

Ruthenium-catalyzed methoxycarbonylation of styrene

Oleg L. Eliseev, Tatyana N. Bondarenko, Anastasia D. Churikova and Albert L. Lapidus

Carbonylation procedure

Representative procedure for the methoxycarbonylation of styrene is as follows. Styrene (0.2 ml, 1.75 mmol), $\text{Ru}_3(\text{CO})_{12}$ (3.7 mg, 5.8 μmol), NaBr (180 mg, 1.75 mmol) and 3 ml of dry methanol were placed in a 50 ml stainless steel reactor equipped with magnetic stirrer and glass liner (Figure S1). The reactor was flushed with CO three times, pressurized to 10 bar and placed to electric oven. Reaction was performed at 130 °C under stirring for 4 h. After that, the reactor was chilled to room temperature, depressurized and opened, the mixture was analyzed chromatographically on an Avtokhrom 3700 instrument (Alltech™ quartz capillary column, stationary phase SE 30, FID, nitrogen as a carrier gas) using n-nonane as an internal standard. For identification, products were separated and analyzed by ^1H NMR.

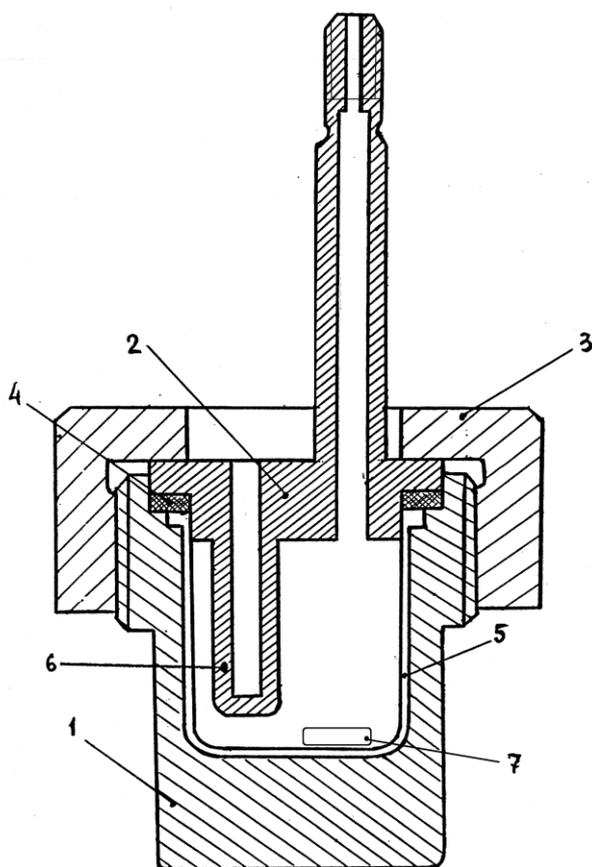


Figure S1 Reactor for carbonylation. 1 – body, 2 – lid, 3 – threaded lid holder, 5 – glass liner, 6 – thermocouple pocket, 7 – Teflon-coated stirrer.

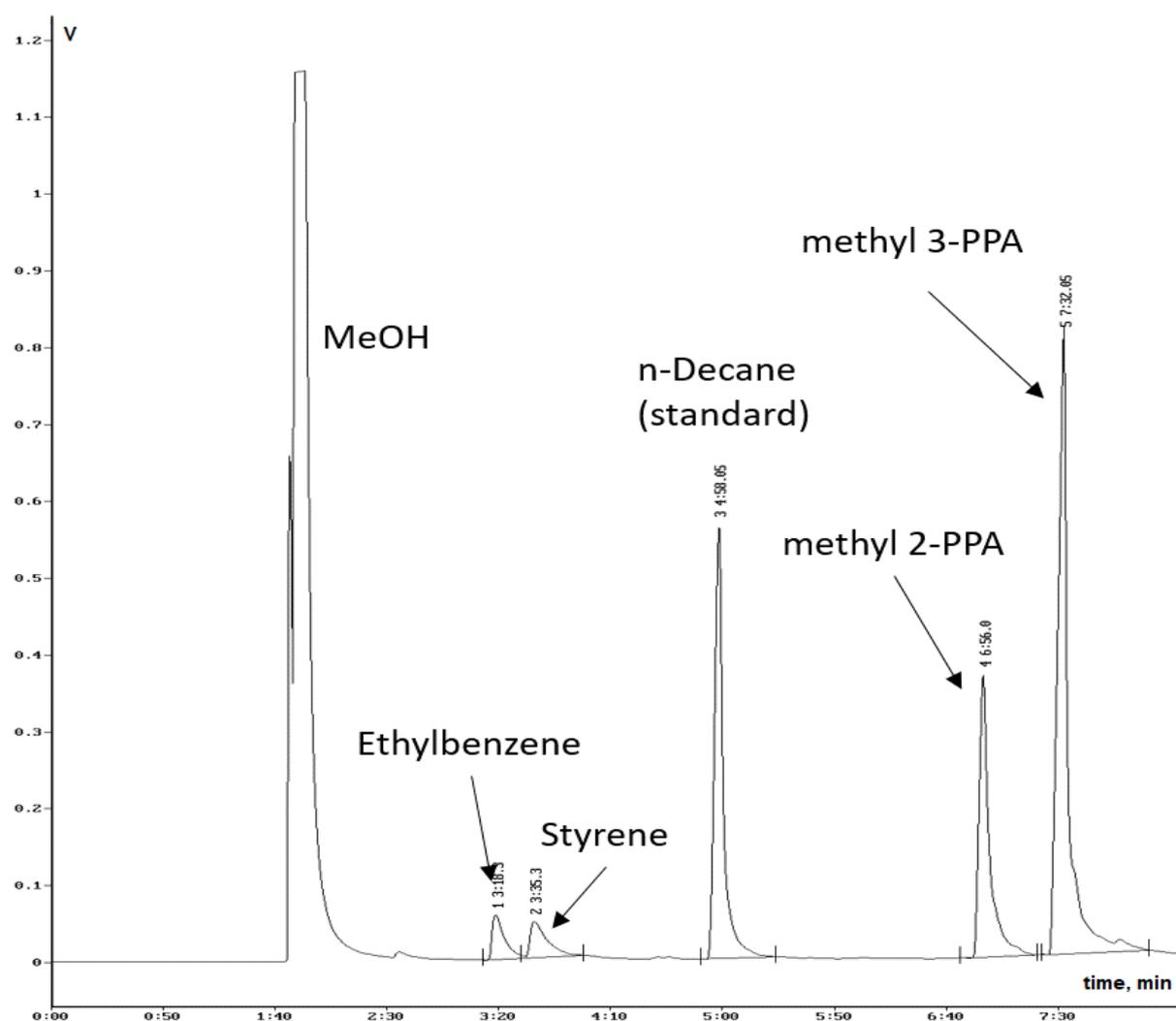


Figure S2 Representative chromatogram of the reaction mixture.

Table S1 Effect of additives on styrene methoxycarbonylation. Reaction conditions: styrene (0.2 ml, 1.75 mmol), $\text{Ru}_3(\text{CO})_{12}$ (3.7 mg, 0.33 mol%), MeOH (3 ml), 130 °C, 10 bar, 4 h.

Entry	Additive (mol%)	Conversion (%)	Esters		Ethylbenzene yield (%)
			yield (%)	Iso : n	
1	[bmim]Br, 200 + TsOH·H ₂ O, 3	44	0	—	7
2	BaCl ₂ ·2H ₂ O, 10	5	0	—	—
3	CoCl ₂ ·6H ₂ O, 100	7	0	—	—
4	CuCl ₂ ·6H ₂ O, 2	50	14	1.14	35
5	Hg ₂ Cl ₂ , 10	3	0	—	—
6	CuCN, 10	0	0	—	—