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A NOVEL SYNTHESIS OF (E,E)-1,4-DIARYL-1,3-BUTADIENES BY THE RUTHENIUM(II) CATALYZED REACTION OF (E)-2-ARYLETHENESULFONYL CHLORIDES WITH VINYLARENES

Nobumasa KAMIGATA,* Jun-ichi OZAKI, and Michio KOBAYASHI
Department of Chemistry, Tokyo Metropolitan University,
Fukazawa, Setagaya-ku, Tokyo 158

Symmetrical and unsymmetrical (E,E)-1,4-diaryl-1,3-butadienes can be prepared in high yields from (E)-2-arylethenesulfonyl chlorides by treating with vinylarenes in the presence of ruthenium(II) phosphine complex in benzene.

Conjugated 1,3-dienes are valuable intermediates in a number of synthetic organic processes, most notably in the Diels-Alder reaction.[1] There have been a number of methods 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 too reactive toward common functional groups, and others require drastic reaction conditions, and/or suffer from rather low stereoselectivity.[2-10] During the course of the studies on the catalytic reactions of the sulfonyl chlorides with olefins in our laboratory,[11] we found that the reactions of (E)-2-arylethenesulfonyl chlorides with vinylarenes in the presence of catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) give (E,E)-1,4-diaryl-1,3-butadienes in a highly stereoselective fashion, hence providing one of the most useful methods for preparation of such compounds. The results are reported in the present communication.

In a typical procedure, a solution of 405 mg (2.0 mmol) of (E)-2-phenylethenesulfonyl chloride, 208 mg (2.0 mmol) of styrene, 20 mg (0.02 mmol) of dichlorotris(triphenylphosphine)ruthenium(II) in 4.0 ml of benzene was heated at 80 °C for 72 hours in a degassed sealed tube. TLC analysis of the resulting mixture indicated that the starting materials were completely consumed and that only one product was formed. The crude mixture was subjected to chromatography on a Florisil column using hexane-ether (1:1) as an eluent to remove the catalyst, and the 1:1 adduct, (E)-2-chloro-2-phenylethyl styryl sulfone (1) was isolated in 98% yield: mp 97-98 °C (from ethanol).

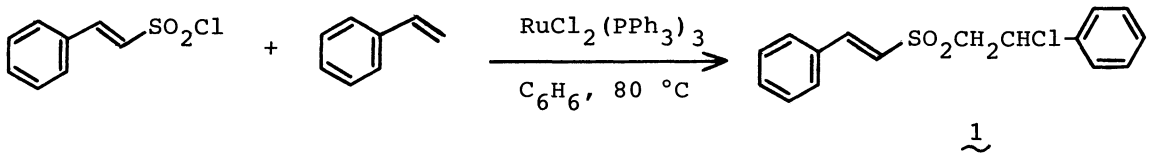

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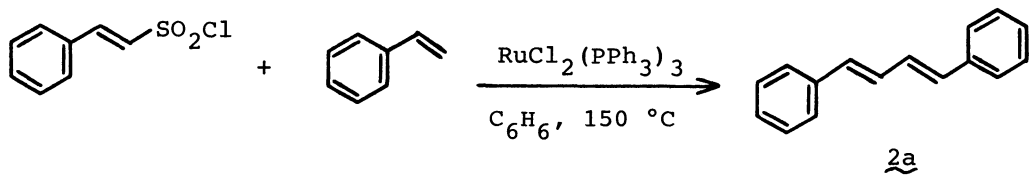
Table 1. Reaction of (E)-2-arylethenesulfonyl chlorides with vinylarenes[a)]

Ar in Ar⟨⟩SO_2Cl	Ar' in $Ar'CH=CH_2$	Reaction time/h	Product	Mp/°C	Yield/%[b)]
C_6H_5	C_6H_5	43	2a	148-149	96
C_6H_5	p-$CH_3C_6H_4$	43	2b	152-153	91
C_6H_5	p-ClC_6H_4	43	2c	161-162	93
C_6H_5	m-$NO_2C_6H_4$	70	2d	142-143	74
p-$CH_3C_6H_4$	C_6H_5	43	2b	148-149	95
p-$CH_3C_6H_4$	p-ClC_6H_4	43	2e	206-207	97
p-ClC_6H_4	p-ClC_6H_4	43	2f	201-202	94

a) The reaction was carried out in a degassed sealed tube containing (E)-2-arylethenesulfonyl chloride (2.0 mmol), vinylarene (2.0 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (20 mg, 0.02 mmol) in 4.0 ml of benzene at 150 °C.

b) The yield refers to the pure isolated product.

The result is quite similar to the reaction of arene- or alkanesulfonyl chloride with olefins reported previously from our laboratory.[11)] However, when the reaction was carried out at 150 °C for 43 hours, no adduct 1 was observed in the reaction mixture, and (E,E)-1,4-diphenyl-1,3-butadiene[12)] (2a) was isolated in 96% yield: mp 148-149 °C (from ethanol, lit. mp 149.7 °C)[13)] after purification by chromatography on Florisil using hexane as an eluent.



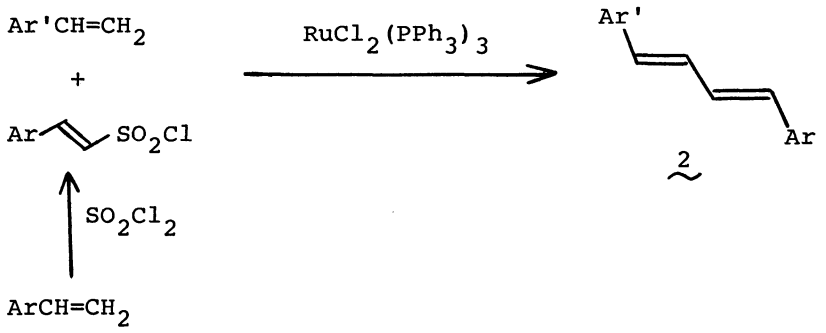
2a

It is quite interesting that the reaction product changed on raising the reaction temperature from 80 °C to 150 °C. The (E,E)-1,4-diphenyl-1,3-butadiene (2a) is presumed to be formed via the adduct 1 by dehydrochlorination and desulfonylation. The mechanism was further supported by the fact that the treatment of the isolated adduct 1 with the ruthenium(II) complex in benzene at 150 °C gave 2a quantitatively.

The reactions of several (E)-2-arylethenesulfonyl chlorides with vinylarenes were carried out under similar conditions to give selectively symmetrical or unsymmetrical (E,E)-1,4-diaryl-1,3-butadienes (2) in high yield. The results

are summarized in Table 1. As shown in Table 1, 1,4-diaryl groups in the product 2 originated from two starting materials: namely, one is aryl group in the (E)-2-arylethenesulfonyl chloride and the other is aryl group from the vinylarene. This means that intramolecular dehydrochlorination and desulfonylation of the adduct 1 take place without the formation of any crossed 1,4-diaryl-1,3-butadiene.

The reaction has several synthetically useful features: (1) the yield of 2 is very high, (2) the reaction is selective and only (E,E)-isomer of 1,4-diaryl-1,3-butadiene is obtained, (3) symmetrical or unsymmetrical 1,4-diaryl-1,3-butadiene is formed specifically, and (4) the reaction is conveniently carried out in one pot. Moreover, (E)-2-arylethenesulfonyl chloride is easily prepared from vinylarenes by treating with sulfuryl chloride in dimethylformamide.[14]



At the present stage, the reaction of alkenesulfonyl chlorides without aryl group does not give 1,3-dienes but 1:1 adduct in high yield. The studies concerning the limitations and the mechanism of the present reaction are now under progress; the details will be reported in another article.

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12) The structure of 2a was determined to be (E,E)-form by comparison of its mp, IR, Mass, and ^{1}H NMR spectra with authentic sample.

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