A NEW ALKYLATION REACTION OF SATURATED HYDROCARBONS

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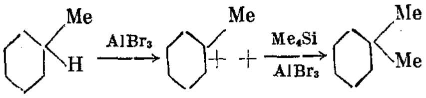
The reaction of electrophilic substitution of hydrogen on the tertiary C atom in saturated hydrocarbons by a CH_3 group from TMS under the influence of $AlBr_3$ is presented. Thus, methylcyclohexane reacts with TMS under the influence of $AlBr_3$ in CH_2Cl_2 with the formation of gem-dimethylcyclohexane. The yield of gem-dimethylcyclohexane reaches 50% with the ratio of the reactants hydrocarbon:silane: $AlBr_3$ = 1:10:3 (50°C, 6 h). Decalin forms 9-methyldecalin under analogous conditions.

Evidently the reaction proceeds according to a scheme including the removal of a hydride ion from the tertiary C atom under the influence of $AlBr_3$ with the formation of a carbene ion and the transfer to it of a CH_3 group from the TMS:



According to [1] the splitting of the Si—C bond does not occur immediately under the influence of the carbene ion. Evidently $AlBr_3$ plays the role of the carrier of the CH_3 group in the reaction. The fact that nonbranched hydrocarbons, for example cyclohexane, not forming a tertiary carbene ion, do not enter into the alkylation reaction speaks in favor of the presented scheme.

The reaction presented here is a new method of synthesis of hydrocarbons with a quaternary C atom. Application of it to saturated bicyclic compounds permits the production of hydrocarbons with an angular CH_3 group.

LITERATURE CITED

1. D. N. Kursanov, Z. N. Parnes, G. D. Kolomnikova, and I. I. Tyulyaev, Izv. Akad. Nauk SSSR, Ser. Khim., 678 (1972).

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