Synthesis of Substituted 1,3-Dienes by the Reaction of Alkenesulfonyl Chlorides with Olefins Catalyzed by a Ruthenium(II) Complex

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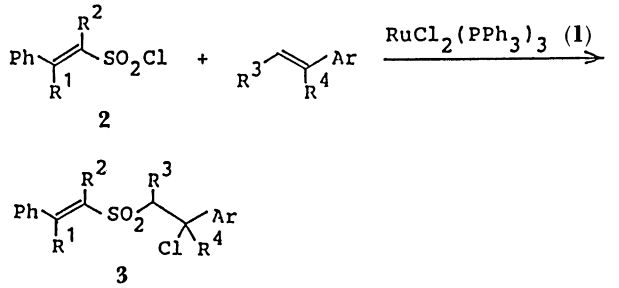
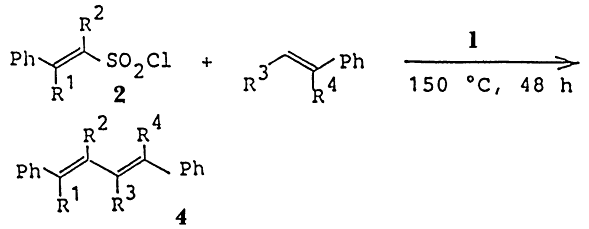
Alkenesulfonyl chlorides reacted with vinylarenes in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) to give substituted 1 : 1 adducts, which were dehydrochlorinated and desulfonylated successively to form substituted (*E*,*E*)-1,3-dienes in good yield.

We have previously reported that the reaction of alkane- and arenesulfonyl chlorides with olefins catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) (**1**) under mild conditions affords 1 : 1 adducts in high yield.[1] We recently found that alkenesulfonyl chlorides reacted with olefins in the presence of the ruthenium(II) catalyst **1** to form 1 : 1 adducts, which were dehydrochlorinated and desulfonylated successively by raising the reaction temperature from 80 to 150 °C to give (*E*,*E*)-1,4-diaryl-1,3-butadienes in high yield.[2,3]However, these reactions were limited to the formation of 1,3-butadienes substituted with aryl groups at the 1- and 4-positions. Here, we report on the formation of substituted 1,3-dienes by the reaction of alkenesulfonyl chlorides with styrenes catalyzed by the ruthenium(II) complex **1**.

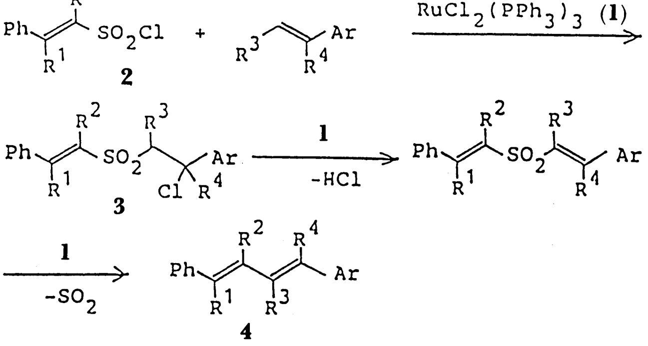
The reaction of (*E*)-2-phenyl-1-propene-1-sulfonyl chloride (**2b**) with styrene was carried out in benzene, in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) (**1**), by heating the reaction mixture at 80 °C under a nitrogen atmosphere to give 1 : 1 adduct **3d** in 89% yield. Similarly, (*E*)-2-phenylethene-, (*E*)-2-phenyl-1-propene-1-, and (*E*)-1-phenyl-1-propene-2-sulfonyl chloride (**2a—c**) were added to substituted vinylarenes using **1** as a catalyst at 80—100 °C to afford 1 : 1 adducts **3** in high yield. The results are summarized in Table 1. Thus, the ruthenium(II)-phosphine catalyzed addition reaction of styrenesulfonyl chlorides possessing methyl group at α- and β-position (**2b** and **2c**) to α- and β-methylstyrenes was found to give 1 : 1 adducts in good yield.



The reaction of (*E*)-2-phenyl-1-propene-1-sulfonylchloride with styrene catalyzed by **1** was also carried out in benzene upon raising the reaction temperature from 80 to 150 °C, to give unsymmetrical 1,4-diphenyl-1,3-pentadiene (**4b**) in 51% yield. Similarly, several alkenesulfonyl chlorides **2a—c** were reacted with substituted vinylarenes in order to study the scope and limitation of the formation of substituted 1,3-dienes. The results are summarized in Table 2.



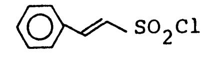
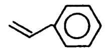
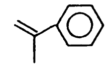
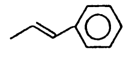
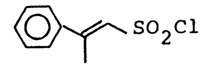
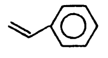
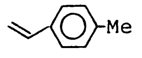
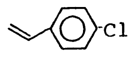
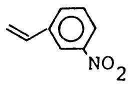
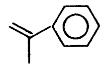
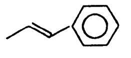
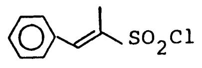
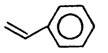
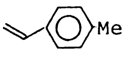
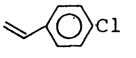
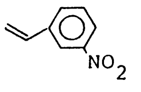
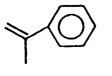
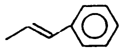
We have previously reported that the reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene catalyzed by **1** proceeds successively via an addition, dehydrochlorination, and desulfonylation to give (*E*)-2-chloro(*p*-tolyl)ethyl styryl sulfone, (*E*,*E*)-*p*-methylstyryl sulfone, and (*E*,*E*)-1-phenyl-4-(*p*-tolyl)-1,3-butadiene, respectively, by studying the time course. Moreover, it was also found that a ruthenium(II) catalyst was effected in each of the three steps.[3] Therefore, the formation of substituted 1,3-diene **4** could be accounted for by the following path-way, as shown in Scheme 1. Alkenesulfonyl chlorides **2** react with the olefins catalyzed by the ruthenium(II) complex **1** to give 1 : 1 adducts **3** during the initial step. Dehydrochlorination and desulfonylation from adducts **3** take place, successively, in the presence of the ruthenium complex **1** to afford substituted 1,3-dienes **4**.



Scheme 1.

There are a number of methods for the preparation of 1,3-dienes;[4-6] however, some of them can prepare

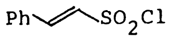
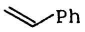
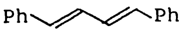
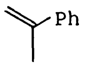
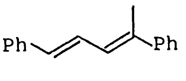
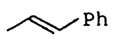
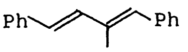
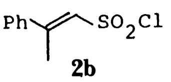
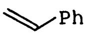
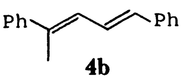
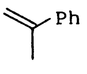
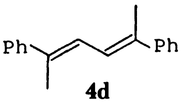
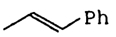
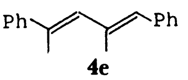
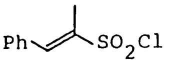
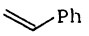
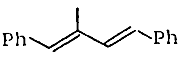
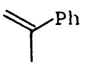
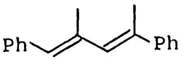
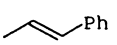
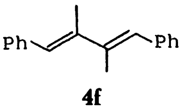
Table 1. Reaction of Alkenesulfonyl Chloride with Olefin Catalyzed by $RuCl_2(PPh_3)_3$ (**1**)

Sulfonyl chloride	Olefin	Temp/°C	Time/h	Product	Yield/%
 **2a**		80	70	**3a**	88
		100	36	**3b**	46[21]
		100	24	**3c**	23
 **2b**		80	24	**3d**	89
		80	21	**3e**	81
		80	13	**3f**	95
		80	24	**3g**	70
		100	36	**3h**	80[21]
		100	24	**3i**	61
 **2c**		80	24	**3j**	84
		80	37	**3k**	74
		80	37	**3l**	76
		80	72	**3m**	70
		100	36	**3n**	80[21]
		100	24	**3o**	53

only symmetrical 1,3-dienes[7–12] and others require sophisticated organometallic reagents.[13–17] On the other hand, the present method can be used to prepare symmetrical and unsymmetrical 1,3-dienes in good yield by the reaction of easily available sulfonyl chlorides with olefin. The reaction of **2c** with 2-phenyl-1-propene afforded 2-methyl-1,4-diphenyl-1,3-pentadiene (**4e**) and (*E*)-2-chloro-2-phenylpropyl 1-methyl-2-phenylethenyl sulfone (**3n**) in 15% and 63% yields, respectively (Run 8 in Table 2). This indicates that the adduct **3n** was not readily dehydrochlorinated and desulfonylated to 1,3-diene **4e** when ethenesulfonyl chloride has a substituent at the *β*-position, probably by the steric effect of the methyl group.

A reaction of (*E*)-1-propene-1-sulfonyl chloride with styrene was carried out at 150 °C using the ruthenium(II) complex **1** while expecting the formation of 1-phenyl-1,3-pentadiene. Unfortunately, the expected 1,3-diene was not obtained, though various transition metal complexes, such as $NiCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pt(PPh_3)_4$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_3$, were used as catalysts. The results show that

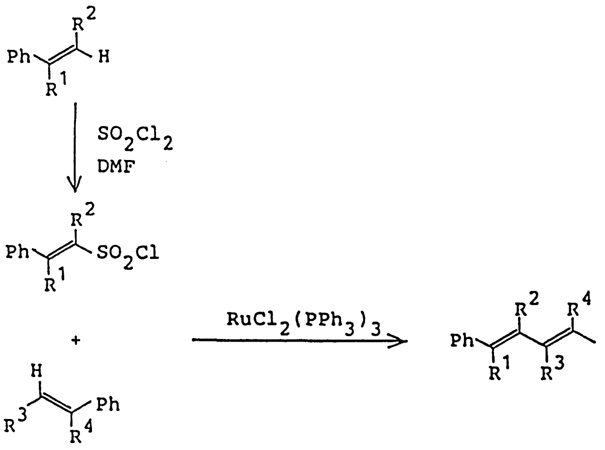
Table 2. Formation of (*E,E*)-1,3-Dienes by the Reaction of (*E*)-Alkenesulfonyl Chlorides with Olefin Catalyzed by the Ruthenium(II) Complex **1**

Run	Sulfonyl chloride	Olefin	Product	Yield/%
1	 **2a**		 **4a**	91
2			 **4b**	56
3			 **4c**	38
4	 **2b**		 **4b**	51
5			 **4d**	80
6			 **4e**	23[a]
7	 **2c**		 **4c**	21
8			 **4e**	15[b]
9			 **4f**	10[c]

a) Isomer of **4e** was isolated in 17% yield. b) Adduct **3n** was formed in 63% yield. c) Isomer of **4f** and adduct **3o** were isolated in 6% and 16% yield respectively.

the reaction of alkenesulfonyl chlorides without an aryl group with vinylarenes did not afford 1,3-dienes, although the reason has not yet been clarified.

In conclusion, symmetrically and unsymmetrically substituted 1,4-diaryl-1,3-dienes were formed by the reaction of alkenesulfonyl chlorides with olefins catalyzed by the ruthenium(II) complex. The present method involves a very excellent one-pot synthesis of symmetrical and unsymmetrical (*E,E*)-1,4-diaryl-1,3-dienes, since substituted ethenesulfonyl chloride can be prepared very easily by treating vinylarenes with sulfuryl chloride in *N,N*-dimethylformamide.[18] The present reaction can be regarded as an oxidative coupling reaction of each terminal carbon atom of two kinds of vinylarenes by using sulfuryl chloride and ruthenium(II) catalyst. Since a direct oxidative coupling of vinylarenes is impossible, the present reaction offers a novel and convenient synthetic method of symmetrical and unsymmetrical (*E,E*)-1,4-diaryl-1,3-dienes.



Experimental

Measurement. Melting points and boiling points were uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer with samples as either neat liquids or KBr disks. The proton magnetic resonance spectra were recorded at 60 MHz by using a JMX-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. Mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with JEOL 5000 Mass Data System at an ionizing voltage of 20—70 eV. The gel-permeation chromatography was accomplished on a JAI LC-08 liquid chromatograph with a JAIGEL-1H column (20ϕX600 mmX2) using chloroform as an eluent.

Materials. Dichlorotris(triphenylphosphine)ruthenium(II) (**1**) was prepared according to a procedure described in the literature.[19] (*E*)-2-Phenylethenesulfonyl chloride (**2a**) was prepared from styrene by treatment with sulfuryl chloride in *N,N*-dimethylformamide by the method described in the literature:[18] yield 50%; mp 87—88 °C (from ethanol-hexane; lit, mp 89—90 °C). (*E*)-2-Phenyl-1-propene-1-sulfonyl chloride (**2b**) or (*E*)-1-phenyl-1-propene-2-sulfonyl chloride (**2c**) were prepared from 2-phenyl-1-propene or 1-phenyl-1-propene by treating with sulfuryl chloride in *N,N*-dimethylformamide–dichloromethane and then with triethylamine in ether: (**2b**) yield 29%; bp 96—98 °C/0.2 mmHg (1 mmHg=133.322 Pa); IR (neat) 1370 and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.65 (3H, s), 6.90 (1H, s), and 7.40 (10H, s); MS *m/z* 216 (M^+): (**2c**) yield 68%; bp 95—96 °C/0.2 mmHg; IR (neat) 1370, 1355, and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.45 (3H, s), 7.35 (5H, s), and 7.65 (1H, s); MS *m/z* 216 (M^+). (*E*)-1-Propene-1-sulfonyl chloride was prepared from propylene oxide by treatment with sodium hydrogensulfite, phosphorus pentachloride, and then triethylamine in ether according to the literature:[20] yield 68%; bp 88—89 °C/21 mmHg. Styrene, *p*-methylstyrene, *p*-chlorostyrene (Tokyo Kasei Chemicals), *m*-nitrostyrene (Aldrich Chemicals), 2-phenyl-1-propene, and 1-phenyl-1-propene (Wako Chemicals) were purified by distillation prior to use.

Formation of 1 : 1 Adducts by the Reaction of Alkenesulfonyl Chlorides with Olefins. To a solution of 1.0 mmol of alkenesulfonyl chloride and 1.5 mmol of olefin in 2.0 cm^3 of benzene or toluene was added 0.01 mmol of dichlorotris(triphenylphosphine)ruthenium(II) (**1**) and heated at 80—100 °C under a nitrogen atmosphere. The reaction mixture was chromatographed on florisil by using benzene as an eluent to separate polar substances. Nonpolar substances were purified by gel-permeation chromatography using chloroform as an eluent to isolate 1 : 1 adducts **3a**—**o**.

The physical and spectral data of compounds **3a**—**o** are as follows:

(*E*)-2-Chloro-2-phenylethyl Styryl Sulfone (3a): Mp 97—98 °C; IR (KBr) 1310 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.78 (1H, d, *J*=7.8 Hz), 3.82 (1H, d, *J*=7.8 Hz), 5.33 (1H, t, *J*=7.8 Hz), 6.33 (1H, d, *J*=15 Hz), 7.10—7.40 (10H, m), and 7.35 (1H, d, *J*=15 Hz); MS *m/z* 306 (M^+).

(*E*)-2-Chloro-2-phenylpropyl Styryl Sulfone (3b): IR (neat) 1310 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.20 (2H, s), 5.42 (1H, s), 5.60 (1H, s), 6.43 (1H, d, *J*=16 Hz), 7.00—7.30 (10H, m), and 7.32 (1H, d, *J*=16 Hz);[21] MS *m/z* 321 (M^+ +1);[22] HRMS, Found *m/z* 320.0743, Calcd for $C_{17}H_{17}O_2SCl$: M, 320.0637.

(*E*)-2-Chloro-1-methyl-2-phenylethyl Styryl Sulfone (3c): Mp 95—96 °C; IR (KBr) 1310 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.53 (3H, d, *J*=8.0 Hz), 3.22—3.63 (1H, m), 5.59 (1H, d, *J*=4.0 Hz), 6.38 (1H, d, *J*=15 Hz), 7.27 (10H, s), and 7.38 (1H, d, *J*=15 Hz); MS *m/z* 320 (M^+); HRMS, Found: *m/z* 319.0577, Calcd for $C_{17}H_{16}O_2SCl$: M, 319.0559.

(*E*)-2-Chloro-2-phenylethyl 2-Phenyl-1-propenyl Sulfone (3d): Mp 95—96 °C; IR (KBr) 1305 and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.40 (3H, s), 3.70—3.85 (2H, m), 5.36 (1H, t, *J*=6.0 Hz), 6.07 (1H, s), and 7.00—7.80 (10H, m); MS *m/z* 320 (M^+); HRMS, Found: *m/z* 320.0644, Calcd for $C_{17}H_{17}O_2SCl$: M, 320.0637.

(*E*)-2-Chloro-2-(*p*-tolyl)ethyl 2-Phenyl-1-propenyl Sulfone (3e): IR (neat) 1310 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 2.17 (3H, s), 2.37 (3H, s), 3.79 (2H, d, *J*=6.0 Hz), 5.33 (1H, t, *J*=6.0 Hz), 5.93 (1H, s), and 6.70—7.70 (9H, m); MS *m/z* 298 (M^+ −HCl); HRMS, Found: *m/z* 298.0993, Calcd for $C_{18}H_{17}O_2S$: M, 298.1027.

(*E*)-2-Chloro-2-(*p*-chlorophenyl)ethyl 2-Phenyl-1-propenyl Sulfone (3f): Mp 58—60 °C; IR (neat) 1310 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 3.76—3.85 (2H, m), 5.36 (1H, t, *J*=6.0 Hz), 6.06 (1H, s), and 7.00—7.50 (9H, m); MS *m/z* 354 (M^+); HRMS, Found *m/z* 354.0222, Calcd for $C_{17}H_{16}O_2SCl_2$: M, 354.0248.

(*E*)-2-Chloro-2-(*m*-nitrophenyl)ethyl 2-Phenyl-1-propenyl Sulfone (3g): Mp 101—102 °C; IR (KBr) 1540, 1350, 1310, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.48 (3H, s), 3.75—3.90 (2H, m), 5.47 (1H, t, *J*=6.0 Hz), 6.13 (1H, s), and 7.18—8.21 (9H, m); MS *m/z* 365 (M^+); HRMS, Found: *m/z* 365.0523, Calcd for $C_{17}H_{16}O_4NSCl$: M, 365.0488.

(*E*)-2-Chloro-2-phenylpropyl 2-Phenyl-1-propenyl Sulfone (3h): IR (neat) 1305 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.33 (3H, s), 4.13 (2H, s), 5.39 (1H, s), 5.57 (1H, s), 6.30 (1H, m), and 6.70—7.40 (10H, m);[16] MS *m/z* 335 (M^+ +1);[17] HRMS, Found: *m/z* 299.1125, Calcd for $C_{18}H_{19}O_2S$: M, 299.1105.

(*E*)-2-Chloro-1-methyl-2-phenylethyl 2-Phenyl-1-propenyl Sulfone (3i): IR (neat) 1300 and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 (1H, d, *J*=7.0 Hz), 1.54 (2H, d, *J*=7.0 Hz), 2.48 (3H, s), 3.10—3.65 (1H, m), 5.40—5.64 (1H, m), 6.00—6.10 (1H, m), and 6.90—7.30 (10H, s); MS *m/z* 335 (M^+ +1);[17] HRMS, Found: *m/z* 299.1105, Calcd for $C_{18}H_{19}O_2S$: M, 299.1105.

(*E*)-2-Chloro-2-phenylethyl 1-Methyl-2-phenylethenyl Sulfone (3j): Mp 93—95 °C; IR (neat) 1300 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (3H, d, *J*=1.2 Hz), 3.76 (2H, d, *J*=6.0 Hz), 5.26 (1H, t, *J*=6.0 Hz), and 7.00—7.40 (11H, m); MS *m/z* 320 (M^+); HRMS, Found: *m/z* 284.0831, Calcd for $C_{17}H_{16}O_2S$: M, 284.0871.

(*E*)-2-Chloro-2-(*p*-tolyl)ethyl 1-Methyl-2-phenylethenyl Sulfone (3k): Mp 91—92 °C; IR (neat) 1305 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.09—2.15 (6H, m), 3.77 (2H, d, *J*=6.0 Hz), 5.26 (1H, t, *J*=6.0 Hz), and 7.00—7.30 (10H, m); MS *m/z* 334 (M^+); HRMS, Found: *m/z* 298.1036, Calcd for $C_{18}H_{17}O_2S$: M, 298.1027.

(*E*)-2-Chloro-2-(*p*-chlorophenyl)ethyl 1-Methyl-2-phenylethenyl Sulfone (3l): Mp 91—92 °C; IR (KBr) 1310 and 1140 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.14 (3H, s), 3.75 (2H, d, *J*=6.0 Hz), 5.28 (1H, t, *J*=6.0 Hz), and 7.10—7.40 (10H, m); MS *m/z* 354 (M^+); HRMS, Found: *m/z* 354.0267, Calcd for $C_{17}H_{16}O_2SCl_2$: M, 354.0248.

(*E*)-2-Chloro-2-(*m*-nitrophenyl)ethyl 1-Methyl-2-phenylethenyl Sulfone (3m): IR (neat) 1540, 1360, 1310, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.21 (3H, s), 3.73—3.88 (2H, m), 5.41 (1H, t, *J*=6.0 Hz), and 7.00—8.20 (10H, m); MS *m/z* 365 (M^+); HRMS, Found: *m/z* 365.0452, Calcd for $C_{17}H_{16}O_4NSCl$: M, 365.0488.

(*E*)-2-Chloro-2-phenylpropyl 1-Methyl-2-phenylethenyl Sulfone (3n): IR (neat) 1300 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.40 (3H, s), 4.13 (2H, s), 5.04 (1H, s), 5.20 (1H, s), and 6.90—7.30 (11H, m);[16] MS *m/z* 335 (M^+ +1);[17] HRMS, Found: *m/z* 299.1167, Calcd for $C_{18}H_{19}O_2S$: M, 299.1105.

(*E*)-2-Chloro-1-methyl-2-phenylethyl 1-Methyl-2-phenylethenyl Sulfone (3o): Mp 112—113 °C; IR (KBr) 1300 and 1140 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.25 (1H, d, *J*=7.0 Hz), 1.55 (2H, d, *J*=7.0 Hz), 2.10—2.30 (3H, m), 3.28—3.86 (1H, m), 5.14—5.53 (1H, m), and 7.00—7.60 (10H, m); MS *m/z* 335 (M^+ +1);[17] HRMS, Found: *m/z* 334.0762, Calcd for $C_{18}H_{19}O_2SCl$: M, 334.0794.

The Formation of 1,3-Dienes by the Reaction of Alkenesulfonyl Chlorides with Olefins. A solution containing of 1.0 mmol of alkenesulfonyl chloride, 1.5 mmol of olefin, and 0.01 mmol of the ruthenium(II) complex **1** in 2.0 cm^3 of benzene was degassed and heated in a sealed tube at 150 °C for 48 h. Gel-permeation chromatography using chloroform as an eluent was performed to isolate 1,3-dienes.

The physical and spectral data of the compounds **4a**—**f** are as follows:

(*E,E*)-1,4-Diphenyl-1,3-butadiene (4a): Mp 148—149 °C (lit,[23] mp 149.7 °C); IR (KBr) 3010, 1490, 1440, 990, 740, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.10—6.80 (4H, m) and 6.90—7.40 (10H, m); MS *m/z* 206 (M^+).

(*E,E*)-1,4-Diphenyl-1,3-pentadiene (4b): Mp 95—96 °C (lit,[24] mp 95.5—97 °C); IR (KBr) 3030, 1595, 1490, 1440, 970, 750, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.21 (3H, s), 6.36—6.89 (2H, m), and 7.00—7.50 (11H, m); MS *m/z* 220 (M^+).

(*E,E*)-2-Methyl-1,4-diphenyl-1,3-butadiene (4c): Mp 76—77 °C (lit,[5] mp 78—80 °C); IR (KBr) 3020, 1490, 1440, 960, 740, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (3H, s) and 6.17—7.40 (13H, m); MS *m/z* 220 (M^+).

(*E,E*)-2,5-Diphenyl-2,4-hexadiene (4d): Mp 130—132 °C (lit,[8] mp 136—137.5 °C); IR (KBr) 3030, 2960, 1495, 1445, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (6H, s), 6.70 (2H, s), and 7.03—7.50 (10H, m); MS *m/z* 234 (M^+).

(*E*,*E*)-2-Methyl-1,4-diphenyl-1,3-pentadiene (4e): IR (neat) 3030, 2850, 1600, 1490, 1440, 1380, 1025, 880, 750, and 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.27 (6H, s), 6.81 (2H, m), and 7.15—7.60 (10H, m); MS *m*/*z* 234 (M$^+$); HRMS, Found: *m*/*z* 234.1408, Calcd for $C_{18}H_{18}$: M, 234.1408.

(*E*,*E*)-2,3-Dimethyl-1,4-diphenyl-1,3-butadiene[13] **(4f):** IR (neat) 2900, 1490, 1450, 750, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.79 (6H, s) and 6.80—7.40 (12H, m); MS *m*/*z* 234 (M$^+$); HRMS, Found: *m*/*z* 234.1404, Calcd for $C_{18}H_{17}$: M, 234.1408.

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