METHYLATION OF OLEFINS WITH ORGANIC REAGENTS IN THE PRESENCE OF RHODIUM COMPOUNDS

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It is known [1-3] that a vinyl hydrogen in compounds containing a C =C bond can be replaced by an aryl, benzyl or a styryl radical by using the appropriate halides in the presence of palladium compounds. However, olefins could not be alkylated in this manner [3].

We found that olefins are alkylated by systems that contain an organic reagent (methyl iodide or dimethyl sulfate), $RhCl_3$ and a suitable reducing agent, like a primary or a secondary alcohol or stannous chloride. When styrene is alkylated with CH_3I the yields of the products, when based on $RhCl_3$, are quite high, but they are not catalytic (Table 1).

The yields are lower (5-15%) when ethylene, 1-octene and cyclohexene are methylated. The alcohol can also serve as a source of the methyl group: small amounts of propenylbenzene were obtained from styrene, $RhCl_3$ and methanol. The considered reactions probably begin with a reduction of Rh(III) to Rh(I), which then reacts further according to the scheme:

$$[Rh^{I}]^{+} + CH_3I \longrightarrow [CH_3Rh^{III}I]^{+}$$

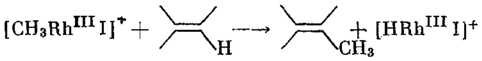

TABLE 1

Molar ratio of CH_3I: $RhCl_3$: PhCH = CH_2	Reducing agent	Medium	T., °C	Yield, %	
				propenylbenzene	isopropenylbenzene
1,3 : 1 : 40	C_2H_5OH	C_2H_5OH	100	18	—
1,3 : 1 : 40	CH_3OH	CH_3OH	160	33	—
1,3 : 1 : 40	CH_3OH	$CH_3OH—CH_3CN$	160	63	—
1,3 : 1 : 40	$SnCl_2$	DMF	100	60	10

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