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

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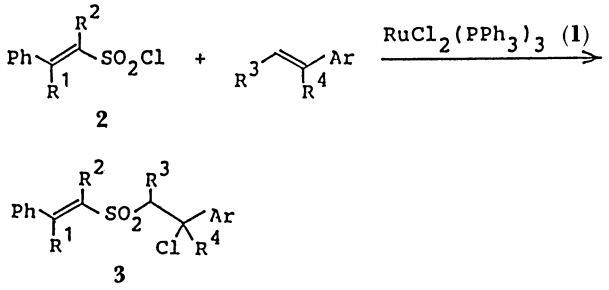
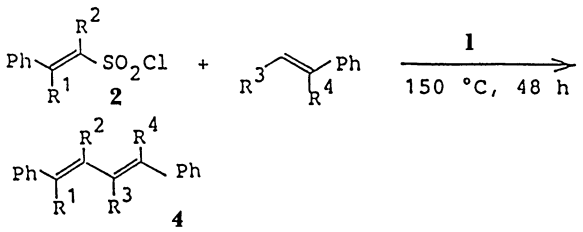
Alkenesulfonyl chlorides reacted with vinylarenes in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) to give substituted 1 : 1 adducts, which were dehydrochlorinated and desulfonylated successively to form substituted (*E,E*)-1,3-dienes in good yield.

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**.

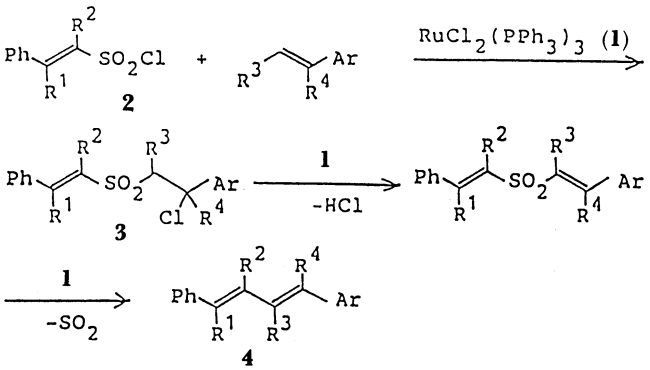
The reaction of (*E*)-2-phenyl-1-propene-1-sulfonyl chloride (**2b**) with styrene was carried out in benzene, in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) (**1**), by heating the reaction mixture at 80 °C under a nitrogen atmosphere to give 1 : 1 adduct **3d** 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-sulfonyl-chloride 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.



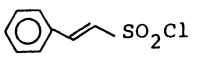
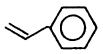
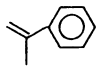
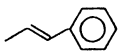
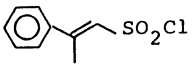
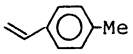
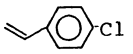
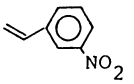
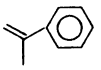
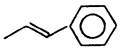
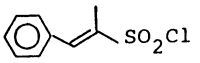
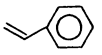
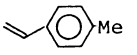
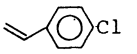
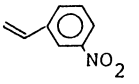
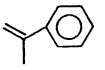
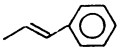
We have previously reported that the reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene catalyzed by **1** proceeds successively via an addition, dehydrochlorination, and desulfonylation to give (*E*)-2-chloro(*p*-tolyl)ethyl styryl sulfone, (*E,E*)-*p*-methylstyryl sulfone, and (*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

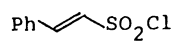
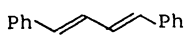
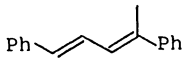
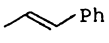
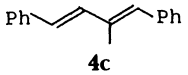
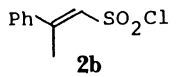
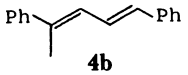
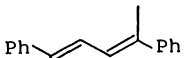
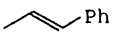
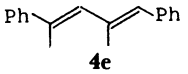
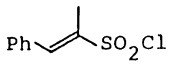
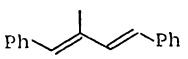
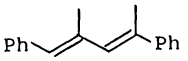
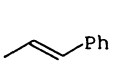
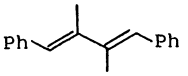
Table 1. Reaction of Alkenesulfonyl Chloride with Olefin Catalyzed by $RuCl_2(PPh_3)_3$ (**1**)

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

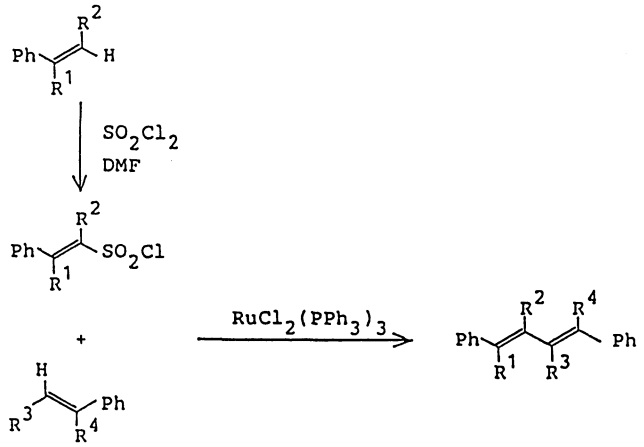
Table 2. Formation of (*E,E*)-1,3-Dienes by the Reaction of (*E*)-Alkenesulfonyl Chlorides with Olefin Catalyzed by the Ruthenium(II) Complex **1**

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 (20ϕ×600 mm×2) 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}; ^1H 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}; ^1H 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}; ^1H 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}; ^1H 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.

References

1) N. Kamigata, H. Sawada, and M. Kobayashi, *J. Org. Chem.*, **48**, 3793 (1983); N. Kamigata, H. Sawada, N. Suzuki, and M. Kobayashi, *Phosphorus and Sulfur*, **19**, 199 (1984); N. Kamigata, N. Suzuki, and M. Kobayashi, *ibid.*, **20**, 139 (1984).

2) N. Kamigata, J. Ozaki, and M. Kobayashi, *Chem. Lett.*, **1985**, 705.

3) N. Kamigata, J. Ozaki, and M. Kobayashi, *J. Org. Chem.*, **50**, 5045 (1985).

4) G. Wilke and H. Muller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960); G. Zweifel and R. L. Miller, *J. Am. Chem. Soc.*, **92**, 6678 (1970).

5) W. Fischetti, K. T. Mak, F. G. Stakem, J. I. Kim, A. L. Rheingold, and R. F. Heck, *J. Org. Chem.*, **48**, 948 (1983).

6) E. Wenkert, M. H. Leftin, and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, **1984**, 617; S. Yamada, H. Ohsawa, T. Suzuki, and H. Takayama, *J. Org. Chem.*, **51**, 4934 (1986).

7) R. C. Larock, *J. Org. Chem.*, **41**, 2241 (1976).

8) R. Levene, J. Y. Becker, and J. Klein, *J. Organomet. Chem.*, **67**, 467 (1974).

9) Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S-I. Murahashi, *J. Am. Chem. Soc.*, **99**, 5652 (1977).

10) K. Tamao, H. Matsumoto, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, **1979**, 1137, 1141.

11) W. P. Weber, R. A. Felix, A. K. Willard, and K. E. Koenig, *Tetrahedron Lett.*, **1971**, 4701.

12) M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *J. Am. Chem. Soc.*, **94**, 9234 (1972).

13) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1960).

14) A. Suzuki, *Pure. Appl. Chem.*, **57**, 1749 (1985) and references cited therein.

15) E. Negishi, *Acc. Chem. Res.*, **15**, 340 (1982) and references cited therein; E. Negishi, T. Takahashi, S. Baba, D. E. Van Horn, and N. Okukado, *J. Am. Chem. Soc.*, **109**, 2393 (1987).

16) N. Jabri, A. Alexakis, and J. F. Normant, *Tetrahedron Lett.*, **22**, 959 (1981) and references cited therein.

17) J. K. Stille and B. L. Groh, *J. Am. Chem. Soc.*, **109**, 813 (1987).

18) B. M. Culbertson and S. Dietz, *J. Chem. Soc. C*, **1968**, 992.

19) T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966); T. A. Stephenson, G. Wilkinson, *J. Chem. Soc. A*, **1970**, 2497; P. S. Hallam, T. A. Stephenson, and G. Wilkinson, *Inorg. Synth.*, **12**, 238 (1972).

20) A. Goldberg, *J. Chem. Soc.*, **1945**, 464; C. S. Rondestvedt, *J. Am. Chem. Soc.*, **76**, 1926 (1954); C. S. Rondestvedt and P. K. Chang., *ibid.*, **77**, 6532 (1955).

21) The adduct formed was readily dehydrochlorinated on working up by elution chromatography to give divinyl sulfone, therefore the spectral data are shown the dehydrochlorinated divinyl sulfone. The mass spectrum was obtained by the crude product and showed the parent peak of the adduct. The yield of the adduct was caluculated from the isolated divinyl sulfone.

22) We often observed the parent peak of sulfones showed $M^+ + 1$.

23) B. B. Corson, *Org. Synth.*, Coll. Vol. II, 229 (1943).

24) L. A. Paquett, R. P. Henzel, and S. E. Wilson, *J. Am. Chem. Soc.*, **94**, 7780 (1972).