Dimethylaminotrimethylstannane, a Powerful Dehydrochlorinating Reagent

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WE have found that dimethylaminotrimethylstannane is a remarkably powerful dehydrochlorinating reagent (see equation 1).

$$Me_3Sn{-}NMe_2 + Cl{-}(A){-}H \rightarrow Me_3SnCl{\cdot}HNMe_2 + (A) \qquad (1)$$

A selection of some reactions which follow this pattern is shown below.

$$IrHCl_2(PPh_3)_3 \xrightarrow[\text{2 hr.}]{\text{xylene (80–100°)}} IrCl(PPh_3)_3 \text{ (I)} \qquad (2)$$

$$IrH_2Cl(PPh_3)_3 \xrightarrow[1\frac{1}{2}\text{ hr.}]{\text{xylene (80–100°)}} IrH(PPh_3)_3 \text{ (II)} \qquad (3)$$

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl \xrightarrow[\text{4 hr.}]{(40°)} cis\text{-}(5{\cdot}2\%) \text{ and } trans\text{-}(88{\cdot}5\%)\ CH_3{\cdot}CH{:}CH{\cdot}CH_3, \text{ and } CH_3{\cdot}CH_2{\cdot}CH{:}CH_2\ (6{\cdot}3\%)$$

Noteworthy features are (a) the mild reaction conditions, (b) the ease of separation of products ($Me_3SnCl{\cdot}HNMe_2$ is insoluble in aromatic solvents, ether, and alkanes), (c) the near quantitative conversions, and (d) the difficulty, in some cases, of achieving alternative syntheses. As an example of (d), the transformation (2) could be not effected even with 1,5-diazabicyclo[4,3,0]non-5-ene[1] even under vigorous conditions [in contrast to $(Ph_3P)_2HIr(CO)Cl_2$, which is dehydrochlorinated instantly to *trans*-$(Ph_3P)_2Ir(CO)Cl$ by both reagents].

The efficacy of Me_3SnNMe_2 as a dehydrochlorinating reagent is attributed to a combination of factors, which include (a) the weak and highly polar Sn–N bond,[2] (b) the high basicity of Me_3SnNMe_2, (c) the high value of the heat of formation of crystalline $Me_3SnCl{\cdot}HNMe_2$, and (d) for the inorganic reactions, the intermediate formation of compounds having metal–tin bonds. Additionally (e), attention is drawn to the capacity of amido-derivatives of tin (unlike organic bases) to exercise a synergic effect, since they are able to behave both as proton-[2] and halide ion[4] abstractors. The evidence for (d) rests on the possibility, in favourable circumstances, of isolating compounds having tin–metal bonds as intermediates. For example, we have previously shown[5] that interaction of *trans*-$(Ph_3P)_2Pt(Cl)H$ and Me_3SnNMe_2 affords *trans*-$(Ph_3P)_2Pt(Cl)SnMe_3$ (III). We now find that prolonged heating of (III) in xylene affords the known[6] bis(triphenylphosphine)platinum(0). As for (e), it is not invariably the case that Me_3Sn/H exchange [in the sense of equation (1)] precedes dehydrochlorination. For instance, we find that $Ph_2SiH(Cl)$, when treated with Me_3SnNMe_2, afforded $Ph_2Si(NMe_2)H$ and Me_3SnCl, thus demonstrating[4] Me_2N/Cl exchange; dehydrochlorination to form a silylene was therefore not accomplished.

It is likely that other amido-compounds [*e.g.*, $(Me_3Sn)_3N$, and derivatives of the more electropositive elements] will behave similarly. The dehydrochlorination reactions of amido-tin compounds are clearly capable of wide extension. The utility of organotin–nitrogen derivatives as synthetic intermediates have previously been demonstrated in other connections.[2,4,5]

The chemistry of the species (I)[7,8] and (II)[8] is of particular interest. An experiment closely related to those summarised in equations (2) and (3) involved the new[9] paramagnetic hydride $OsHCl_2(PBu^n{}_2Ph)_3$, which quantitatively afforded $Me_3SnCl,HNMe_2$.

(*Received, August 30th,* 1967; *Com.* 923.)

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