ENE REACTIONS OF METHYL TRIFLUOROPYRUVATE

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Reactions of methyl trifluoropyruvate (I) with alkenes containing an allylic hydrogen atom have been studied. Reactions of (I) with terminal alkenes proceed slowly at 20°C and rapidly at 100°C. Similar reactions of (I) with cycloalkenes and allyl iodide occur above 100°C. It is found that all these reactions yield methyl esters of α -oxy- α -trifluoromethyl- γ , δ -unsaturated acids. Catalysis of these reactions with SnCl₄ reduces reaction times and temperatures to -40-20°C. With terminal alkenes, the use of catalyst does not change the direction of the reaction. With cycloalkenes, methyl esters of α -oxy- α -trifluoromethyl- β , γ -unsaturated acids are obtained. Both allyl methyl ether and allylbenzene react with (I) yielding substituted tetrahydrofurans (II-III) as main products.

$$CF_3$$
 CH_3OOC
 $R = OCH_3$ (II); $R = Ph$ (III)

The reactions of (I) with terminal acetylenes have been studied. 1-Hexyn gives the allene derivative. The reaction of (I) with propargyl methyl ether yields a mixture of dihydrofuran (IY) and oxetane (Y)

The obtained products are useful as synthons for the synthesis of lactones, lactams, substituted dioxans and morpholines.