REACTION BETWEEN TRIMETHYLPHOSPHITE AND SODIUM TETRAPHENYLBORONATE

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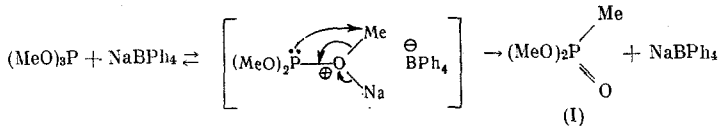
It is well known that the instability of phosphonium betaines can be stabilized in the form of phosphonium salts by the action of sodium tetraphenylboronate [1]. With an attempt to stabilize bipolar adducts of trimethylphosphite (TMP) in unsaturated compounds, forming at high temperatures, in the form of phosphonium tetraphenylboronates, it was found that, in the interval 90-120°C, TMP reverts to dimethylmethylphosphonate (I) (method of differential thermal analysis), probably according to the scheme:



(I)

In the nuclear magnetic resonance spectrum-^{31}P, there appears a singlet with δ_{31P}—32 ppm. and, in the paramagnetic resonance spectrum, two doublets of the methyl groups with 3.69 ($^3J_{PH}$ = 11 Hz) and 1.4 ppm. ($^2J_{PH}$ = 18 Hz), which is identical to the signals of (I), obtained by the action of MeI on $P(OMe)_3$. It must be noted that thermal isomerization of TMP takes place only with > 300°C [2].

An attempt to isomerize $P(OEt)_3$ and $P(OPh)_3$ by the action of $NaBPh_4$ was unsuccessful; no traces of phosphonates were observed with heating to 290°C. An attempt to isomerize TMP by the action of $NaBF_4$ was also unsuccessful, which is obviously explained by a reaction in the heterogeneous system ($NaBF_4$, in distinction from $NaBPh_4$, is practically insoluble in TMP).

Using an excess of TMP, the reaction does not go to completion, which is obviously explained by the deactivation of $NaBPh_4$ as a result of its strong solvation by the forming (I). The solvating properties of (I) are obviously close to the solvating properties of phosphates [3].

Thus, under the action of $NaBPh_4$, TMP undergoes non-classical Arbuzov regrouping.

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