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Preliminary communication

Base-catalyzed disproportionation of unsymmetrical hexaalkylditins. Addition reactions of hexaalkyl-ditins and -digermanes to unsaturated systems

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Contrary to hexaphenylethane hexaorgano-ditins and -digermanes do not dissociate into free radicals $R_3M^{\bullet}$ ($\dot{M}$ = Ge, Sn). For example, $Me_3SnSnEt_3$ can be distilled at 235° without disproportionation. Likewise, a 1/1 mixture of Me_6Sn_2 and Et_6Sn_2 remains unaltered when heated for 25 h at 150°[1].

$$Me_6M_2 + Et_6M_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2\,Me_3MMEt_3 \qquad (1)$$

(M = Ge, Sn)

We have now found* that reaction (1) (M = Sn) occurs even at room temperature if polar conditions are applied, as observed previously for the corresponding organogermanes[2]. Thus, with equimolar amounts of Me_6Sn_2 and Et_6Sn_2 in hexamethylphosphoric triamide (HMPT) (concentration of the reactants 0.5 mmole/ml) equilibrium (1) is reached in $\leqslant$ 1 h to give about 50% of $Me_3SnSnEt_3$. In THF and acetonitrile at room temperature reaction (1) takes place only in the presence of a catalytic amount of base, *e.g.* MeONa or MeMgBr.

Using GLC analysis, the equilibrium constant K_{-1} for reaction (1) was shown to be 0.22 ± 0.02 in THF and 0.24 ± 0.02 in acetonitrile, indicating an almost random distribution of the trimethyltin and triethyltin groups. For the analogous base-catalyzed disproportionation (1) for M = Ge in HMPT the equilibrium constant is 0.12 ± 0.02[2]. Reactions of type (1) offer an attractive method for the preparation of mixed-alkyl substituted ditins and digermanes.

The considerably enhanced reactivity of the Sn—Sn and Ge—Ge bonds in the presence of bases suggested to us that organo-ditins and -digermanes might add to unsaturated systems under appropriate polar conditions; information on such addition reactions is limited to the reaction of Me_6Sn_2 with perfluoroolefins and perfluoroacetylenes under free radical conditions[3-6].

In the reaction of equimolar amounts of Me_6Sn_2 and diphenylacetylene in HMPT

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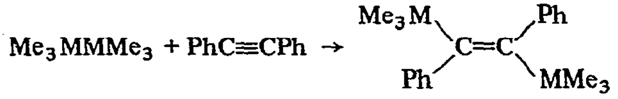
*E.J. Bulten and J.G. Noltes, paper presented at the Fourth International Conference on Organometallic Chemistry, Bristol, 1969.

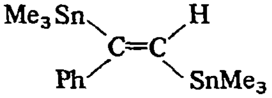
in the presence of 5 mole % of MeONa for 2 h at 50° and subsequently for 60 h at room temperature about 70% of the ditin was consumed (GLC) and a crystalline product 1,2-bis(trimethylstannyl)-1,2-diphenylethylene (I) (m.p. 130–131°) was isolated. Cleavage of (I) with bromine or with methanolic MeONa gave exclusively *trans*-dibromostilbene or *trans*-stilbene. The reaction with phenylacetylene was found to be generally applicable to hexaalkylditins as well as to hexaalkyldigermanes. Thus Et_6Sn_2 afforded 1,2-bis(triethylstannyl)-1,2-diphenylethylene (m.p. 59–60°) in 82% yield. 1,2-Bis(trimethylgermyl)-1,2-diphenylethylene (m.p. 123–124°) was obtained analogously.



$$Me_3MMMe_3 + PhC{\equiv}CPh \rightarrow (Me_3M)(Ph)C{=}C(Ph)(MMe_3) \qquad (2)$$

(M = Ge, Sn) (I)

In order to determine the scope of this new type of reaction a series of small scale experiments (GLC) were performed with Me_6Sn_2 and various unsaturated species in solvents of different polarity. With diphenylacetylene reaction (2) proceeds only in HMPT and in the presence of base; under these conditions Me_6Sn_2 likewise reacts smoothly with phenylacetylene (ratio 1/1) and with diphenylbutadiyne (ratio 2/1) to give 1,2-bis(trimethylstannyl)phenylethylene (II, b.p. 95–96°/0.2 mm; n_D^{20} 1.5670 and 1,4-diphenyl-1,2,3,4-tetrakis(trimethylstannyl)-1,3-butadiene (III, m.p. 240–242°), respectively. From the pattern of the $^{117,119}Sn$–H coupling constants (*cf.* ref.7) compound (II) appears to be the *trans*-isomer. 1-Hexyne reacts more slowly than phenylacetylene. Reaction of Me_6Sn_2 with diethyl azodicarboxylate in HMPT proceeds even without a catalyst to give 1,2-bis(trimethylstannyl)diethyl-1,2-hydrazinedicarboxylate (IV) in good yield.



$$(Me_3Sn)(Ph)C{=}C(H)(SnMe_3)$$

(II)

$$Ph{-}C(SnMe_3){=}C(SnMe_3){-}C(SnMe_3){=}C(SnMe_3){-}Ph$$

(III)

$$EtOOC{-}N(SnMe_3){-}N(SnMe_3){-}COOEt$$

(IV)

Further investigations are in progress.

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