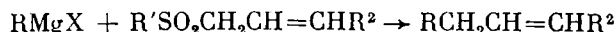


CROSS COUPLING OF ORGANOALUMINUM COMPOUNDS WITH PHENYL  
ALLYL SULFONE, CATALYZED BY TRANSITION METAL COMPLEXES

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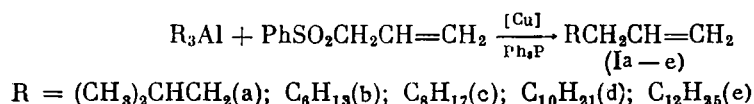
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Recently a number of papers was published in which it was shown that it is theoretically possible to use transition metal complexes to catalyze the cross coupling of Grignard reagents with allyl sulfones of diverse structure [1-3], which leads to obtaining a new carbon-carbon bond.



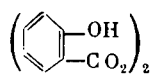
In order to develop a new method for obtaining olefins of a given structure using readily available organoaluminum compounds and allyl sulfones we studied the reaction of some di- and trialkylalanes with phenyl allyl sulfone, catalyzed by transition metal complexes. On the example of reacting triisobutylaluminum (TBA) with phenyl allyl sulfone we studied the effect of the nature of the metal and structure of the activating additives (cocatalyst) on the yield and composition of the cross-coupling products.

Of the tested compounds of the transition metals (Cu, Ti, Zr, Fe, Co, Ni, Cr, Pd) the most catalytically active in the given reaction proved to be the Fe and Cu salts, activated by  $Ph_3P$ . Thus, the catalytic systems  $Li_2CuCl_4 - PPh_3$  and  $Cu(\text{salicylate})_2 - PPh_3$  permitted obtaining 5-methyl-1-hexene (Ia) from TBA and phenyl allyl sulfone (1:1) in 92-94% yield (Table 1).



The insertion of alkyl and aryl phosphites into the catalyst composition leads to a noticeable decrease in the yield of (Ia) (Table 2).

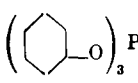
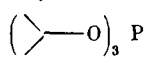
TABLE 1. Effect of Nature of Catalyst on Yield of 5-Methyl-1-hexene (Ia) in Reaction of TBA with Phenyl Allyl Sulfone\*

Catalyst	Yield of (Ia), %	Catalyst	Yield of (Ia), %
$Li_2CuCl_4$	94	$Cp_2TiCl_2$	20
 Cu	92	$Cr(\text{acac})_3$	18
$Cu(\text{acac})_2$	82	$Cp_2ZrCl_2$	17
$Fe(\text{acac})_3$	46	$Al(\text{acac})_3$	15
$CuI$	33	$Zr(\text{acac})_4$	9
$CuBr$	29	$Ni(\text{acac})_2$	8
$Co(\text{acac})_2$	23	$Pd(\text{acac})_2$	8

\*50°C, 20 mmoles of TBA and sulfone, and 1 mmole of catalyst and  $Ph_3P$ ; solvent = octane.

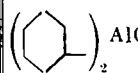
Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 675-677, March, 1984. Original article submitted February 14, 1983.

TABLE 2. Effect of Nature of Cocatalyst on Yield of 5-Methyl-1-hexene (Ia) in Reaction of TBA with Phenyl Allyl Sulfone\*

Cocatalyst	Yield of (Ia), %	Cocatalyst	Yield of (Ia), %
Ph <sub>3</sub> P	94		30
α,α'-Bipyridyl	48		
Bu <sub>3</sub> P	42	(PhO) <sub>3</sub> P	22
	34	(EtO) <sub>3</sub> P	10

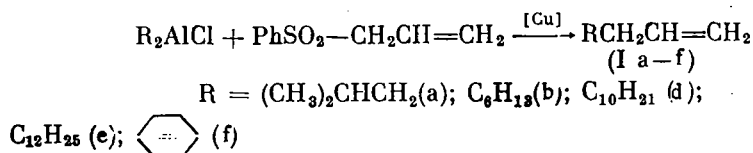
\*Li<sub>2</sub>CuCl<sub>4</sub>:Ph<sub>3</sub>P:PhSO<sub>2</sub>-CH=CH<sub>2</sub>:i-Bu<sub>3</sub>Al = 1:1:20:20, mmoles, 50°C, 4 h; solvent = octane.

TABLE 3. Effect of Structure of Trialkylalane on Yield of 1-Alkenes\*

Alkylalane	1-Alkene	Yield of (I), %	Alkylalane	1-Alkene	Yield of (I), %
i-Bu <sub>3</sub> Al	(Ia)	94	i-Bu <sub>2</sub> AlCl	(Ia)	58
(C <sub>6</sub> H <sub>13</sub> ) <sub>3</sub> Al	(Ib)	78	(C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> AlCl	(Ib)	56
(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> Al	(Ic)	74	(C <sub>10</sub> H <sub>21</sub> ) <sub>2</sub> AlCl	(Id)	52
(C <sub>10</sub> H <sub>21</sub> ) <sub>3</sub> Al	(Id)	68	(C <sub>12</sub> H <sub>25</sub> ) <sub>2</sub> AlCl	(Ie)	46
(C <sub>12</sub> H <sub>25</sub> ) <sub>3</sub> Al	(Ie)	66		(If)	22

\*1 mmole of Li<sub>2</sub>CuCl<sub>4</sub> and Ph<sub>3</sub>P, 20 mmoles of sulfone and either R<sub>3</sub>Al or R<sub>2</sub>AlCl, solvent = octane, 50°C, 5 h.

The maximum yield of (Ia) was obtained by using the catalytic system Li<sub>2</sub>CuCl<sub>4</sub>-PPh<sub>3</sub> and running the reaction in octane solution at 50°C (4 h) and a Cu:P:sulfone:AlR<sub>3</sub> ratio = 1:1:20:20. Replacing the TBA by higher trialkylalanes in the reaction with phenyl allyl sulfone decreases the yield of the corresponding 1-alkenes to 66-78% (Table 3). A comparison of the reactivity of trialkylalanes with dialkylhaloalanes in the reaction with phenyl allyl sulfone revealed that diisobutylaluminum chloride and the higher C<sub>6</sub>-C<sub>12</sub> dialkylhaloalanes are less active in the formation of 1-alkenes (see Table 3).



It is probable that under the cross-coupling conditions the low-valence Cu(0)-L complexes are easily oxidized by an excess of R<sub>2</sub>AlCl to either CuCl or CuCl<sub>2</sub>, which exhibit a low catalytic activity in this reaction.

The high yields of the cross-coupling products of alkylalanes with phenyl allyl sulfone, the ease of running the reaction, and also the ready availability of the starting reactants, all permit using this reaction as a method for obtaining 1-alkenes.

#### EXPERIMENTAL

The phenyl allyl sulfone was 98% pure. The reaction products were identified by comparing with known compounds. The GLC analysis was run on a Chrom-41 instrument, which was equipped with a flame-ionization detector and a 3.7 m × 3 mm column packed with 15% Carbowax-6000 deposited on Chromaton N-AW. Helium (60 ml/min) was used as the carrier gas.

With stirring, to a solution of 0.22 g (1 mmole) of Li<sub>2</sub>CuCl<sub>4</sub> and 0.262 g (1 mmole) of Ph<sub>3</sub>P in 10 ml of octane at 0°C was added in drops 20 mmoles of either R<sub>3</sub>Al or R<sub>2</sub>AlCl and the

mixture was kept at this temperature for  $\sim 15$  min in an argon atmosphere. The obtained catalyzed solution was transferred to a thermostatted glass reactor, in which 3.64 g (20 mmoles) of phenyl allyl sulfone had been previously placed, and the reaction mixture was heated for 4 h at 50°C, diluted with an equal volume of  $\text{CHCl}_3$ , washed in succession with 5% HCl solution and water, and then dried over  $\text{MgSO}_4$ .

The 1-alkene was isolated by distilling the residue that remained after removal of the solvent. The following alkenes were obtained by the described method: 5-methyl-1-hexene, bp 84–85°,  $n_D^{20}$  1.3971,  $M^+$  98 (cf. [4]); 1-nonene, bp 55–56° (20 mm),  $n_D^{20}$  1.4159,  $M^+$  126 (cf. [4]); 1-undecene, bp 63–64° (5 mm);  $n_D^{20}$  1.4260,  $M^+$  154 (cf. [4]); 1-tridecene, bp 66–70° (1 mm)  $n_D^{20}$  1.4338,  $M^+$  182 (cf. [4]); 1-pentadecene, bp 87–88° (1 mm),  $n_D^{20}$  1.4394,  $M^+$  210 (cf. [4]); allylcyclohexane, bp 57–58° (20 mm),  $n_D^{20}$  1.4498,  $M^+$  124 (cf. [5]).

#### CONCLUSIONS

A method was developed for obtaining 1-alkenes by reacting di- and trialkylalanes with phenyl allyl sulfone, catalyzed by copper complexes.

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#### TRANSFORMATIONS OF EPOXYKETONES OF THE CARANE SERIES

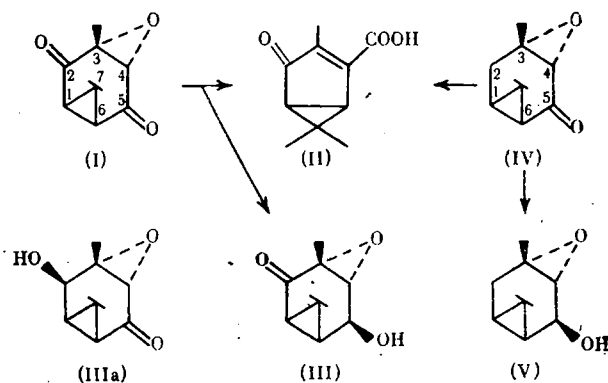
##### USING BASES

A. N. Karaseva, V. V. Karlin,  
I. S. Ikhtonova, and Z. G. Isaeva

UDC 542.97:547.597

As a supplement to the previously obtained data [1] on the transformations of epoxyketones of the carane series using bases we studied the reaction of the diketo-substituted epoxide (I) (scheme 1) with alcoholates and alkalis in alcohol, and also of (I) and the mono-substituted epoxide (IV) with  $\text{MeONa}$  in dioxane.

Scheme 1



A. E. Arbusov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 677–679, March, 1984. Original article submitted February 14, 1983.