, 5 H); mass spectrum, m/e (relative intensity) 306 (M^+, 1), 199 (43), 133 (62), 110 (96), 107 (100), 81 (29). Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.55; H, 8.55; O, 10.44. Found: C, 70.41; H, 8.58; O, 10.68.

19 (n = 6): bp 200 °C (0.01 mmHg); IR (neat film) 2920 (s), 1624 (w), 1308 (s), 1240 (s), 762 (m), 696 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.80 (m, 10 H), 1.63 (s, 6 H), 1.86–2.56 (m, 4 H), 3.00 (d, J = 7.5 Hz, 2 H), 3.13 (s, 2 H), 5.18 (br t, J = 7.5 Hz, 1 H), 7.10–7.66 (m, 5 H); mass spectrum, m/e (relative intensity) 334 (M^+, 4), 137 (100), 91 (98), 81 (100). Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.81; H, 9.04; O, 9.57. Found: C, 71.56; H, 8.84; O, 9.77.

19 (n = 6, *p*-tolylsulfonyl derivative): mp 49–50 °C (benzene–*n*-hexane); IR (KBr) 2930 (s), 1650 (w), 1315 (m), 1150 (s), 745 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.80 (m, 10 H), 1.80–2.37 (m, 4 H), 2.46 (s, 3 H), 3.83 (d, J = 8.0 Hz, 2 H), 5.23 (t, J = 8.0 Hz, 1 H), 7.21–7.48, 7.66–7.91 (m, AA′BB′, 2 H each); mass spectrum, m/e (relative intensity) 292 (M^+, 0.7), 137 (90), 95 (90), 81 (100). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27; O, 10.94. Found: C, 69.65; H, 8.43; O, 11.15.

19 (n = 8): bp 215 °C (0.01 mmHg); IR (neat film) 2930 (s), 1656 (w), 1310 (s), 1284 (s), 1136 (s), 1284 (s), 1136 (s), 1118 (s), 698 (s), 676 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–1.60 (m, 14 H), 1.64

(32) Wadsworth, W. S., Jr. *Org. React.* **1977**, *25*, 73.

(s, 6 H), 1.80–2.50 (m, 4 H), 3.26 (d, J = 2.6 Hz, 2 H), 3.30 (s, 2 H), 5.20 (t, J = 8.0 Hz, 1 H), 7.12–7.56 (m, 5 H); mass spectrum, m/e (relative intensity) 362 (M^+, 0.04), 296 (1), 164 (78), 133 (51), 109 (58), 83 (100), 81 (57). Anal. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45; O, 8.83. Found: C, 72.91; H, 9.38; O, 9.13.

19 (n = 10): bp 215 °C (0.01 mmHg); IR (neat film) 2930 (s), 1658 (w), 1310 (s), 1116 (s), 762 (m), 696 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.60 (m, 16 H), 1.65 (s, 6 H), 1.72–2.20 (m, 4 H), 3.24 (d, J = 7.6 Hz, 2 H), 3.25 (s, 2 H), 5.25 (t, J = 7.6 Hz, 1 H), 7.12–7.56 (m, 5 H); mass spectrum, m/e 390 (M^+). Anal. Calcd for $C_{24}H_{38}O_2S$: C, 73.79; H, 9.81; O, 8.19; S, 8.21. Found: C, 73.56; H, 9.97; O, 8.48; S, 8.27.

19a: oil; IR (neat film) 1630 (w), 1605 (w), 1310 (s), 1115 (s), 835 (m), 785 (s), 755 (s), 700 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.62 (s, 6 H), 1.50–2.00 (m, 2 H), 2.15–2.55 (m, 2 H), 2.74 (t, J = 6.0 Hz, 2 H), 3.24 (s, 2 H), 3.27 (d, J = 8.0 Hz, 2 H), 5.87 (t, J = 8.0 Hz, 1 H), 7.03–7.73 (m, 9 H); mass spectrum, m/e 354 (M^+). Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.54; H, 7.39; O, 9.03. Found: C, 74.36; H, 7.53; O, 9.15.

19b: oil; IR (neat film) 2905 (s), 1655 (w), 1300 (s), 1150 (s), 1080 (m), 735 (m), 685 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.58 (s, 3 H), 1.21 (s, 3 H), 1.57–2.61 (m, 8 H), 3.77 (d, J = 8 Hz, 2 H), 5.00 (t, J = 8 Hz, 1 H), 7.48–8.13 (m, 5 H); mass spectrum, m/e 290 (M^+). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64; O, 11.02. Found: C, 70.58; H, 7.82; O, 10.87.

19c: oil; IR (neat film) 2960 (m), 1600 (w), 1310 (s), 1120 (s), 1085 (s), 770 (m), 700 (.(m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52–1.82 (m, 2 H), 1.64 (s, 6 H), 2.24 (t, J = 6.5 Hz, 2 H), 3.14 (d, J = 8.0 Hz, 2 H), 3.24 (s, 2 H), 3.72 (t, J = 5.4 Hz, 2 H), 4.00 (s, 2 H), 5.20 (br t, J = 8.0 Hz, 1 H), 7.22–7.54 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.27, 27.22 (C-5, C-6), 28.52 (C-6′), 37.80 (C-5′), 53.53 (C-2′), 64.63 (C-4′), 68.18 (C-4), 73.51 (C-2), 109.70 (C-1′), 125.87, 128.60 (C-8′, C-9′), 126.91 (C-10′), 144.60 (C-7′), 145.94 (C-1); mass spectrum, m/e (relative intensity) 308 (M^+, 3), 244 (8), 199 (100), Calcd for $C_{17}H_{24}O_3S$ m/e 308.1446, found m/e 308.1476.

22: oil; IR (neat film) 3480 (br s), 2960 (m), 1600 (w), 1305 (s), 1115 (s), 960 (w), 840 (m), 770 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.62 (s, 3 H), 1.78–2.10 (m, 2 H), 3.13 (dd, J = 8.0, 4.0 Hz, 2 H), 3.31 (s, 2 H), 3.62–3.82 (m, 2 H, collapsing to a br s upon irradiation at 1.95), 4.05 (s, 2 H), 4.44 (t, J = 4.5 Hz, 1 H, collapsing to a singlet upon irradiation at 1.95), 5.44 (t, J = 8.0 Hz, 1 H, collapsing to a singlet upon irradiation at 3.13), 5.58–5.96 (br, 1 H), 7.22–7.56 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.30, 28.95 (2 C-6′), 31.55 (C-5), 37.80 (C-5′), 53.31 (C-2′), 63.72 (C-2, C-4), 65.19 (C-4′), 82.27 (C-6), 114.34 (C-1′), 125.92, 128.73 (C-8′, C-9′), 127.09 (C-10′), 142.12 (C-7′), 145.47 (C-1); mass spectrum, m/e 324 (M^+). A satisfactory analysis was not obtained for this compound due to impurities not separable by preparative TLC [benzene–EtOA (2:1) or $CHCl_3$–EtOAc (2:1)].

19d: bp 195 °C (0.01 mmHg); IR (neat film) 2950 (s), 1672 (w), 1606 (w), 1308 (s), 1136 (s), 1118 (s), 766 (m), 698 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (s, 6 H), 1.46 (t, J = 7.6 Hz, 2 H), 1.63 (s, 6 H), 2.09 (br s, 2 H), 2.23 (br t, J = 7.6 Hz, 2 H, sharpens upon irradiation at 5.21, collapsing to a br s upon irradiation at 1.46), 3.13 (d, J = 7.6 Hz, 2 H), 3.24 (s, 2 H), 5.21 (tt, J = 7.6, 1.5 Hz, 1 H, collapsing to a t, J = 7.6 Hz, upon irradiation at 2.23), 7.18–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.18 (C-6), 27.74 (C-5), 28.26 (C-6′), 37.58, 38.32 (C-3, C-5′), 39.56 (C-4), 48.85 (C-2), 56.13 (C-2′), 64.02 (C-4′), 106.45 (C-1′), 125.53 (C-8′), 126.52 (C-10′), 128.34 (C-9′), 146.16 (C-7′), 154.35 (C-1); mass spectrum, m/e (relative intensity) 320 (M^+, 0.04), 133 (7), 123 (100), 91 (35), 81 (53). Anal. Calcd for $C_{19}H_{28}O_2S$: C, 71.21; H, 8.81; O, 9.98; S, 10.00. Found: C, 70.97; H, 9.03; O, 9.91; S, 10.12.

19e: bp 200 °C (0.01 mmHg); IR (neat film) 2925 (m), 1655 (m)8, 1310 (s), 1135 (m), 1115 (s), 765 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 6.6 Hz, 3 H), 1.66 (s, 6 H), 1.16–2.56 (m, 9 H), 3.26 (s, 2 H), 3.26 (d, J = 8.0 Hz, 2 H), 5.09 (t, J = 8.0 Hz, 1 H), 7.20–7.59 (m, 5 H); mass spectrum, m/e (relative intensity) 320 (M^+, 0.8), 256 (3), 133 (31), 123 (100), 122 (100), 91 (39), 81 (100), 67 (100). Anal. Calcd for $C_{19}H_{28}O_2S$: C, 71.21; H, 8.80; O, 9.98. Found: C, 71.40; H, 8.94, O, 9.77. An authentic sample of **19e** was prepared by sulfonylation [sodium neophylsulfinate (2.0 equiv) and NaI (1.2 equiv) in MeOH at 65 °C for 0.5 h; 54% isolated yield] of the tosylate of (*E*)-1-(2-hydroxyethylidene)-2-methylcyclohexane. The alcohol was prepared by hydrolysis (1.5 equiv KOH in MeOH at 40 °C for 1 h; 87% yield) of the corresponding acetate, which was produced as a single product by the Pd(II)-catalyzed rearrangement of 1-acetoxy-1-vinyl-2-methylcyclohexane (2:1 diastereomeric mixture).[28] The *E* structure of this alcohol was determined on the basis of a greater europium-(III)-induced shift of the allylic methylene protons in the cyclohexane ring than of the methyl or allylic methyne protons.

19f (mixture of *E* and *Z* isomers): bp 200 °C (0.01 mmHg); IR (neat film) 2950 (s) 1665 (w), 1605 (w), 1310 (s), 1120 (s), 840 (m), 770 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (d, J = 5.2 Hz, 3 H), 0.93 (s, 3 H), 0.96 (s, 3 H), 1.64 (s, 6 H), 1.18–2.44 (m, 7 H), 3.04–3.36 (m, 2 H), 3.24 (s, 2 H), 4.92–5.32 (m, 1 H), 8.16–8.54 (m, 5 H); mass spectrum, m/e (relative intensity) 348 (M^+, 1), 284 (6), 165 (32), 151 (100), 109 (66), 95 (99), 81 (81). Anal. Calcd for $C_{21}H_{32}O_2S$: C, 72.37; H, 9.25; O, 9.18. Found: C, 72.16; H, 9.27; O, 8.91.

19g (mixture of *E* and *Z* isomers): bp 210 °C (0.01 mmHg); IR (neat film) 2950 (s), 2925 (s), 1310 (s), 1135 (m), 1120 (s), 840 (w), 765 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (br s, 6 H), 1.24 (br s, 6 H), 1.34–1.72 (m, 1 H), 1.63 (s, 6 H), 1.90–2.51 (m, 5 H), 3.14 (d, J = 8 Hz, 2 H), 3.24 (s, 2 H), 5.22 (br t, J = 8 Hz, 1 H), 7.14–7.52 (m, 5 H); mass spectrum, m/e (relative intensity) 362 (M^+, 1), 305 (67), 165 (99), 164 (99), 123 (79), 109 (99), 108 (100), 107 (93), 95 (99), 81 (98). Anal. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45; O, 8.83. Found: C, 73.08; H, 9.46; O, 9.13.

General Procedure for the Degradation of [1-(Arylmethyl)-π-allyl]palladium Complexes 8 and 9. The [1-(arylmethyl)-π-allyl]palladium complexes **8** and **9** were degradated in a manner similar to that for the cases of **3** and **6** by treatment with 2 equiv of DMG at room temperature under air: **8b,c,d,f** in CH_3OH, **8h** in CH_3OH in the presence of 4.5 equiv of pyridine, and **9** in AcOH–$CHCl_3$. A mixture of products was separated by means of preparative VPC (SiDC 550, He carrier).

2-Methyl-4-*p*-tolyl-1-butene: bp 140 °C (34 mmHg); IR (neat film) 2940 (s), 1655 (m), 1520 (m), 1460 (m), 1380 (w), 900 (s), 810 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.77 (s, 3 H), 2.33 (s, 3 H), 2.2–2.45 (m, 4 H), 2.7–2.9 (m, 2 H), 4.77 (s, 2 H), 7.07 (s, 4 H); mass spectrum, m/e (relative intensity) 160 (58), 145 (17), 106 (26), 105 (100), 91 (16).

2-Methyl-4-*p*-tolyl-2-butene: IR (neat film) 2980 (m), 2930 (s), 1520 (s), 1450 (s), 1380 (w), 1100 (m), 860 (m), 810 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.70 (s, 6 H), 2.27 (s, 3 H), 3.23 (d, J = 11 Hz, 2 H)8, 5.26 (t, J = 11 Hz, 1 H), 6.93 (s, 4 H); mass spectrum, m/e (relative intensity) 160 (M^+, 47), 145 (100), 130 (19), 105 (36), 91 (33), 77 (23).

2,3-Dimethyl-4-*p*-tolyl-1-butene: bp 145 °C (22 mmHg); IR (neat film) 2940 (s), 1650 (m), 1520 (s), 1460 (s), 1380 (m), 900 (s), 810 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (d, J = 10 Hz, 3 H), 1.6 (m, 7 H), 1.70 (m, 3 H), 2.30 (s, 3 H), 2.5 (m, 2 H), 4.67 (m, 2 H), 6.97 (s, 4 H); mass spectrum, m/e (relative intensity) 174 (M^+, 29), 159 (14), 166 (39), 105 (100), 103 (15), 91 (14), 77 (30). Anal. Calcd for $C_{13}H_{18}$: C, 89.96; H, 10.04. Found: C, 90.08; H, 10.29.

1-*p*-Tolyl-3-(4-methyl-3-penten-1-yl)-2-butene: bp 148 °C (2 mmHg); IR (neat film) 2930 (s), 1520 (m), 1450 (m), 1380 (m), 800 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.58 (s, 3 H), 1.66 (br s, 6 H), 2.03 (br s, 4 H), 2.26 (s, 3 H), 3.25 (d, J = 7 Hz, 2 H), 5.02 (m, 1 H), 5.28 (t, J = 7 Hz, 1 H), 6.92 (s, 4 H); mass spectrum, m/e (relative intensity 228 (M^+, 26), 185 (52), 150 (100), 145 (66), 123 (82), 105 (100), 91 (66). Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.61; H, 10.55.

***cis*-1-*p*-Tolyl-5-phenyl-3-hexene (10)**: bp 160 °C (0.1 mmHg) (as a mixture with **11**); IR (neat film) 3030 (m), 3010 (m), 2960 (s), 2930 (s), 1600 (w), 1515 (m), 1495 (m), 1450 (s), 810 (m), 755 (m), 740 (br s) cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (d, J = 7 Hz, 3 H), 2.30 (s, 3 H), 2.34–2.72 (m, 4 H), 5.44–5.64 (m, 2 H), 7.0–7.3 (m, 10 H); mass spectrum, m/e (relative intensity) 250 (M^+, 22), 145 (42), 105 (100).

***cis*-1-*p*-Tolyl-5-phenyl-2-hexene (11)**: IR (neat film) 3020 (m), 2960 (s), 2920 (m), 1600 (w), 1515 (m), 1490 (m), 1450 (s), 800 (s), 760 (s), 695 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.30 (d, J = 7 Hz, 3 H), 2.30 (s, 3 H), 2.43 (t, J = 6 Hz, 2 H), 2.78 (center of m, 1 H), 3.30 (d, J = 6 Hz, 2 H), 5.3–5.7 (m, 2 H), 6.9–7.3 (m, 5 H); mass spectrum, m/e (relative intensity) 250 (M^+, 7), 145 (10), 105 (100).

(2-Phenylethylidene)cyclopentane: IR (neat film) 3170 (m), 3040 (m), 2950 (s), 1672 (w), 1604 (w), 734 (s), 694 (s); ^1H NMR ($CDCl_3$) δ 1.44–1.88 (m, 4 H), 2.10–2.44 (m, 4 H), 3.33 (dd, J =

7.2, 1.6 Hz, 2 H), 5.45 (tt, J = 7.2, 2.4 Hz, 1 H), 7.03–7.46 (m, 5 H); mass spectrum, m/e (relative intensity) 172 (M^+, 100), 143 (32), 129 (63), 104 (100), 91 (71), 81 (88); calcd for $C_{13}H_{16}$ m/e 172.1251, found m/e 172.1222.

Partial Hydrogenation of 3f in the Presence of Pyridine (Eq 5b). Complex **3f** (0.4 mmol) was dissolved in 10 mL of MeOH containing 0.1 mL of pyridine. The mixture was stirred at ambient temperature under H_2 until an uptake of 9 mL of H_2 was observed. The usual workup and purification by column chromatography (silica gel, benzene) provided a mixture of **16f** and **17f** (1:1) in 63% yield.

(*E*)-1-(Neophylsulfonyl)-3-hexene (16f): bp 160 °C (0.1 mmHg) (as a mixture of **16f** and **17f**); IR (neat film) 2960 (s), 1605 (w), 1445 (m), 1310 (s), 1285 (m), 1130 (s), 1120 (s), 970 (m), 840 (m), 770 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (t, J = 7 Hz, 3 H), 1.2 (m, 2 H), 1.62 (s, 6 H), 1.92–2.16 (m, 2 H), 2.22 (d, J = 3 Hz, 2 H), 3.10 (s, 2 H), 5.2–5.53 (m, 2 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 10), 199 (100), 133 (96), 119 (100). Anal. (mixture of **16f** and **17f**) Calcd for $C_{16}H_{24}SO_2$: C, 68.63; H, 8.63; O, 11.41. Found: C, 68.65; H, 8.74; O, 11.71.

(*E*)-1-(Neophylsulfonyl)-2-hexene (17f): IR (neat film) 2950 (s), 1600 (w), 1285 (m), 1130 (s), 1120 (s), 970 (m), 840 (m), 765 (m), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.91 (t, J = 7 Hz, 3 H), 1.25–1.54 (m, 2 H), 1.62 (s, 6 H), 2.06 (m, 2 H), 2.93 (d, J = 7 Hz, 2 H), 3.05 (s, 2 H), 5.1–5.6 (m, 2 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 280 (M^+, 1), 199 (92), 133 (100), 119 (67), 91 (100).

Reduction of 3f with $NaBH_4$ (Eq 5c). A methanol solution of $NaBH_4$ (0.56 mmol in 5 mL of MeOH) was added to the solution of complex **3f** (1.7 mmol) in methanol (70 mL) with stirring at 0 °C. The reaction mixture was allowed to stir at 0 °C for an additional 1 h. After evaporation of the methanol, the residue was extracted with ether. The extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent and column purification (silica gel, benzene as an eluent) gave 1-(neophylsulfonyl)-hexa-1,3-diene: 63% yield; bp 163 °C (0.15 mmHg); IR (neat film) 2970 (s), 1640 (m), 1600 (m), 1310 (s), 1280 (sh), 1130 (s), 1115 (s), 995 (m), 850 (m), 765 (m), 700 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.02 (t, J = 7 Hz, 3 H), 1.60 (s, 6 H), 2.16 (dq, J = 6, 7 Hz, 2 H), 3.24 (s, 2 H), 5.56 (d, J = 15 Hz, 1 H), 5.77 (dd, J = 15, 10 Hz, 1 H), 6.17 (td, J = 15, 6 Hz, 1 H), 6.82 (dd, J = 15, 10 Hz, 1 H), 7.4 (m, 5 H); mass spectrum, m/e (relative intensity) 199 ($M^+ - C_6H_7$, 2), 157 (13), 133 (31), 119 (23), 105 (17), 91 (100). Anal. Calcd for $C_{16}H_{22}SO_2$: C, 69.02; H, 7.97; O, 11.49. Found: C, 69.22; H, 8.14; O, 11.74.

Acknowledgment. We acknowledge support for this work provided by the ministry of Education, Science and Culture (Grant in Aid for Special Profect Research No. 57118006 and for Scientific Research B No. 58470066).

Registry No. **1a**, 106-99-0; **1b**, 78-79-5; **1c**, 513-81-5; **1d**, 123-35-3; **1e**, 504-60-9; **1f**, 592-48-3; **1g**, 2783-10-0; **1h**, 64255-45-4; **1i**, 4549-74-0; **1j**, 4549-74-0; **1k**, 37580-41-9; **3a**, 87567-02-0; **3c**, 67677-32-1; **3c** *tert*-butylsulfonyl derivative, 87585-74-8; **3e**, 87567-03-1; **3e** *tert*-butylsulfonyl derivative, 87567-04-2; **3f**, 87567-05-3; **3f** *tert*-butylsulfonyl derivative, 87567-06-4; **3g**, 87567-07-5; **3h**, 87567-08-6; **3i**, 87567-09-7; **3j**, 87567-10-0; **3k**, 87567-11-1; **5** (n = 3), 28638-58-6; **5** (n = 4), 2622-21-1; **5** (n = 6), 80304-18-3; **5** (n = 8), 72315-25-4; **5** (n = 10), 75531-52-1; **5a**, 57065-77-7; **5b**, 473-00-7; **5c**, 87567-27-9; **5d**, 87567-28-0; **5e** (isomer 1), 23155-97-7; **5e** (isomer 2), 87567-29-1; **5f** (isomer 1), 62008-31-5; **5f** (isomer 2), 62008-26-8; **5g** (isomer 1), 87567-30-4; **5g** (isomer 2), 87567-31-5; **6** (n = 3), 87585-75-9; **6** (n = 4), 87567-12-2; **6** (n = 6), 87567-13-3; **6** (n = 6) *p*-toluenesulfonyl derivative, 87567-14-4; **6** (n = 8), 87567-15-5; **6** (n = 10), 87567-16-6; **6a**, 87567-17-7; **6b**, 87567-18-8; **6b** phenylsulfonyl derivative, 87567-19-9; **6c**, 87567-20-2; **6d**, 87585-76-0; **6e**, 87567-21-3; **6f** (isomer 1), 87585-77-1; **6f** (isomer 2), 87567-69-9; **6g**, 87567-70-2; **6g** (isomer 2), 87585-81-7; **8b**, 87567-22-4; **8c**, 87585-78-2; **8d**, 87567-23-5; **8f**, 87567-24-6; **8h**, 87567-25-7; **9**, 87567-26-8; **10**, 77944-33-3; **11**, 77944-34-4; **12a**, 87567-32-6; **12b**, 87567-33-7; **12c**, 67686-38-8; **12d**, 67686-39-9; **12e**, 87567-34-8; **12f**, 77944-25-3; **12g**, 77944-26-4; **12h**, 77944-27-5; **12i**, 77944-28-6; **12j**, 77944-29-7; **12k**, 87567-35-9; **13a**, 87567-36-0; **13k**, 87567-37-1; **14e**, 77944-30-0; **14f**, 77944-31-1; **15j**, 87567-38-2; **16f**, 77944-36-6; **17f**, 77944-35-5; **19** (n = 3), 87567-39-3; **19** (n = 4), 87567-40-6; **19** (n = 6), 87567-41-7; **19** (n = 6) *p*-tolylsulfonyl derivative, 87567-42-8; **19** (n = 8), 87567-43-9; **19** (n = 10), 87567-44-0; **19a**, 87567-45-1; **19b**, 87567-46-2; **19c**, 87567-47-3; **19d**, 87567-48-4; **19e**, 87567-49-5; (*E*)-**19f**, 87567-50-8; (*Z*)-**19f**, 87567-51-9; (*E*)-**19g**, 87567-52-0; (*Z*)-**19g**, 87567-53-1; **20** (n = 8), 87567-54-2; **20** (n = 10), 87567-55-3; **21** (n = 6), 87567-56-4; **21** (n = 8), 87567-57-5; **21** (n = 10), 87567-58-6; **22**, 87567-59-7; 2-methyl-4-*p*-tolyl-1-butene, 56818-01-0; 2-methyl-4-*p*-tolyl-2-butene, 32094-39-6; 2,3-dimethyl-4-*p*-tolylbutene, 87567-61-1; 2-methoxy-2,3-dimethyl-4-*p*-tolylbutane, 87567-61-1; 1-*p*-tolyl-3-(4-methyl-3-penten-1-yl)-2-butene, 87585-79-3; (2-phenylethylidene)cyclopentane, 87567-62-2; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; 1-(neophylsulfonyl)-*trans*-pent-3-ene, 87567-63-3; neophyl methyl sulfone, 87567-64-4; *trans*-crotyl chloride, 4894-61-5; 1-(neophylsulfonyl)-(*E*)-3-methylpent-3-ene, 87567-65-5; (*E*)-2-methyl-2-butenyl bromide, 57253-30-2; (*Z*)-2-methyl-2-butenyl bromide, 57253-29-9; (*E*)-2-phenyl-2-butenyl tosylate, 87585-80-6; phenyl ethyl ketone, 93-55-0; ethyl (dimethylphosphono)acetate, 311-46-6; (*E*)-ethyl 3-phenyl-2-butenoate, 1504-72-9; (*Z*)-ethyl 3-phenyl-2-butenoate, 87567-66-6; (*E*)-1-(2-hydroxyethylidene)-2-methylcyclohexane, 87637-55-6; sodium neophylsulfinate, 67686-36-6; *cis*-1-acetoxy-1-vinyl-2-methylcyclohexane, 67902-66-3; *trans*-1-acetoxy-1-vinyl-2-methylcyclohexane, 67902-67-4; 1-(neophylsulfonyl)-hexa-1,3-diene, 87567-67-7; palladium chloride, 7647-10-1; (*E*)-4-(neophylsulfonyl)-2-butene, 87567-68-8.

Polystyrene-Supported Carbodiimide Catalysts

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Received January 27, 1983

Polystyrene-anchored triphenylarsine oxide **8** has been prepared from brominated polystyrene beads by a lithium-mediated arsenation–hydrogen peroxide oxidation sequence. Compound **8** with only 0.6 mequiv of As/g has been found to be a highly effective, insoluble catalyst for the conversion of aryl isocyanates to diarylcarbodiimides in high yield. Up to 5.6×10^4 turnovers of the catalyst **8** in the carbodiimide-forming reaction have been measured when appropriate measures are taken to prevent its deactivation. Several arylcarbodiimides have been prepared in high yield by using **8**.

Carbodiimides are often used in polyurethane technology as a functionality to either lower the melting point of the diisocyanate monomer (as an aid to processing) or to prevent the aging and hydrolysis of the polymeric

0022-3263/83/1948-4681$01.50/0 © 1983 American Chemical Society