Reaction of Alkenesulfonyl Chlorides with Olefins Catalyzed by a Ruthenium(II) Complex. A Novel Method for Synthesis of (*E*,*E*)-1,4-Diaryl-1,3-butadienes

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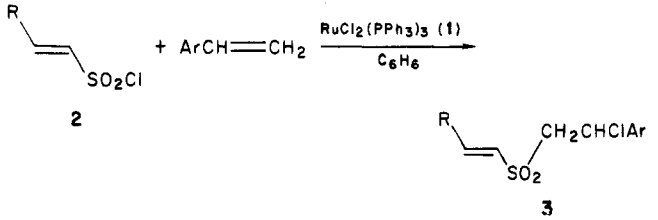
Received May 9, 1985

In the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) (**1**), alkenesulfonyl chloride (**2**) was found to react with vinylarenes to give 1:1 adducts (**3**) in high yield under mild conditions. Dehydrochlorination from the adducts **3** to afford divinyl sulfones (**4**) takes place by raising the reaction temperature from 80 to 130 °C. Upon further reaction at 150 °C, (*E*,*E*)-1,4-diaryl-1,3-butadienes (**5**) are formed in high yield if both of the alkenyl substituents of the sulfonyl chloride and the alkene have aryl groups. The time course of the reaction indicates that the addition of **2** to vinylarenes giving 1:1 adducts **3**, dehydrochlorination from the adducts **3** giving divinyl sulfones **4**, and desulfonylation from the divinyl sulfone **4** giving 1,3-butadienes **5** proceed successively. The usefulness of the reaction for the syntheses of (*E*,*E*)-1,4-diaryl-1,3-butadiene is described. On the other hand, **2** reacts with alkyl olefins in the presence of **1** to give 1:1 adducts (**12**) with extrusion of sulfur dioxide.

Synthetic application of the radical reactions brought about by the interaction of a transition metal salt or complex with organic halides has received considerable attention.[1] For example, γ-butyrolactones were synthesized in high yield by the reaction of trimethylsilyl α-chloro carboxylates with olefins in the presence of a ruthenium(II) catalyst.[2] Recently, we have reported that the reaction of alkane- and arenesulfonyl chloride with olefins catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) (**1**) under mild conditions affords 1:1 adducts in high yield.[3] On the other hand, the reaction of trichloromethanesulfonyl chloride with olefins catalyzed by **1** affords 1:1 adducts with extrusion of sulfur dioxide.[4] We report here the reactions of alkenesulfonyl chloride with olefins catalyzed by a ruthenium(II) complex **1**.

Results and Discussion

The reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene was carried out in benzene, using dichlorotris(triphenylphosphine)ruthenium(II) (**1**) as a catalyst, by heating the reaction mixture at 80 °C in a degassed sealed tube. The starting materials were completely consumed after 70 h, a clean conversion to a single product occurred, and this product was identified as (*E*)-2-chloro-2-(*p*-tolyl)ethyl styryl sulfone (**3a**) on the basis of its spectral properties. Similarly, (*E*)-2-arylethene, (*E*)-1-propene-1-, and ethenesulfonyl chloride were reacted with vinylarenes in the presence of **1** at 80–100 °C to afford 1:1 adducts **3** in high yield. The results are summarized



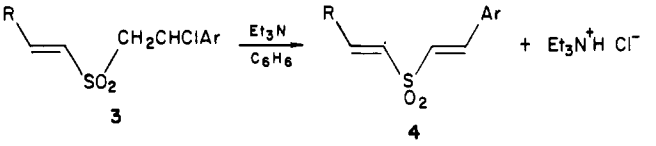
in Table I. NMR spectra indicated that the trans configuration of the starting alkenesulfonyl chloride was retained in the product **3** when R = aryl and methyl.

Table I. Reaction of Alkenesulfonyl Chloride with Vinylarenes Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II)

R in **2**	Ar in $ArCH{=}CH_2$	temp, °C	reaction time, h	product	yield,[a] %
C_6H_5	*p*-$CH_3C_6H_4$	80	70	**3a**	90
C_6H_5	C_6H_5	80	70	**3b**	88
C_6H_5	*p*-ClC_6H_4	80	70	**3c**	86
C_6H_5	*m*-$NO_2C_6H_4$	80	140	**3d**	87
p-$CH_3C_6H_4$	C_6H_5	80	70	**3e**	98
p-ClC_6H_4	C_6H_5	80	70	**3f**	92
CH_3	*p*-$CH_3C_6H_4$	100	15	**3g**	98
CH_3	C_6H_5	100	15	**3h**	91
CH_3	*p*-$CH_3C_6H_4$	100	15	**3i**	87
CH_3	*m*-$NO_2C_6H_4$	100	15	**3j**	86
H	*p*-$CH_3C_6H_4$	80	20	**3k**	77
H	C_6H_5	80	20	**3l**	65
H	*p*-ClC_6H_4	80	20	**3m**	77
H	*m*-$NO_2C_6H_4$	90	70	**3n**	80
C_6H_5	*p*-$CH_3C_6H_4$	130	5	**3a**	38
				4a	41
C_6H_5	C_6H_5	130	5	**3b**	84
C_6H_5	*p*-ClC_6H_4	130	5	**3c**	85
C_6H_5	*m*-$NO_2C_6H_4$	130	20	**3d**	80

[a] The yields refer to pure isolated products.

The adducts **3** were dehydrochlorinated to (*E*,*E*)-2,2′-disubstituted divinyl sulfone **4** in greater yield than 95% by treating all of the adducts **3** with equimolar amounts of triethylamine in benzene at room temperature.



Therefore, the present reaction is an excellent preparative method for divinyl sulfones. However, the addition reaction requires very long times, i.e., 70–140 h is required in the reactions of (*E*)-2-arylethenesulfonyl chloride with vinylarene catalyzed by **1** at 80 °C. So, we carried out the reaction at 130 °C to shorten the reaction time. The reaction was completed in 5–20 h at this temperature, and the adducts **3** were isolated in high yields as shown in Table I.

Here, it is noteworthy that (*E*,*E*)-*p*-methylstyryl styryl sulfone (**4a**) was formed in 41% yield with the adduct **3a**

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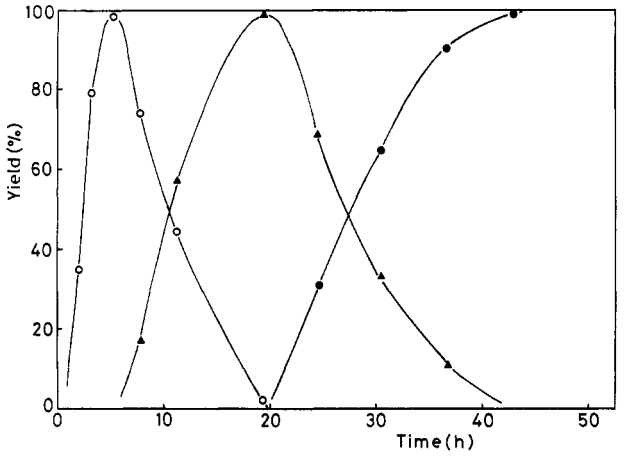
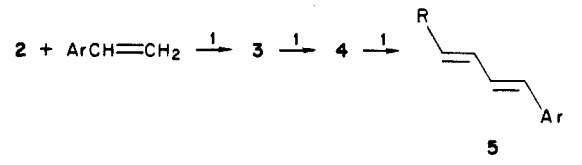


Figure 1. Time course in the reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene catalyzed by ruthenium(II) complex (1): (○) (*E*)-2-chloro-2-(*p*-tolyl)ethyl styryl sulfone (**3a**); (▲) (*E*,*E*)-*p*-methylstyryl styryl sulfone (**4a**); (●) (*E*,*E*)-1-phenyl-4-(*p*-tolyl)-1,3-butadiene (**5a**).

(38% yield) in the reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene catalyzed by 1 at 130 °C. This suggests that **3a** is also dehydrochlorinated thermally in the presence of a ruthenium(II) catalyst. The reactions of (*E*)-2-phenylethenesulfonyl chloride with vinylarene catalyzed by 1 were carried out at 130 °C for 45 h. As expected, (*E*,*E*)-2,2′-disubstituted divinyl sulfones (**4**) were formed in greater yields than 95% in all of the examples, with one exception. The formation of **4** under these conditions suggests that the reaction of (*E*)-2-arylethenesulfonyl chloride with vinylarene catalyzed by 1 to give **3** and dehydrochlorination of **3** to give **4** proceed successively.

$$2 + \mathrm{ArCH{=}CH_2} \xrightarrow{1} 3 \xrightarrow{1} 4 + \mathrm{HCl}$$

To establish that the reaction of (*E*)-2-arylethenesulfonyl chloride with vinylarenes catalyzed by 1 proceeds stepwise to give **3** and then **4**, the time course was studied in the reaction of (*E*)-2-phenylethenesulfonyl chloride with *p*-methylstyrene in the presence of 1 at 150 °C. The result is shown in Figure 1. The addition of (*E*)-2-phenylethenesulfonyl chloride to *p*-methylstyrene forming **3a** occurred very rapidly at this temperature and was completed in 5 h. Then, the disappearance of the adduct **3a** started and at the same time the formation of **4a** was observed. After 20 h, the adduct **3a** was completely consumed and the formation of **4a** became maximum. The results support our presumption of stepwise formation of **3a** and **4a**, respectively, in the reaction of (*E*)-2-arylethenesulfonyl chloride with vinylarenes in the presence of 1. Surprisingly, upon further heating of the reaction mixture, the divinyl sulfone **4a** gradually disappeared and at the same time the formation of (*E*,*E*)-1-phenyl-4-(*p*-tolyl)-1,3-butadiene (**5a**) was observed which became the only product after 43 h. This means that the ruthenium(II) complex catalyzes not only the addition reaction of sulfonyl chloride **2** with olefin but also dehydrochlorination reaction of the adduct **3** and desulfonylation reaction of divinyl sulfones **4**.



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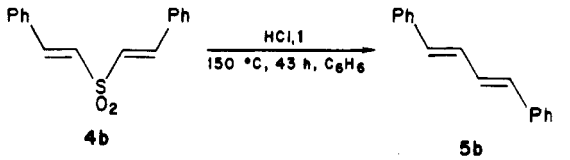
To test if the catalyst 1 is really needed in the dehydrochlorination of **3** and desulfonylation of **4**, the isolated **3b** was heated at 150 °C in benzene in the absence of 1 for 43 h, but no reaction was observed and the starting material **3b** was recovered quantitatively. However, when the same reaction was carried out in the presence of the ruthenium(II) catalyst 1, (*E*,*E*)-1,4-diphenyl-1,3-butadiene (**5b**) was formed in high yield. Interestingly, when the isolated (*E*,*E*)-distyryl sulfone (**4b**) was treated at 150 °C in benzene for 43 h in the presence of 1, no reaction was observed and the starting material **4b** was recovered quantitatively. In spite of the ruthenium(II)-catalyzed reaction **3** → **4** → **5** proceeding stepwise, the observation of no reaction of isolated **4b** suggests that hydrogen chloride will act an important role in the desulfonylation reaction of **4b** to **5b**. So, isolated **4b** in benzene in the presence of the catalyst 1 and hydrogen chloride was allowed to stand at 150 °C for 43 h, and **5b** was isolated in high yield in this case.

Table II. Formation of (*E*,*E*)-1,4-Diaryl-1,3-butadienes by Reaction of (*E*)-2-Arylethenesulfonyl Chloride with Vinylarenes Catalyzed by a Ruthenium(II) Complex (1) in Benzene at 150 °C

R in **2**	Ar in ArCH=CH$_2$	reaction time, h	product	yield, %[a]
C_6H_5	*p*-$CH_3C_6H_4$	43	**5a**	91
C_6H_5	C_6H_5	43	**5b**	91
C_6H_5	*p*-ClC_6H_4	43	**5c**	93
C_6H_5	*m*-$NO_2C_6H_4$	70	**5d**	74
p-$CH_3C_6H_4$	*p*-ClC_6H_4	43	**5e**	97
p-ClC_6H_4	*p*-ClC_6H_4	43	**5f**	94

[a] The yields refer to pure isolated products.



4b **5b**

This finding shows that hydrogen chloride activated the ruthenium(II) catalyst in the desulfonylation of divinyl sulfone **4**, and the catalytic effect of the ruthenium(II) catalyst is different in the addition reaction of **2** to olefin and in the dehydrochlorination of **3** from desulfonylation of **4**, although at present the mechanistic implications of hydrogen chloride on the structure and catalytic property of the ruthenium(II) complex are not clear.

As we have proposed a redox transfer radical chain mechanism in the ruthenium(II)-catalyzed addition of aryl- or methanesulfonyl chlorides to olefin,[3,5] we speculate that the mechanism is as shown in Scheme I in the reaction of (*E*)-2-arylethenesulfonyl chloride with vinylarene catalyzed by 1. At the begining of the reaction, ruthenium(II) catalyst 1 reacts with sulfonyl chloride to form the sulfonyl radical **6** which adds to vinylarene to give radical intermediate **7**, and the addition reaction will be completed by chlorine abstraction from $Ru^{III}Cl$. Then the ruthenium(II) catalyst acts in the dehydrochlorination and desulfonylation reaction. The 1,3-diene **5** will be formed from divinyl sulfone **4** via such complexes as **8**, **9**, and **10**.

To study the scope and limitation of the formation of 1,3-dienes, the reaction of (*E*)-2-arylethenesulfonyl chloride with several vinylarenes was carried out in benzene in the presence of 1 at 150 °C for 43 h, and 1,4-diaryl-1,4-butadienes (**5**) were isolated in high yield. The results are summarized in Table II.

The fact that each of the substituents R and Ar groups in (*E*)-2-arylethenesulfonyl chloride and vinylarene occu-

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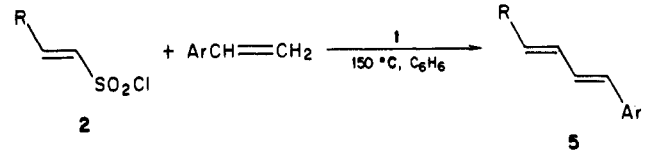


pied the 1,4-position of the 1,3-butadienes formed supports the intramolecular desulfonylation as shown in Scheme I. Although the synthetic use of carbon–carbon bond formation by thermal desulfonylation of sulfone is known, such pyrolysis reaction without catalyst have to raise the reaction temperature at 500–710 °C.[6] In contrast, the present 1,3-butadiene formation catalyzed by a ruthenium(II) complex can be performed under very mild conditions (at 150 °C) in solution. Transition metal complex catalyzed desulfonylation of arenesulfonyl chlorides forming chloroarenes is known;[7] however, we emphasize that this is the first example of the carbon–carbon bond formation by desulfonylation catalyzed by a transition metal complex. There have been a number of method for preparation of 1,3-dienes, but most of them bring some limitations and difficulties into practice, because some require air-sensitive or sophisticated organometallic reagents, many of which are reactive enough toward common functional groups, and others require drastic reaction conditions, and/or suffer from rather low stereoselectivity.[8-16] The present method is a very excellent one-pot synthesis of symmetrical and unsymmetrical (*E,E*)-1,4-diaryl-1,3-butadienes (**5**) since (*E*)-2-arylethenesulfonyl chloride can be prepared very easily by treating vinylarenes with sulfuryl chloride in dimethyl formamide.

The present reaction can be regarded as the oxidative coupling reaction of each terminal carbon atom of two kinds of vinyl arenes by using sulfuryl chloride and ruthenium(II) catalyst. Since, the direct oxidative coupling of vinylarenes is impossible, the present reaction offers a novel and convenient synthetic method of symmetrical and

Scheme I

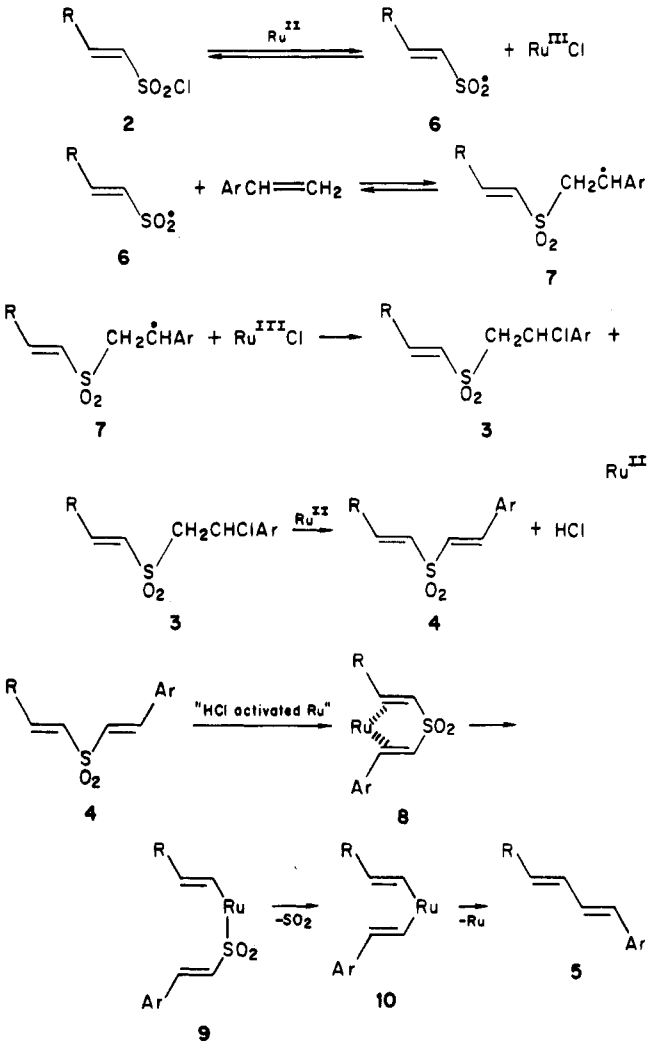
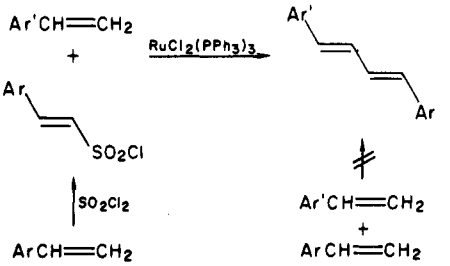


Table III. Reaction of (*E*)-2-Phenylethenesulfonyl Chloride with Alkyl Olefins in the Presence of 1 in Benzene at 150 °C for 70 h

alkyl olefin	product	yield, %[a]
$CH_3(CH_2)_3CH{=}CH_2$	**12a**	53
$CH_3(CH_2)_4CH{=}CH_2$	**12b**	52
$CH_3(CH_2)_5CH{=}CH_2$	**12c**	53
$c\text{-}C_6H_{11}\text{-}CH{=}CH_2$	**12d**	46

[a] The yields refer to pure isolated products.

unsymmetrical 1,3-dienes. However, at the present time, the reactions of (*E*)-1-propene-1- and ethenesulfonyl chloride with vinylarenes do not afford 1,3-dienes under similar reaction conditions.



The reactions of (*E*)-2-phenylethenesulfonyl chloride in the presence of 1 in benzene were carried out also with alkyl olefin. In this case, no reaction occurred at 130 °C, and all the starting materials were recovered. By raising the reaction temperature to 150 °C the reaction between

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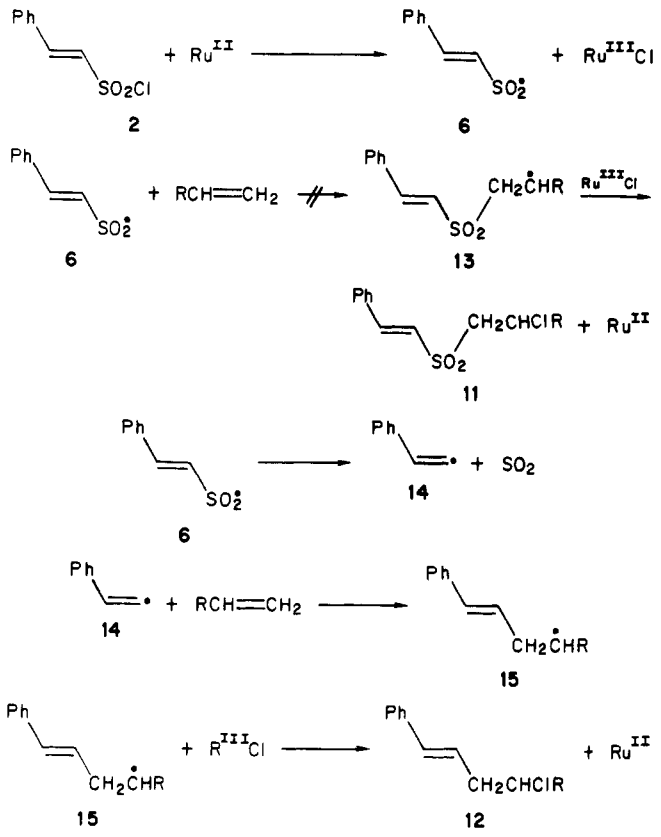
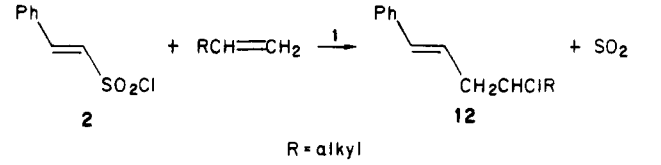
Scheme II



(*E*)-2-phenylethenesulfonyl chloride with alkyl olefin was observed; however, the reaction product was not the expected 1:1 adduct, (*E*)-2-alkyl-2-chloroethyl styryl sulfone (**11**), but the 1:1 adduct, (*E*)-4-alkyl-4-chloro-1-phenyl-1-butene (**12**) with extrusion of sulfur dioxide. The results



are summarized in Table III. Addition of sulfonyl chloride to olefins catalyzed by **1** with extrusion of sulfur dioxide was observed in the reaction of trichloromethanesulfonyl chloride with olefin; however, in this case, sulfur dioxide was released in both the reactions with alkyl olefins and vinylarenes.[4] In the present case, it is of interest that (*E*)-2-phenylethenesulfonyl chloride reacts in a different manner with alkyl olefins and with vinylarenes. The reaction mechanism is proposed as shown in Scheme II.

The sulfonyl radical **6** formed by the interaction of (*E*)-2-phenylethenesulfonyl chloride and ruthenium(II) catalyst **1** could not add to the carbon–carbon double bond because the adduct radical **13** is not resonance-stabilized, in contrast with the radical intermediate formed by addition of **2** to vinylarenes **7** in Scheme I, the activation energy of addition of sulfonyl radical **6** being too high to realize smooth addition. So, sulfonyl radical **6** releases the sulfur dioxide to form vinyl radical **14**. The vinyl radical **14** could react with the alkyl olefin to give the radical intermediate **15** which abstracts the chlorine atom from $Ru^{III}Cl$ to afford the final product **12**.

Experimental Section

Measurement. Melting points and boiling points are 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 JNM-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. Mass spectra were determined with a JEOL JMS-DX 300 mass spectrometer with JEOL JMA 5000 Mass Data System at an ionizing voltage of 20–70 eV. Iatroscan was used on a IATROSCAN Laboratory Model TH-10 on a silica gel rod using hexane–benzene as an eluent.

Materials. Dichlorotris(triphenylphosphine)ruthenium(II) (**1**) were prepared by the method described in the literature.[17] Ethenesulfonyl chloride was prepared from 1,2-dibromoethane by treating with sodium sulfite, phosphorus pentachloride, and then triethylamine according to the literature:[18] yield 45%; bp 52–55 °C (1 mmHg) (lit. bp 52–56 °C (1 mmHg).[18] (*E*)-1-Propene-1-sulfonyl chloride was prepared from propylene oxide by treatment with sodium bisulfite, phosphorus pentachloride, and then with triethylamine in ether according to the literature:[19] yield 76%; bp 38 °C (2 mmHg). (*E*)-2-Phenylethenesulfonyl chloride was prepared according to the method described in the literature by treating with sulfuryl chloride in dimethylformamide: yield 70%; mp 89–90 °C (from chloroform–petroleum ether; lit. mp 89–90 °C).[20] Styrene, *p*-methylstyrene, *p*-chlorostyrene, *m*-nitrostyrene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and vinylcyclohexane from Tokyo Kasei Chemicals were purified by distillation under nitrogen prior to use.

General Procedure for the Reaction of Alkenesulfonyl Chlorides with Olefins. A solution containing 2.0 mmol of alkenesulfonyl chloride, 2.0 mmol of olefin, and 0.02 mmol of dichlorotris(triphenylphosphine)ruthenium(II) (**1**) in 4.0 mL of benzene was degassed and heated in a sealed tube at 80–150 °C. The reaction mixture was chromatographed on Florisil by using hexane–ether as the eluent. The results are given in Tables I–III.

Treatment of the Adducts 3a–d and 3g–n with Triethylamine. To a solution of 1.0 mmol of adduct **3** in 3.0 mL of benzene was added 121 mg (1.2 mmol) of triethylamine in 1.0 mL of benzene, and the mixture was stirred at room temperature for 2 h. The reaction mixture was chromatographed on Florisil by using hexane–benzene as an eluent. Divinyl sulfones **4a–d** and **4g–n** were isolated in greater yield than 95% in all the cases, with one exception.

Measurement of the Time Course in the Reaction of (*E*)-2-Phenylethenesulfonyl Chloride with *p*-Methylstyrene Catalyzed by 1. A mixture containing 2.04 g (10 mmol) of (*E*)-2-phenylethenesulfonyl chloride, 1.18 g (10 mmol) of *p*-methylstyrene, and 95.9 mg (0.10 mmol) of ruthenium(II) catalyst **1** in 20.0 mL of benzene was prepared. This solution was divided equally into ten glass tubes, which were degassed, sealed, and then heated at 150 °C. After an adequate reaction time interval, one sealed tube was taken out from the thermostat, and progress of reaction was determined by using IATROSCAN.

The physical and spectral data of the compounds **3–5** are as follows: **(*E*)-2-Chloro-2-(*p*-tolyl)ethyl styryl sulfone (3a)**: mp 83.5–84.0 °C (from ethanol); IR (KBr) 1130 and 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (3 H, s), 3.79 (1 H, d, J = 8.4 Hz), 3.80 (1 H, d, J = 7.2 Hz), 5.28 (1 H, dd, J = 7.2 and 8.4 Hz), 6.21 (1 H, d, J = 15.0 Hz), 7.0–7.4 (9 H, m), and 7.28 (1 H, d, J = 15.0 Hz); MS, m/z 320 and 322 (M^+). Anal. Calcd for $C_{17}H_{17}O_2SCl$: C, 63.64; H, 5.34. Found: C, 63.50; H, 5.16.

(*E*)-2-Chloro-2-phenylethyl styryl sulfone (3b): mp 97–98 °C (from ethanol); IR (KBr) 1120 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (1 H, d, J = 7.8 Hz), 3.82 (1 H, d, J = 7.8 Hz), 5.33 (1 H, t, J = 7.8 Hz), 6.33 (1 H, d, J = 15.0 Hz), 7.1–7.4 (10 H, m), and 7.35 (1 H, d, J = 15.0 Hz); MS, m/z 306 and 308 (M^+). Anal. Calcd for $C_{16}H_{15}O_2SCl$: C, 62.73; H, 4.93. Found: C, 62.84; H, 4.89.

(*E*)-2-Chloro-2-(*p*-chlorophenyl)ethyl styryl sulfone (3c): mp 94–95 °C (from ethanol); IR (KBr) 1125 and 1310 cm^{-1}; ^1H

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NMR ($CDCl_3$) δ 3.75 (1 H, d, J = 7.8 Hz), 3.78 (1 H, d, J = 6.6 Hz), 5.29 (1 H, dd, J = 6.6 and 7.8 Hz), 6.21 (1 H, d, J = 15.0 Hz), 7.1–7.4 (9 H, m), and 7.28 (1 H, d, J = 15.0 Hz); MS, m/z 340, 342, and 344 (M^+). Anal. Calcd for $C_{16}H_{14}O_2SCl_2$: C, 56.31; H, 4.14. Found: C, 56.35; H, 4.12.

(*E*)-2-Chloro-2-(*m*-nitrophenyl)ethyl styryl sulfone (3d): mp 99–100 °C (from ethanol); IR (KBr) 1120, 1310, 1360, and 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (1 H, d, J = 8.4 Hz), 3.82 (1 H, d, J = 7.2 Hz), 5.42 (1 H, dd, J = 7.2 and 8.4 Hz), 6.60 (1 H, d, J = 15.0 Hz), 7.29 (5 H, s), 7.37 (1 H, d, J = 15.0 Hz), and 6.9–8.2 (4 H, m); MS, m/z 351 and 353 (M^+). Anal. Calcd for $C_{16}H_{14}O_4NSCl$: C, 54.62; H, 4.01; N, 3.98. Found: C, 54.32; H, 3.91; N, 4.01.

(*E*)-2-Chloro-2-phenylethyl *p*-methylstyryl sulfone (3e): mp 121–122 °C (from ethanol); IR (KBr) 1120 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s), 3.81 (1 H, d, J = 7.2 Hz), 3.82 (1 H, d, J = 7.2 Hz), 5.35 (1 H, t, J = 7.2 Hz), 6.29 (1 H, d, J = 15.0 Hz), 7.12 (5 H, s), 7.2–7.4 (4 H, m), and 7.32 (1 H, d, J = 15.0 Hz); MS, m/z 320 and 322 (M^+). Anal. Calcd for $C_{17}H_{17}O_2SCl$: C, 63.64; H, 5.34. Found: C, 63.67; H, 5.29.

(*E*)-2-Chloro-2-phenylethyl *p*-chlorostyryl sulfone (3f): mp 109–110 °C (from ethanol); IR (KBr) 1120 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.79 (1 H, d, J = 6.6 Hz), 3.81 (1 H, d, J = 6.6 Hz), 5.32 (1 H, t, J = 6.6 Hz), 6.30 (1 H, d, J = 15.0 Hz), 7.1–7.4 (9 H, m), and 7.30 (1 H, d, J = 15.0 Hz); MS, m/z 340, 342, and 344 (M^+). Anal. Calcd for $C_{16}H_{14}O_2SCl_2$: C, 56.31; H, 4.14. Found: C, 56.23; H, 4.05.

(*E*)-2-Chloro-2-(*p*-tolyl)ethyl 1-propenyl sulfone (3g): mp 62.5–63.5 °C (from hexane–ethanol); IR (KBr) 1130 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (3 H, dd, J = 0.6 and 6.6 Hz), 2.30 (3 H, s), 3.69 (1 H, d, J = 7.8 Hz), 3.72 (1 H, d, J = 7.8 Hz), 5.27 (1 H, t, J = 7.8 Hz), 5.94 (1 H, dq, J = 0.6 and 14.4 Hz), 6.72 (1 H, dq, J = 6.6 and 14.4 Hz), and 7.21 (4 H, s); MS, m/z 258 and 260 (M^+). Anal. Calcd for $C_{12}H_{15}O_2SCl$: C, 55.70; H, 5.84. Found: C, 57.76; H, 5.78.

(*E*)-2-Chloro-2-phenylethyl 1-propenyl sulfone (3h): mp 99.5–100.5 °C (from ethanol); IR (KBr) 1125 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (3 H, dd, J = 1.8 and 6.6 Hz), 3.63 (1 H, d, J = 7.2 Hz), 3.66 (1 H, d, J = 7.2 Hz), 5.28 (1 H, t, J = 7.2 Hz), 5.80 (1 H, dq, J = 1.8 and 13.8 Hz), 6.58 (1 H, dq, J = 6.6 and 13.8 Hz), and 7.32 (5 H, s); MS, m/z 244 and 246 (M^+). Anal. Calcd for $C_{11}H_{13}O_2SCl$: C, 53.98; H, 5.35. Found: C, 53.85, H, 5.29.

(*E*)-2-Chloro-2-(*p*-chlorophenyl)ethyl 1-propenyl sulfone (3i): mp 78–79 °C (from ethanol); IR (KBr) 1120 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (3H, dd, J = 1.2 and 6.6 Hz), 3.53 (1 H, d, J = 7.2 Hz), 3.57 (1 H, d, J = 7.2 Hz), 5.13 (1 H, t, J = 7.2 Hz), 5.86 (1 H, dq, J = 1.2 and 15.0 Hz), 6.59 (1 H, dq, J = 6.6 and 15.0 Hz), and 7.15 (4 H, s); MS, m/z 278, 280, and 282 (M^+). Anal. Calcd for $C_{11}H_{12}O_2SCl$: C, 47.32; H, 4.33. Found: C, 47.38; H, 4.25.

(*E*)-2-Chloro-2-(*m*-nitrophenyl)ethyl 1-propenyl sulfone (3j): mp 111–112 °C (from ethanol); IR (KBr) 1120, 1300, 1355, and 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (3 H, dd, J = 0.6 and 6.6 Hz), 3.59 (1 H, d, J = 7.2 Hz), 3.64 (1 H, d, J = 7.2 Hz), 5.31 (1 H, t, J = 7.2 Hz), 5.9–6.2 (1 H, m), 6.3–7.2 (1 H, m), and 7.3–8.3 (4 H, m); MS, m/z 289 and 291 (M^+). Anal. Calcd for $C_{11}H_{12}O_4NSCl$: C, 45.60; H, 4.17; N, 4.83. Found: C, 45.53; H, 4.15; N, 4.78.

2-Chloro-2-(*p*-tolyl)ethyl vinyl sulfone (3k): mp 71–72 °C (from ethanol); IR (KBr) 1135 and 1315 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (3 H, s), 3.56 (1 H, d, J = 7.2 Hz), 3.61 (1 H, d, J = 7.2 Hz), 5.15 (1 H, t, J = 7.2 Hz), 5.6–6.3 (3 H, m), and 6.9–7.3 (4 H, m); MS, m/z 244 and 246 (M^+). Anal. Calcd for $C_{11}H_{13}O_2SCl$: C, 53.98; H, 5.35. Found: C, 53.85; H, 5.20.

2-Chloro-2-phenylethyl vinyl sulfone (3l): mp 75–76 °C (from ethanol); IR (KBr) 1120 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.69 (1 H, d, J = 7.2 Hz), 3.73 (1 H, d, J = 7.2 Hz), 5.29 (1 H, t, J = 7.2 Hz), 5.8–6.4 (3 H, m), and 7.32 (5 H, s); MS, m/z 230 and 232 (M^+). Anal. Calcd for $C_{10}H_{11}O_2SCl$: C, 52.06; H, 4.81. Found: C, 52.15; H, 4.76.

2-Chloro-2-(*p*-chlorophenyl)ethyl vinyl sulfone (3m): mp 94–95 °C (from ethanol); IR (KBr) 1130 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (1 H, d, J = 7.2 Hz), 3.59 (1 H, d, J = 7.2 Hz), 5.17 (1 H, t, J = 7.2 Hz), 5.7–6.4 (3 H, m), and 7.19 (4 H, s); MS, m/z 264, 266, and 268 (M^+). Anal. Calcd for $C_{10}H_{10}O_2SCl_2$: C, 45.29; H, 3.80. Found: C, 45.29; H, 3.58.

2-Chloro-2-(*m*-nitrophenyl)ethyl vinyl sulfone (3n): mp 119–120 °C (from ethanol). IR (KBr) 1115, 1310, 1350, and 1535 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.93 (2 H, d, J = 6.6 Hz), 5.44 (1 H, t, J = 6.6 Hz), 5.99 (1 H, d, J = 10.2 Hz), 6.12 (1 H, d, J = 15.6 Hz), 6.73 (1 H, dd, J = 10.2 and 15.6 Hz), and 7.3–8.4 (4 H, m); MS, m/z 275 and 277 (M^+). Anal. Calcd for $C_{10}H_{10}O_4NSCl$: C, 43.56; H, 3.66; N, 5.08. Found: C, 43.79; H, 3.49; N, 5.01.

(*E*,*E*)-*p*-Methylstyryl styryl sulfone (4a): mp 124–125 °C (from ethanol); IR (KBr) 1130 and 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (3 H, s), 6.75 (1 H, d, J = 14.4 Hz), 6.80 (1 H, d, J = 14.4 Hz), 7.0–7.5 (9 H, m), 7.59 (1 H, d, J = 14.4 Hz), and 7.60 (1 H, d, J = 14.4 Hz); MS, m/z 284 (M^+); HRMS, m/z 284.0897 ($C_{17}H_{16}O_2S$ requires 284.0871).

(*E*,*E*)-Distyryl sulfone (4b): mp 91–92 °C (lit.[21] mp 92 °C); IR (KBr) 1130 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.70 (2 H, d, J = 15.0 Hz), 7.1–7.3 (10 H, m), and 7.48 (2 H, d, J = 15.0 Hz); MS, m/z 270 (M^+).

(*E*,*E*)-*p*-Chlorostyryl styryl sulfone (4c): mp 150–151 °C (from ethanol); IR (KBr) 1125 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (2 H, d, J = 15.0 Hz), 7.1–7.6 (9 H, m), 7.57 (1 H, d, J = 15.0 Hz), and 7.61 (1 H, d, J = 15.0 Hz); MS, m/z 304 and 306 (M^+); HRMS, m/z 304.0411 ($C_{16}H_{13}O_2SCl$ requires 304.0324).

(*E*,*E*)-*m*-Nitrostyryl styryl sulfone (4d): mp 91–92 °C (from ethanol); IR (KBr) 1125, 1300, 1355, and 1525 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.74 (1 H, d, J = 15.0 Hz), 6.89 (1 H, d, J = 15.0 Hz), 7.33 (5 H, s), and 7.4–8.3 (6 H, m); MS, m/z 315 (M^+); HRMS, m/z 315.0523 ($C_{16}H_{13}O_4NS$ requires 315.0565).

(*E*,*E*)-*p*-Methylstyryl 1-propenyl sulfone (4g): mp 132–133 °C (from ethanol); IR (KBr) 1125 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (3 H, dd, J = 1.2 and 6.6 Hz), 2.32 (3 H, s), 6.30 (1 H, dq, J = 1.2 and 15.6 Hz), 6.68 (1 H, d, J = 15.6 Hz), 6.88 (1 H, dq, J = 1.2 and 6.6 Hz), 6.98 (1 H, dq, J = 1.2 and 15.6 Hz), 7.15 (2 H, d, J = 7.8 Hz), 7.36 (2 H, d, J = 7.8), and 7.51 (1 H, d, J = 15.6 Hz); MS, m/z 222 (M^+); HRMS, m/z 222.0691 ($C_{12}H_{14}O_2S$ requires 222.0715).

(*E*,*E*)-1-Propenyl styryl sulfone (4h): mp 69–70 °C (from ethanol); IR (KBr) 1125 and 1305 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (3 H, dd, J = 1.2 and 6.6 Hz), 6.28 (1 H, dq, J = 1.2 and 15.6 Hz), 6.72 (1H, d, J = 15.6 Hz), 6.99 (1 H, dq, J = 6.6 and 15.6 Hz), 7.39 (5 H, s), and 7.53 (1 H, d, J = 15.6 Hz); MS, m/z 208 (M^+); HRMS, m/z 208.0554 ($C_{11}H_{12}O_2S$ requires 208.0558).

(*E*,*E*)-*p*-Chlorostyryl 1-propenyl sulfone (4i): mp 112–113 °C (from ethanol); IR (KBr) 1130 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (3 H, dd, J = 1.2 and 6.6 Hz), 6.28 (1 H, dq, J = 1.2 and 15.6 Hz), 6.70 (1 H, d, J = 15.6 Hz), 6.83 (1 H, d, J = 6.6 and 15.6 Hz), 6.96 (1 H, dq, J = 6.6 and 15.6 Hz), 7.27 (2 H, d, J = 7.8 Hz), 7.44 (2 H, d, J = 7.8 Hz), and 7.47 (1 H, d, J = 15.6 Hz); MS, m/z 242 and 244 (M^+). HRMS, m/z 242.0093 ($C_{11}H_{11}O_2SCl$ requires 242.0168).

(*E*,*E*)-*m*-Nitrostyryl 1-propenyl sulfone (4j): mp 117.5–118.5 °C (from ethanol); IR (KBr) 1125, 1300, 1350, and 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (3 H, dd, J = 1.2 and 6.6 Hz), 6.27 (1 H, dq, J = 1.2 and 15.0 Hz), 6.90 (1 H, d, J = 15.0 Hz), 7.01 (1 H, dq, J = 6.6 and 15.0 Hz), 7.60 (1 H, d, J = 15.0 Hz), 7.4–8.3 (4 H, m); MS, m/z 253 (M^+); HRMS, m/z 253.0428 ($C_{11}H_{11}O_4NS$ requires 253.0409).

(*E*)-*p*-Methylstyryl vinyl sulfone (4k): mp 86–87 °C (from ethanol); IR (KBr) 1130 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (3 H, s), 5.8–6.4 (3 H, m), 6.56 (1 H, d, J = 15.6 Hz), 7.14 (2 H, d, J = 8.4 Hz), 7.26 (2 H, d, J = 8.4 Hz), and 7.43 (1 H, d, J = 15.6 Hz); MS, m/z 208 (M^+); HRMS, m/z 208.0567 ($C_{11}H_{12}O_2S$ requires 208.0557).

(*E*)-Styryl vinyl sulfone (4l): mp 72–73 °C (from ethanol); IR (KBr) 1130 and 1305 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.9–6.6 (3 H, m), 6.79 (1 H, d, J = 15.0 Hz), 7.42 (5 H, s), and 7.60 (1 H, d, J = 15.0 Hz); MS, m/z 194 (M^+); HRMS, m/z 194.0412 ($C_{10}H_{10}O_2S$ requires 194.0402).

(*E*)-*p*-Chlorostyryl vinyl sulfone (4m): mp 60–61 °C (from ethanol); IR (KBr) 1130 and 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.9–6.6 (3 H, m), 6.73 (1 H, d, J = 15.0 Hz), 7.36 (4 H, s), and 7.53 (1 H, d, J = 15.0 Hz); MS, m/z 228 and 230 (M^+); HRMS, m/z 228.0034 ($C_{10}H_9O_2SCl$ requires 228.0011).

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(*E*)-*m*-Nitrostyryl vinyl sulfone (4n): mp 117–118 °C (from ethanol); IR (KBr) 1130, 1305, 1365, and 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.9–7.3 (5 H, m) and 7.4–8.5 (4 H, m); MS, *m/z* 239 (M^+); HRMS, *m/z* 239.0256 ($C_{10}H_9O_4NS$ requires 239.0252).

(*E,E*)-1-Phenyl-4-(*p*-tolyl)-1,3-butadiene (5a): mp 152–153 °C (lit.[22] mp 155–156 °C), IR (KBr) 3030, 2920, 995, 805, 750, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s), 6.3–6.8 (4 H, m), and 6.9–7.6 (9 H, m); MS, *m/z* 220 (M^+).

(*E,E*)-1,4-Diphenyl-1,3-butadiene (5b): mp 148–149 °C (from ethanol, lit.[23] mp 149.7 °C); IR (KBr) 3010, 1490, 1440, 990, 740, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.1–6.8 (4 H, m) and 6.9–7.4 (10 H, m); MS, *m/z* 206 (M^+).

(*E,E*)-1-(*p*-Chlorophenyl)-4-phenyl-1,3-butadiene (5c): mp 161–162 °C (from ethanol, lit.[22] mp 161 °C); IR (KBr) 3010, 1480, 1090, 980, 840, 745, and 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6–6.9 (4 H, m) and 7.0–7.6 (9 H, m); MS, *m/z* 240 and 242 (M^+).

(*E,E*)-1-(*m*-Nitrophenyl)-4-phenyl-1,3-butadiene (5d): mp 142–143 °C (from ethanol; lit.[24] mp 146 °C); IR (KBr) 3020, 1535, 1350, 990, 755, 735, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.5–6.9 (4 H, m) and 7.0–8.4 (9 H, m); MS, *m/z* 251 (M^+).

(*E,E*)-1-(*p*-Chlorophenyl)-4-(*p*-methylphenyl)-1,3-butadiene (5e): mp 206–207 °C (from benzene); IR (KBr) 3020, 1490, 995, 990, 850, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s), 6.3–6.8 (4 H, m), and 6.9–7.6 (8 H, m); MS, *m/z* 254 and 256 (M^+). Anal. Calcd for $C_{17}H_{15}Cl$: C, 80.15; H, 5.94. Found: C, 80.12; H, 5.91.

(*E,E*)-1,4-Bis(*p*-chlorophenyl)-1,3-butadiene (5f): mp 201–202 °C (from benzene); IR (KBr) 3020, 1490, 1400, 1095, 1000, 855, and 800 cm^{-1}; ^1H NMR (C_6D_6) δ 6.0–6.8 (2 H, m) and 6.9–7.5 (10 H, m); MS, *m/z* 274, 276, and 278 (M^+). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40. Found: C, 69.80; H, 4.38.

(22) Leznoff, C. C. *Can. J. Chem.* **1970**, *48*, 1842.
(23) Corson, B. B. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 228.
(24) Bergmann, F.; Schapiro, D. *J. Org. Chem.* **1947**, *12*, 57.

(*E*)-4-Chloro-1-phenyl-1-octene (12a): IR (neat) 3025, 2925, 2860, 1595, 1490, 1450, 965, 745, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.0 (9 H, m), 2.2–2.7 (2 H, m), 3.3–3.9 (1 H, m), and 6.0–7.5 (7 H, m); MS, *m/z* 222 and 224 (M^+); HRMS, *m/z* 222.1157 ($C_{14}H_{19}Cl$ requires 222.1175).

(*E*)-4-Chloro-1-phenyl-1-nonene (12b): IR (neat) 3025, 2950, 2925, 2850, 1595, 1490, 1450, 965, 790, 760, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.0 (11 H, m), 2.3–2.7 (2 H, m), 3.3–4.0 (1 H, m), and 5.9–7.4 (7 H, m); MS, *m/z* 236 and 238 (M^+): HRMS, *m/z* 236.1325 ($C_{15}H_{21}Cl$ requires 236.1332).

(*E*)-4-Chloro-1-phenyl-1-decene (12c): IR (neat) 3020, 2940, 2920, 2850, 1490, 1450, 1375, 960, 740, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.0 (13 H, m), 2.4–2.7 (2 H, m), 3.6–4.2 (1 H, m), and 6.2–7.4 (7 H, m); MS, *m/z* 250 and 252 (M^+); HRMS, *m/z* 250.1420 ($C_{16}H_{23}Cl$ requires 250.1488).

(*E*)-4-Chloro-4-cyclohexyl-1-phenyl-1-butene (12d): IR (neat) 3060, 3040, 2920, 2850, 1593, 1490, 1445, 960, 740, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.1 (11 H, m), 2.3–2.8 (2 H, m), 3.5–4.1 (1 H, m), and 6.1–7.5 (7 H, m); MS, *m/z* 248 and 250 (M^+); HRMS, *m/z* 248.1283 ($C_{16}H_{21}Cl$ requires 248.1332).

Registry No. 2a, 52147-97-4; **2e**, 98821-28-4; **2f**, 52147-98-5; **2g**, 98821-29-5; **2l**, 6608-47-5; **3a**, 98821-15-9; **3b**, 68667-91-4; **3c**, 98821-16-0; **3d**, 98821-17-1; **3e**, 98821-18-2; **3f**, 98821-19-3; **3g**, 98821-20-6; **3h**, 98821-21-7; **3i**, 98821-22-8; **3j**, 98821-23-9; **3k**, 98821-24-0; **3l**, 98821-25-1; **3m**, 98821-26-2; **3n**, 98821-27-3; **4a**, 98821-30-8; **4b**, 65350-60-9; **4c**, 98821-31-9; **4d**, 98821-32-0; **4g**, 98821-33-1; **4h**, 98821-34-2; **4i**, 98821-35-3; **4j**, 98821-36-4; **4k**, 98821-37-5; **4l**, 98821-38-6; **4m**, 98821-39-7; **4n**, 98821-40-0; **5a**, 37985-11-8; **5b**, 538-81-8; **5c**, 37985-13-0; **5d**, 57668-32-3; **5e**, 98821-41-1; **5f**, 88539-06-4; **12a**, 98821-42-2; **12b**, 98821-43-3; **12c**, 98821-44-4; **12d**, 98821-45-5; *p*-$CH_3C_6H_4CH{=}CH_2$, 622-97-9; $C_6H_5CH{=}CH_2$, 100-42-5; *p*-$ClC_6H_4CH{=}CH_2$, 1073-67-2; *m*-$NO_2C_6H_4CH{=}CH_2$, 586-39-0; $CH_3(CH_2)_3CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_4CH{=}CH_2$, 592-76-7; $CH_3(CH_2)_5CH{=}CH_2$, 111-66-0; *c*-$C_6H_{11}CH{=}CH_2$, 695-12-5.

Magnetic Circular Dichroism of Cyclic π-Electron Systems. 27.[1] Mesoionic Compounds

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Received June 11, 1985

Magnetic circular dichroism of a series of mesoionic heterocycles derived from a (4*n* + 2)-electron perimeter has been measured and calculated. The spectra permit an identification of L_1 and L_2 bands. The observed MCD signs agree with simple qualitative arguments based on the perimeter model.

Absolute signs of low-energy $\pi\pi^*$ transitions in the magnetic circular dichroism (MCD) spectra of cyclic π-electron systems formally derived from (4*n* + 2)-electron perimeters are frequently very sensitive to the details of molecular structure, such as the nature and position of substituents and heteroatoms. These signs are usually readily predictable from the knowledge of the perturbations which convert the parent (4*n* + 2)-electron perimeter into the molecule in question.[2] The predictions can be semiquantitative, based on explicit MO calculations, typically of the PPP or INDO/S variety, or qualitative, based on the perimeter model, which requires only the knowledge of the relative size of the gaps between the two highest occupied molecular orbitals (ΔHOMO) and between the two lowest unoccupied MO's (ΔLUMO) derived from the perimeter. The relative size may be obvious by inspection, using the PMO theory. In particularly complicated cases, it may have to be obtained from a calculation. The simplicity of the perimeter model is appealing not only for facile predictions of MCD signs but also for providing physical insight into the origin of the signs obtained using computer programs. Perhaps equally important is its contribution to the organization of knowledge concerning UV and MCD spectra of large classes of compounds which may appear widely dissimilar at first sight.

Since the perimeter model is based on perturbation theory, it is interesting to ask how strong a perturbation is needed before the model fails to account for the observed MCD signs. From this point of view, mesoionic compounds[3] represent a challenging test case. The electronic

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0022-3263/85/1950-5050$01.50/0