



## Titanium(IV) Isopropoxide-catalysed Reaction of Ethylmagnesium Bromide with Ethyl Acetate in the Presence of Styrene

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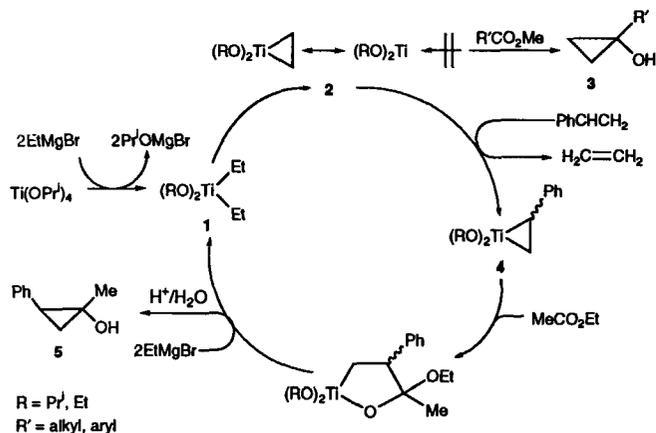
Reaction of ethylmagnesium bromide with ethyl acetate in the presence of styrene and titanium(IV) isopropoxide as a catalyst leads to (*Z*)-1-methyl-2-phenylcyclopropanol in 42% yield.

Recently we have shown that the titanium(IV) isopropoxide-catalysed reaction of methyl alkanecarboxylates with ethylmagnesium bromide yields 1-substituted cyclopropanols.<sup>1</sup> It was supposed that the key step in the process is disproportionation of diisopropoxydiethyltitanium **1** into the corresponding titanacyclopropane **2**, which is further transformed into the 1-substituted cyclopropanols **3** by reaction with ester (Scheme 1). Use of substituted ethylmagnesium bromide in this reaction yields the corresponding 1,2-disubstituted cyclopropanols.<sup>2</sup> We supposed that an alternative method of preparation of 1,2-disubstituted cyclopropanols might be ethylene displacement from the intermediate **2** by the other unsaturated compounds. In fact, dropwise addition of an ethylmagnesium bromide ether solution to a boiling ether solution of ethyl acetate, styrene and

titanium(IV) isopropoxide forms, in addition to a small amount of 1-methylcyclopropanol, the known<sup>2,3</sup> (*Z*)-1-methyl-2-phenylcyclopropanol in 42% yield.

Data on the composition of evolved gases, which were studied by GLC (Table 1), seem to provide indirect evidence for the formation of **5** by ethyl acetate double-alkylation with phenyl-substituted titanacyclopropane **4**. Table 1 shows that the gaseous products of the ethylmagnesium bromide and titanium(IV) isopropoxide reaction in the presence of, as well as in the absence of, ethyl acetate and styrene are ethane and ethylene. The standard procedure<sup>1</sup> for 1-methylcyclopropanol preparation carried out in the absence of styrene leads only to ethane evolution.

We also established that using other esters in the reaction of



Scheme 1

ethylmagnesium bromide, styrene and titanium(IV) isopropoxide yields the corresponding 1-substituted-2-phenylcyclopropanols. However, we cannot extend this method to the preparation of other 1,2-disubstituted cyclopropanols by using the hept-1-ene,  $\alpha$ -methylstyrene and ethyl vinyl ether as the olefinic component.

**Table 1** Yields and composition of the gaseous products of the ethylmagnesium bromide reaction with titanium(IV) isopropoxide in the presence of ethyl acetate and styrene.

		Molar ratio of reagents and gaseous products				
		Reagents		Gaseous products		
EtMgBr	Ti(OPr <sup>i</sup> ) <sub>4</sub>	EtOAc	PhCH=CH <sub>2</sub>	Ethane	Ethylene	Yield(%)
2	0.05	—	—	1.1	0.5	80
2	0.05	1	—	1.0	0.0	45
2	0.05	1	2	0.9	0.6	75

## References

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