STUDY OF THE EFFECT OF HIGH PRESSURE ON THE DIRECTION OF THE GRIGNARD REACTION

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The Grignard reaction under pressure was not studied previously. We studied the effect of pressures up to 5000 kg/cm² at 25° on the ratio of the addition and reduction products in the reaction of C₂H₂MgBr with pinacolone. Mixing the reactants at the desired moment under pressure was accomplished using a technique that was somewhat improved over that given in [1]. The reactants were found in two parts of a thin-walled Teflon ampul, that were separated by a thin Teflon film. The ampul was placed in a thermostatted highpressure vessel, which was filled with a liquid; the pressure inside the ampul was transmitted through its thin walls. After creating the pressure and holding, the high-pressure vessel was inverted; here the partition in the ampul was broken by a heavy hammer and the reactants became mixed. The reaction was run at a concentration of 0.25 mole of C₂H₅MgBr and 0.025 mole of (CH₃)₃CCOCH₃. The reaction mass after being worked up was analyzed by gas chromatography. The study disclosed that pressure has little effect on the ratio of the products of the addition and reduction reductions, namely 2,2,3-trimethyl-3-pentanol and 2,2-dimethyl-3-butanol; the amount of the latter in the mixture of alcohols was equal to 25.4 ± 1.4% at atmospheric pressure and 22.8 ± 0.4 at 5000 kg/cm² (the errors represent the mean arithmetic deviations from the average value in parallel experiments). These results lead to the conclusion that the formation of the transition states in the studied addition and reduction reactions is accompanied by approximately the same change in the volume.

LITERATURE CITED

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