REACTION OF PICRYL HALIDES WITH HEXAMETHYLDISTANNANE

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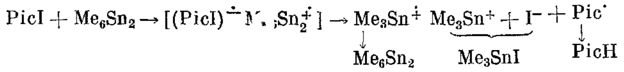
We have studied the reaction of picryl halides PicX (X = F, Cl, I) with hexamethyldistannane ($\mathrm{Me_6Sn_2}$) in tetrahydrofuran in vacuo. It was found that the direction of the reaction depended on the nature of PicX. Thus, with PicF the reaction went to completion at 50°C in 36 h, and its products were $\mathrm{PicOSnMe_3}$ (~50%) (identified according to PMR and UV spectra) and $\mathrm{Me_3SnF}$ (quantitatively). The reaction of $\mathrm{Me_6Sn_2}$ with PicI (50°C, 96 h) gave 1,3,5-trinitrobenzene in quantitative yield together with $\mathrm{Me_3SnI}$. PicCl did not react with $\mathrm{Me_6Sn_2}$ at all: After prolonged (7-12 days) holding of the reaction mixture in vacuo at 50°C, the starting compounds were recovered.

The obtained facts indicate that the reaction mechanism changes in going from PicF to PicI. The mechanism of the reaction of $\mathrm{Me_6Sn_2}$ with PicF is not completely clear, but $\mathrm{PicSnMe_3}$ is apparently formed in the first step (as indicated by the presence of 1,3,5-trinitrobenzene in the products of decomposition of the reaction mixture by HCl in vacuo), and the $\mathrm{PicSnMe_3}$ subsequently undergoes addition at the nitro group of the starting PicF. The obtained adduct is converted to the picrate by a mechanism similar to the one proposed for the reaction of 1,3,5-trinitrobenzene with $\mathrm{Me_3SnM}$ [1].

For the reaction of PicI with $\mathrm{Me_6Sn_2}$, the simplest and most logical mechanism is the radical mechanism



$$\mathrm{PicI} + \mathrm{Me_6Sn_2} \rightarrow [(\mathrm{PicI})^{\dot{-}}\,\mathrm{Me_6Sn_2^{\dot{+}}}] \rightarrow \underset{\substack{\downarrow\\ \mathrm{Me_6Sn_2}}}{\mathrm{Me_3Sn}^{\dot{+}}}\ \underbrace{\mathrm{Me_3Sn^+} + \mathrm{I^-}}_{\mathrm{Me_3SnI}} + \underset{\substack{\downarrow\\ \mathrm{PicH}}}{\mathrm{Pic}^{\cdot}}$$

The inertness of PicCl in this reaction is apparently due to the great hindrances for the possible occurrence of both the first and the second reaction mechanism.

LITERATURE CITED

1. G. A. Artamkina, M. P. Egorov, I. P. Beletskaya, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 242, 107 (1978).

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