

REACTIONS OF ORGANOMAGNESIUM COMPOUNDS
WITH ALLYL SULFONES, CATALYZED BY
TRANSITION METAL SALTS

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According to [1, 2], the cross-coupling of Grignard reagents with allyl sulfones in the presence of Cu or Ni salts constitutes a promising route to unsaturated hydrocarbons.

This report deals with the possible participation in this reaction of various organomagnesium compounds and allyl sulfones, and new catalysts capable of effecting this reaction have been sought. Taking the cross-coupling of phenylmagnesium bromide with phenyl allyl sulfone as an example, we have established the optimum reaction conditions, and we have studied the effects of the type of transition metal, ligand, and solvent on the yields and selectivity of formation of allylbenzene.

It has been found that of the compounds of the transition metals tested as catalysts (Cu, Ti, Zr, Cr, Mn, Fe, Co, Ni, and Pd), the most efficient were CuCl_2 , Li_2CuCl_4 , $\text{Cu}(\text{acac})_2$, and modified PPh_3 (Table 1).

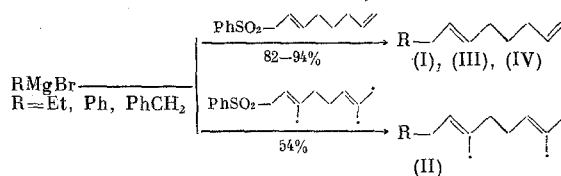
The nature of the electron-donor ligand in the catalyst has a marked effect on the yields of allylbenzene. For example, the yields of allylbenzene in the series PPh_3 , α, α' -bipyridyl, Bu_3P , $(\text{EtO})_3\text{P}$, $(\text{C}_6\text{H}_{11}\text{O})_3\text{P}$, and $(\text{PhO})_3\text{P}$ decrease from 96 to 15% (Table 2). In all probability, arylphosphines favor the activation and stabilization of the intermediate complexes responsible for the formation of the allylbenzene molecule.

Table 3 shows that when the reaction is carried out in ethereal solvents, the yields of allylbenzene reach 80-96%, the highest yield of allylbenzene from PhMgBr and phenyl allyl sulfone being obtained in THF with CuCl_2 in the presence of Ph_3P (60°C, 4 h).

For this reason, subsequent experiments on the reactions of organomagnesium compounds with allyl sulfones were carried out under these optimum conditions. Thus, a variety of alkyl and allylmagnesium halides reacted with phenyl allyl sulfone to give unsaturated hydrocarbons in yields which varied considerably depending on the structure of the Grignard reagent. In particular, replacement of the n-butyl group in n- $\text{C}_4\text{H}_9\text{MgBr}$ by isobutyl and tert-butyl reduced the yields of reaction products. In contrast to these organomagnesium compounds, nonylmagnesium bromide and benzylmagnesium bromide reacted very selectively with phenyl allyl sulfone to give 1-dodecene and 1-phenyl-3-butene in yields of 94 and 90%.

It was found that the nature of the halogen atom in the Grignard reagent had a marked effect on the yields of coupling products. For example, when bromine was replaced by chlorine or iodine in allylmagnesium bromide, the yield of hexadiene in the reaction with phenyl allyl sulfone fell from 87 to 46% (Table 4).

We then examined the possibility of reacting PhMgBr , PhCH_2MgBr , and EtMgBr with higher allyl sulfones (phenyl 2,7-octadienyl sulfone and phenyl 3,7-dimethyl-2,6-octadienyl sulfone).



It was found that EtMgBr reacted readily with these sulfones to give the unsaturated hydrocarbons (I) and (II), whereas PhMgBr and $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ reacted only with phenyl 2,7-octadienyl sulfone to give (III) and (IV). In

TABLE 1. Effect of Catalyst Type on Yields and Product Composition in the Reaction of PhMgBr with Phenyl Allyl Sulfone (M:Ph₃P:PhSO₂-CH=CH-CH₂:PhMgBr = 1:1:20:25; 60°C, 4 h, THF)

Catalyst	Yield of allylbenzene, %	Catalyst	Yield of allylbenzene, %
CuCl ₂	96	Ni(acac) ₂	32
Li ₂ CuCl ₄	94	NiCl ₂	11
(CH ₃) ₂ CO ₂ Cu	92	Ti(OBu) ₄	12
Cu(acac) ₂	92	Cp ₂ TiCl ₂	14
CuBr	55	TiCl ₄	2
CuCl	38	Zr(OBu) ₄	3
CuI	32	(Cp) ₂ ZrCl ₂	15
FeCl ₃	59	Zr(acac) ₄	21
Fe(acac) ₃	55	Cr(acac) ₂	2
Mn(acac) ₂	10	PdCl ₂	18
		Pd(acac) ₂	4

TABLE 3. Effect of Solvent on Yields of Allylbenzene (CuCl₂:Ph₃P:PhSO₂-CH=CH-CH₂:PhMgBr = 1:1:20:25; 60°C, 4 h)

Solvent	Yield of allylbenzene, %
THF	96
1,4-Dioxane	92
Diethyl ether	80
Diglyme	79
Dipropyl ether	68
Benzene	62
CH ₂ Cl ₂	46
Heptane	44
Sulfolan	35

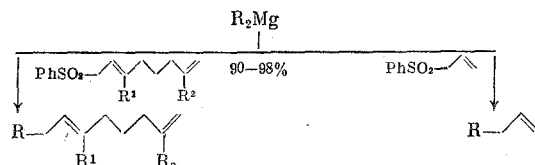
TABLE 2. Effect of Ligand on the Yields and Product Composition in the Reaction of PhMgBr with Phenyl Allyl Sulfone (CuCl₂:L:PhSO₂-CH=CH-CH₂:PhMgBr = 1:1:20:25; 60°C, 4 h, THF)

Ligand	Yield of allylbenzene, %
Ph ₃ P	96
α, x'-Bi-pyridil	46
Bu ₃ P	30
(EtO) ₃ P	22
(C ₆ H ₁₁ O) ₃ P	19
(PhO) ₃ P	15

TABLE 4. Effect of Structure of Grignard Reagent on the Product Yields in Cross-Coupling with Phenyl Allyl Sulfone (CuCl₂:Ph₃P:PhSO₂-CH=CH-CH₂:RMgX = 1:1:20:25; 60°C, THF)

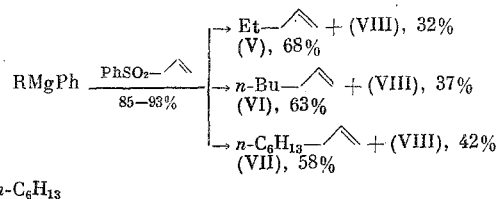
Grignard reagent	Yield of products of reaction with phenyl allyl sulfone, %
<i>n</i> -BuMgBr	<i>n</i> -Bu-CH=CH-CH ₂ (96)
<i>i</i> -BuMgBr	<i>i</i> -Bu-CH=CH-CH ₂ (80)
<i>t</i> -BuMgBr	<i>t</i> -Bu-CH=CH-CH ₂ (52)
C ₉ H ₁₉ MgBr	C ₉ H ₁₉ -CH=CH-CH ₂ (94)
C ₆ H ₅ CH ₂ MgBr	C ₆ H ₅ CH ₂ -CH=CH-CH ₂ (90)
CH ₂ =CH-MgBr	CH ₂ =CH-CH=CH-CH ₂ (87)
CH ₂ =CH-MgCl	CH ₂ =CH-CH=CH-CH ₂ (70)
CH ₂ =CH-MgI	CH ₂ =CH-CH=CH-CH ₂ (46)

order to compare the reactivities of organomagnesium halides with those of magnesium dialkyls in these reactions, the reactions of Et₂Mg, *n*-Bu₂Mg, *n*-hexyl₂Mg, and Ph₂Mg with phenyl allyl sulfone, phenyl 2,7-octadienyl sulfone, and phenyl 3,7-dimethyl-2,6-octadienyl sulfone were studied (50°C, 4 h, THF) in the presence of the catalytic system Cu(acac)₂-PPh₃ (1:1).



R = Et, *n*-Bu, *n*-C₆H₁₃, Ph.
 R = Et, R¹ = R² = H (I); R = Et; R¹ = R² = CH₃ (II);
 R = *n*-Bu; R¹ = R² = H (IX); R = *n*-Bu; R¹ = R² = CH₃;
 R = Et (V); R = *n*-Bu (VI); R = *n*-C₆H₁₃ (VII); R = Ph (VIII)

It is noteworthy that unsymmetrical alkyl aryl magnesium compounds also participate in this reaction with the formation of mixtures of hydrocarbons. For instance, RMgPh (R = Et, *n*-Bu, and *n*-C₆H₁₃) react with phenyl allyl sulfone to give hydrocarbons (V)-(VIII) in high yields. These experiments showed that the alkyl radical in organomagnesium compounds is more reactive towards cross-coupling with allyl sulfones than is the phenyl residue



R = Et, *n*-Bu, *n*-C₆H₁₃

It is evident that, in contrast to the Grignard reagents, magnesium dialkyls are much more reactive, reacting much more readily with allyl sulfones irrespective of the structures of the latter to give unsaturated hydrocarbons in high yields.

EXPERIMENTAL

The allyl sulfones used in this investigation were of purity $\geq 98\%$, obtained as described in [3, 4]. GLC was carried out on a Khrom-41 chromatograph, flame ionization detector, column 1.2×3 mm, 5% elastomer SE-30 on Chromatone N-AW, carrier gas helium. PMR spectra were recorded on a Tesla BS-487B instrument with CCl_4 solutions, internal standard HMDS. IR spectra were obtained on a UR-20 spectrophotometer (films), and mass spectra on an MX-13-06, ionizing electron energy 70 eV, ionization chamber temperature 200°C .

General Method of Reaction of Allyl Sulfones with Organomagnesium Compounds. To a solution of 0.262 g (1 mmole) of $\text{Cu}(\text{acac})_2$, 0.262 g (1 mmole) of PPh_3 , and 20 mmole of the allyl sulfone in 20 ml of THF, cooled to -5°C , was added under argon with rapid stirring 25 mmole of the organomagnesium compound, and the temperature held at -5°C for 15 min. The solution was transferred to a thermostated glass reactor, and heated for 4 h at 60°C . The catalysate was decomposed with 5% HCl and repeatedly extracted with ether, and the extract was washed with water until neutral and dried over MgSO_4 . After removal of the solvent, the residue was distilled in vacuo.

1,6E-Decadiene (I), bp $62-63^\circ\text{C}$ (20 mm), n_D^{20} 1.4353, IR spectrum (ν , cm^{-1}): 915, 1000, 3085 ($-\text{CH}=\text{CH}_2$) 975, 3030 ($\text{trans-CH}=\text{CH}$). PMR spectrum (δ , ppm): 0.78-0.99 m (3H, CH_3), 1.22-1.68 m (4H, CH_2), 1.80-2.18 m (6H, $\text{CH}_2-\text{C}=\text{}$), 4.80-5.04 m (2H $>\text{CH}=\text{CH}_2$), 5.20-5.82 m (3H, $-\text{CH}=\text{}$), m/z 138.

2,6-Dimethyl-2,6-decadiene (II), bp $52-53^\circ\text{C}$ (3 mm), n_D^{20} 1.4515. IR spectrum (ν , cm^{-1}): 830 ($>\text{C}=\text{CH}$). PMR spectrum (δ , ppm): 0.67-0.98 m (3H, CH_3), 1.08-1.43 m (2H, CH_2), 1.58 s (6H, $\text{CH}_3-\text{C}=\text{}$), 1.63 s (3H, $\text{CH}_3-\text{C}=\text{}$), 1.80-2.17 m (6H, $\text{CH}_2-\text{C}=\text{}$), 4.50-5.20 m (2H, $\text{CH}=\text{C}<$), m/z 166.

1-Phenyl-2E,7-octadiene (III), bp $99-100^\circ\text{C}$ (3 mm), n_D^{20} 1.5173. IR spectrum (ν , cm^{-1}): 1600, 1490, 740, 700 (arom.), 915, 1010, 3085 ($\text{CH}=\text{CH}_2$), 975, 3030 ($\text{trans-CH}=\text{CH}$). PMR spectrum (δ , ppm): 1.25-1.63 m (2H, CH_2), 1.85-2.20 m (4H, $\text{CH}_2-\text{C}=\text{}$), 3.15 d (2H, $=\text{C}-\text{CH}_2-\text{C}=\text{}$), 4.70-4.88 m (2H, $\text{CH}_2=\text{C}<$), 4.93-5.83 m (3H, $-\text{CH}=\text{C}<$), 7.08 s (5H, arom.), m/z 186.

1-Phenyl-3E,8-nonadiene (IV), bp $95-96^\circ\text{C}$ (2 mm), n_D^{20} 1.5168. IR spectrum (ν , cm^{-1}): 1603, 1500, 740, 705 (arom.), 920, 1000, 3085 ($\text{CH}=\text{CH}_2$), 975, 3035 ($\text{trans-CH}=\text{CH}$). PMR spectrum (δ , ppm): 1.31-1.67 m (2H, CH_2), 1.75-2.33 m (6H, $\text{CH}_2-\text{C}=\text{}$), 2.50-2.78 m (2H, $=\text{C}-\text{CH}_2$), 4.50-5.08 m (3H, $\text{CH}=\text{CH}_2$), 5.20-5.80 m (2H, $\text{CH}=\text{CH}$), 7.08 s (5H, arom.), m/z 200.

1,6E-Dodecadiene (IX), bp $61-62^\circ\text{C}$ (5 mm), n_D^{20} 1.4438. IR spectrum (ν , cm^{-1}): 920, 1000, 3085 ($\text{CH}=\text{CH}_2$), 975, 3030 ($\text{trans-CH}=\text{CH}$). PMR spectrum (δ , ppm): 0.75-0.97 m (3H, CH_3), 1.28-1.67 m (10H, CH_2), 1.75-2.25 m (6H, $\text{CH}_2-\text{C}=\text{}$), 4.75-5.08 m (3H, $\text{CH}=\text{CH}_2$), 5.20-5.52 m (2H, $\text{CH}=\text{CH}$), m/z 166.

2,6-Dimethyl-2,6-dodecadiene (X), bp $75-76^\circ\text{C}$ (8 mm), n_D^{20} 1.4562. IR spectrum (ν , cm^{-1}): 835 ($>\text{C}=\text{CH}$). PMR spectrum (δ , ppm): 0.80-0.98 m (3H, CH_3), 1.12-1.38 m (6H, CH_2), 1.55 s (6H, $\text{CH}_3-\text{C}=\text{}$), 1.65 s (3H, $\text{CH}_3-\text{C}=\text{}$), 1.75-2.42 m (6H, $\text{CH}_2-\text{C}=\text{}$), 4.98-5.20 m (1H, $\text{CH}=\text{C}<$), m/z 194.

Olefins (V)-(VIII), obtained by reacting phenyl allyl sulfone with the appropriate organomagnesium compounds, were identified by comparison with known samples.

CONCLUSIONS

1. The reactions of Grignard reagents of various types with allyl sulfones in the presence of salts of transition metals have been studied, leading to the formation of unsaturated hydrocarbons. It has been found that Cu and Fe complexes, modified by PPh_3 , are the most active catalysts for this reaction.

2. It has been shown for the first time to be possible to effect the cross-coupling of allyl sulfones with symmetrical and nonsymmetrical magnesium dialkyls in the presence of copper complexes.

LITERATURE CITED

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SYNTHESIS OF AROMATIC AND HETEROAROMATIC
UNSATURATED SULFONES USING PALLADIUM
COMPLEX CATALYSTS

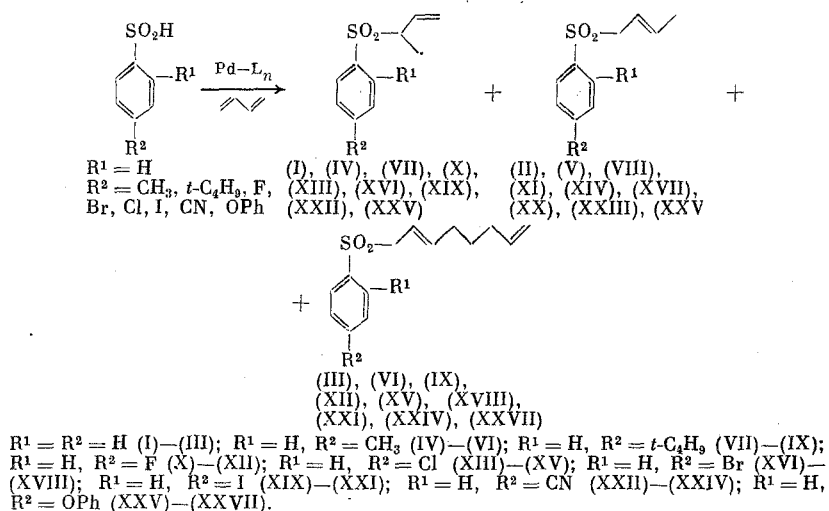
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We have recently [1-5] developed a method for the preparation of difficultly available unsaturated sulfones, based on the reaction of sulfinic acids with 1,3-dienes under the action of palladium and nickel-containing complex catalysts.

To examine the possible use of different aromatic and heteroaromatic sulfinic acids in this reaction, in the present work, we studied the reaction of butadiene with substituted arylsulfinic acids, catalyzed by low-valence Pd complexes.

We have already found [1-5] that low-valence Pd complexes, obtained by reduction of Pd(acac)₂ by triethylalane in the presence of PPh₃, are the most active catalysts in the reaction of sulfinic acids with 1,3-dienes. With this catalytic system, benzene- and toluenesulfinic acids react with butadiene (60°C, 6 h) to give the corresponding butenyl and 2,7-octadienyl sulfones (I)-(VI) in yields of ~ 97%. Replacement of a methyl group in toluenesulfinic acids by F, Cl, Br, and I atoms, and also by tert-butyl, nitrile, and phenoxy groups, practically does not influence the direction, the yield, and the composition of the products of their telomerization with butadiene. In all the experiments, both mono- (VII)-(XX) and diadducts (XXI)-(XXVII) are formed. The ratio of butenyl and octadienyl sulfones changed inappreciably from experiment to experiment, and is on the average 51:34:15, respectively (Table 1).



Similar results were obtained in the study of the telomerization of naphthalenesulfinic acid with butadiene, leading to sulfones (XXVIII)-(XXX) with an overall yield of 91%. In contrast to the above acids, *o*-methoxybenzenesulfinic acid enters into telomerization with butadiene with the exclusive formation of (XXXII), (XXXIII). However, in its reactivity, *o*-chlorophenylsulfinic acid practically does not differ from the above acids, and reacts with butadiene to give sulfones (XXXIV)-(XXXVI) in an overall yield of 85%.

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