

NEW POSSIBILITIES FOR THE USE OF METHOXYALLENE IN CARBON-CARBON BOND-FORMING REACTIONS

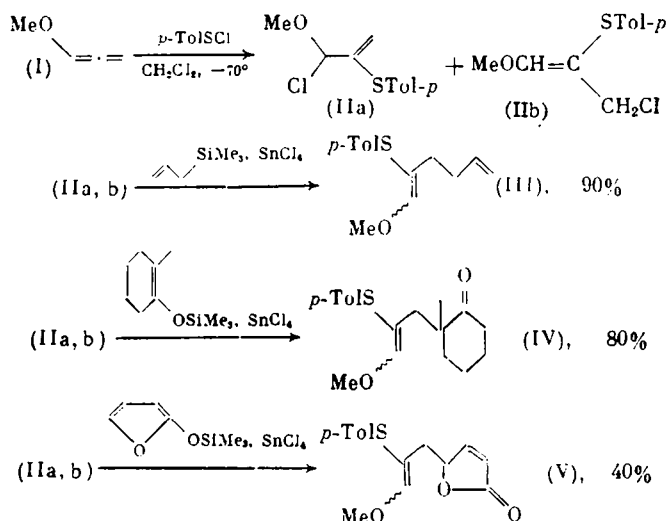
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The usual approaches to the synthetic application of methoxyallene (I) are based on the reactions of its lithium derivative with electrophiles [1] or the reaction of (I) with Grignard reagents by an S_N2' reaction scheme [2].

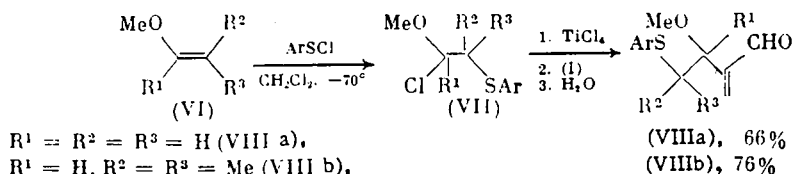
We have developed a new approach for the use of (I) in synthesis based on an Ad_E reaction. In the first variant, (I) reacts with $ArSCl$ to give a mixture of adducts (IIa) and (IIb), which alkylates allylsilane or enol silyl ether π -donors in the presence of Lewis acids to give products (III)-(V). The final result of these transformations corresponds to the addition of an S-electrophile and C-nucleophile at the 2,3-double bond of (I), which is used in

this case as an equivalent of the bipolar C_3 -synthone $\overset{+}{CH_2} - \overset{-}{C} = CHOMe$.



In the second variant, (I) is used as a π -donor in Ad_E reactions with electrophiles such as α -alkoxy- β -arylthioalkyl chlorides (adducts of vinyl ethers with $ArSCl$ (VII) [3]). In this case, addition of the C-electrophile and O-nucleophile at the 1,2-double bond of (I), which

also acts as an equivalent of a different bipolar C_3 -synthone, namely, $CH_2 = \overset{-}{C} - \overset{+}{C}HOMe$



In both variants, the structure of the C-addends may vary in a broad range and all the transformations such as (I) \rightarrow (II) \rightarrow (III) or (VI) \rightarrow (VII) \rightarrow (VIII) are carried out as sequence of operations in a single flask.

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These results indicate promise for the use of readily available methoxyallene (I) in the synthesis of various polyfunctional compounds.

LITERATURE CITED

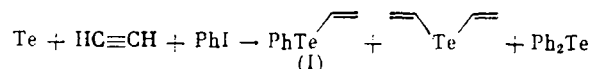
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VINYL PHENYL TELLURIDE FROM METALLIC TELLURIUM, ACETYLENE, AND IODOBENZENE

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The information on the synthesis of vinyl phenyl telluride (I) is extremely limited [1-3]. We have found that the reaction of metallic tellurium with acetylene and iodobenzene in the $\text{KOH-HMPTA-SnCl}_2\text{-H}_2\text{O}$ system in an autoclave at 100-120°C and 10-12 gauge atmospheres leads to telluride (I) in 20% yield relative to the tellurium taken and to divinyl telluride in 17% yield and diphenyl telluride in 2% yield.



The addition of a radical inhibitor such as hydroquinone into the reaction mixture completely suppresses the formation of (I). Upon carrying out the reaction without SnCl_2 , only a trace of telluride (I) is detected. When iodobenzene is replaced by bromobenzene, the yield of (I) is less than 1%, while this product is not formed when chlorobenzene is used.

This behavior indicates a chain radical-anion mechanism for the aromatic nucleophilic substitution [4] of the tellurium-containing anions involving SnCl_2 as the electron donor and initiator. The spectral and physicochemical data for telluride (I) correspond to the values reported by Bychkova [1] and Kauffmann [2].

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