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A CONVENIENT METHOD FOR THE PREPARATION OF ALLYL ETHERS——THE REACTION OF α,β-UNSATURATED ACETALS WITH GRIGNARD REAGENTS ACTIVATED BY TITANIUM TETRACHLORIDE

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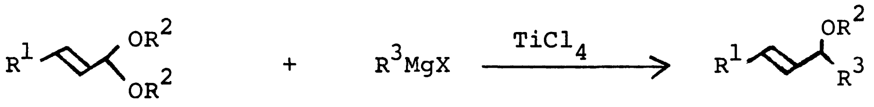
In the presence of $TiCl_4$, α,β-unsaturated acetals[1)] react with Gringard reagents to give the corresponding allyl ethers in good yields.

Acetals have been widely utilized as protected carbonyl compounds and known to be inert toward various nucleophiles such as Grignard reagents and organolithium compounds. Recently, it was found in our laboratory that the trimethylsilyl enol ethers or vinyl acetates react with various acetals in the presence of $TiCl_4$ to give the aldol addition products, β-alkoxyketones,[2),3)] in good yields.

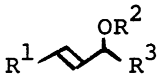
In this communication we report the reaction of α,β-unsaturated acetals with Grignard reagents activated by $TiCl_4$ to result in the replacement of one alkoxy group by an alkyl group to form allyl ethers.



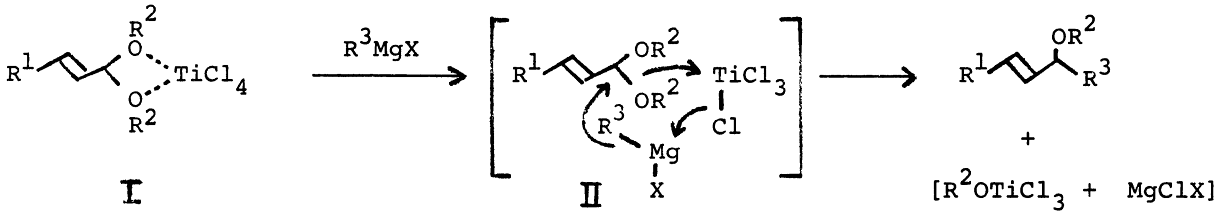
For example, to a mixture of 5 mmol of cinnamaldehyde dimethyl acetal and 5 mmol of $TiCl_4$ in 20 ml of dry THF was added a THF solution of 7.5 mmol of phenethylmagnesium bromide at -78°C under an argon atmosphere, and the reaction mixture was stirred for 6 hr at -78°C. As 20 ml of 10% aqueous potassium carbonate was added to the solution, a white precipitate appeared. After the usual work-up, 3-methoxy-1,5-diphenyl-1-pentene was isolated by silica gel column chromatography in 81% yield. In a similar manner, various allyl ethers such as 3-methoxy-1-phenyl-1-pentene 3-methoxy-1-phenyl-1,5-hexadiene, 4-methoxy-6-phenyl-2-hexene and

3-ethoxy-5-phenyl-1-pentene were obtained by the reactions of the corresponding acetals with Grignard reagents as shown in Table I.

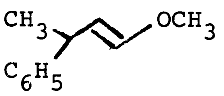
Table I Reaction of α,β-unsaturated acetals with Grignard Reagents

Acetal		Reaction		Yield %
R^1	R^2	Time(hr)	R^3	
C_6H_5	CH_3	6	$C_6H_5CH_2CH_2$	81
C_6H_5	CH_3	6	CH_3CH_2	83
C_6H_5	CH_3	6	$CH_2{=}CH{-}CH_2$	71
CH_3	CH_3	6	$C_6H_5CH_2CH_2$	79
H	CH_3CH_2	6	$C_6H_5CH_2CH_2$	70

The displacement reaction of α,β-unsaturated acetal with Grignard reagnets may be explained as follows: the acetal forms a co-ordinated compound (I) with $TiCl_4$. The (I) subsequently reacts smoothly with the Grignard reagent probably through a six-membered cyclic intermediate (II) to afford allyl ethers as sketched below.



On the other hand, it was found that γ-arylation took place to afford vinyl ethers when phenylmagnesium bromide is employed in the above reaction. For example,



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1-methoxy-3-phenyl-1-butene (1) was obtained in 42% yield by the reaction of crotonaldehyde dimethyl acetal and phenylmagnesium bromide in the presence of $TiCl_4$, and the allyl ether could not be detected.

In summary, it is noted that the present process provides the convenient method of preparing the various allyl ethers in good yields. Further development is now in progress.

REFERENCES

1) The acetals were readily prepared from α,β-unsaturated aldehyde and orthoformic esters in alcoholic solution in the presence of a catalyst such as anhydrous hydrogen chloride.

2) T. Mukaiyama and M. Hayashi, Chem. Lett., 15 (1974).

3) T. Mukaiyama, T. Izawa, and K. Saigo, Chem. Lett., 323 (1974).

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