MECHANISM OF THE THERMOLYSIS AND PHOTOLYSIS OF BIS(TRIORGANYLSTANNYL)-MERCURIALS AND THEIR STABILIZATION

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UDC 541.124:541.11:541.144.8:547.1'13

In contrast to dialkylmercurials R_2HG, whose thermal stability depends on the C–Hg bond energy and decreases with increasing bulk of substituents R in the series Me > Et > i-Pr > t-Bu, the thermal stability of bis(triorganylstannyl)mercurials $(R_3'Sn)_2Hg$ increases with increasing bulk of the R' substituent. This behavior is difficult to explain on the basis of the Sn–Hg bond energy. For example, $(R_3'Sn)_2Hg$ (I) with R' = Ph, CH_2–t-Bu and t-Bu melt at high temperature without decomposition, while their analogs with R' = Me, Et, and n-Bu are stable only at −20°C [1, 2].

Apparently, in contrast to dialkylmercurials, the thermolysis and photolysis of (I) occurs by a chain S_{H_2} mechanism

$$\text{Initiation: } (R_3'Sn)_2Hg \xrightarrow[-Hg]{t,\ h\nu} 2R_3'Sn^{\cdot}$$

$$\text{Chain propagation: } R_3'Sn^{\cdot} + (R_3'Sn)_2Hg \rightleftharpoons \left[\begin{matrix} R_3'Sn\cdots HgSnR_3' \\ \vdots \\ SnR_3' \end{matrix}\right]^{\cdot} \rightleftharpoons R_3'Sn{-}SnR_3' + [{}^{\cdot}HgSnR_3']$$

$$[{}^{\cdot}HgSnR_3'] \rightarrow Hg + {}^{\cdot}SnR_3' \text{ etc.}$$

$$\text{Chain termination: } 2R_3'Sn^{\cdot} \rightarrow R_3'Sn - SnR_3'$$

Since the bimolecular step of this reaction is hindered by bulky substituents and the tin atom, the enhancement of the thermal and photochemical stability of (I) with increasing size of R' is clear. In addition, we showed that small additions of benzophenone and benzaldehyde (1-5 mol. %) increase the thermal and photochemical stability of (I) with R' = Me and Et. For example, these compounds in hexane solution decompose completely at 20°C in 10-20 min to give a hexaalkyldistannane and metallic mercury, while their solution stabilized by 5 mol. % benzophenone is stable at this temperature for more than 24 h. The stabilization of solutions of these compounds is based on trapping of stannyl radicals by benzophenone. The stable radical formed, Ph_2COSnR_3' is incapable of prolonging the chain decomposition of (I).

Thus, we have found effective stabilizers for the storage of unstable bis(triorganylstannyl)mercurials and explained their action on the basis of a radical chain S_{H_2} mechanism for the decomposition of these compounds.

LITERATURE CITED

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 956-957, April, 1987. Original article submitted November 24, 1986.

 0568-5230/87/3604-0884$12.50