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FREE RADICAL DECOMPOSITION OF ORGANOMERCURY DERIVATIVES OF TIN AS SHOWN BY CIDNP

Terence N. Mitchell

Lehrstuhl für Organische Chemie, Universität Dortmund, Germany

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The phenomenon of chemically induced dynamic nuclear polarisation (CIDNP)[1] has been used to confirm the existence of free radical intermediates in many reactions, and is particularly useful when the radicals cannot be directly observed by ESR spectroscopy. The observation of CIDNP during the thermal decomposition of organomercury derivatives of tin is here reported for the first time.

The reaction of an alkyl(trimethylsilyl)mercury compound with a trialkyltin alkoxide results in the formation of the corresponding alkyl(trialkylstannyl)-mercurial and trimethylalkoxysilane[2]:

$$RHgSiMe_3 + R'_3SnOR'' \longrightarrow RHgSnR'_3 + Me_3SiOR'' \qquad 1)$$

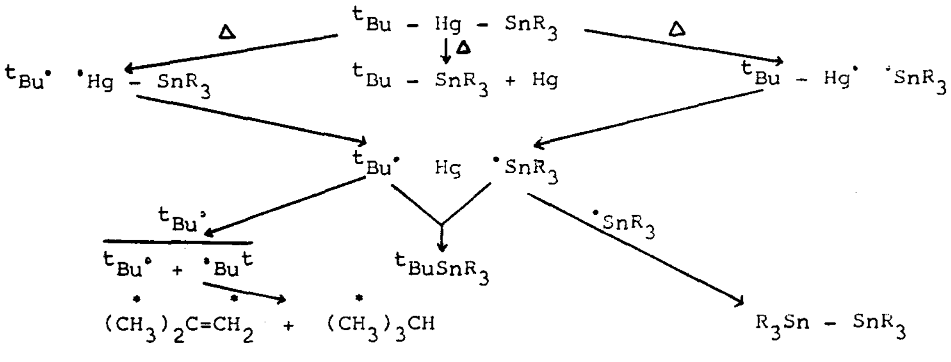
The stannyl mercurials are yellow oils which are extremely sensitive to light and atmospheric oxygen. They cannot be purified by crystallization or distillation. However, the formation of tert-butyl(trialkylstannyl)mercurials can be readily followed by PMR spectroscopy: tert-butyl(trimethylsilyl)mercury has J(^{199}Hg-C-C-H) 96 Hz[3] while the corresponding tert-butyl(trialkylstannyl)-mercurials have J(^{199}Hg-C-C-H) in the range 123-126 Hz (cf. tert-Bu_2Hg 104 Hz).

During the decomposition of $^tBuHgSnMe_3$ and $^tBuHgSnEt_3$ (in benzene solution) in the NMR spectrometer at 37°, CIDNP was observed for the protons of isobutylene and isobutane (see Scheme I). In all cases AE multiplets[4] were observed, as during the photolysis of pinacolone[5]. The amplitude of the multiplets was increased on increasing the temperature to 50-60°; at these temperatures the decomposition of the mercurial was faster: it was observed by following the decrease in the size of the tert-butylmercury resonance. However, amplification factors greater than ca. 15 were not observed, indicating a low stationary concentration of tert-butyl radicals. The CIDNP phenomenon was observable until the mercurial had decomposed, that is for up to 40 minutes at 37°. Tert-butyl(tributylstannyl)mercury exhibited no CIDNP at 75°; because of its enhanced thermal stability the stationary radical concentration is apparently much lower. The amplitude of the CIDNP effect was increased by a factor 2-3 on adding air to the sample in the NMR tube: it is not clear whether this is an effect of oxygen acting as a triplet radical or whether it merely reflects a higher radical concentration due to rapid oxidation of the sample. As yet, no CIDNP has been observed for mercurials having primary or secondary alkyl groups R attached to mercury; relatively stable alkyl radicals are therefore required in order that CIDNP may be observed.

The first step in the decomposition involves homolytic dissociation of the Hg-Sn or Hg-C bond; evidence that the latter is first cleaved may be provided by the observation that only tert-butyl stannyl mercurials $^{t}BuHgSnR_3$ add to malonodinitrile derivatives to give stannyl ketenimines: other alkyl stannyl mercurials $RHgSnR_3$ are unreactive[6].

$$^{t}BuHgSnR_3 \; + \; XC_6H_4CH{=}C(CN)_2 \longrightarrow XC_6H_4CH{}^{t}Bu.C(CN){=}C{=}NSnR_3 \qquad 2)$$

However, the two possible initial steps (see Scheme I) both lead to the formation of tert-butyl and stannyl radicals, the latter recombining to give ditins (the major tin product). The polarized products isobutylene and isobutane are almost certainly formed in a cage containing two tert-butyl radicals. Trialkyl tert-butyltins are obtained in only small yields as shown by PMR spectroscopy, corresponding to a unimolecular decomposition or to recombination of two free radicals.



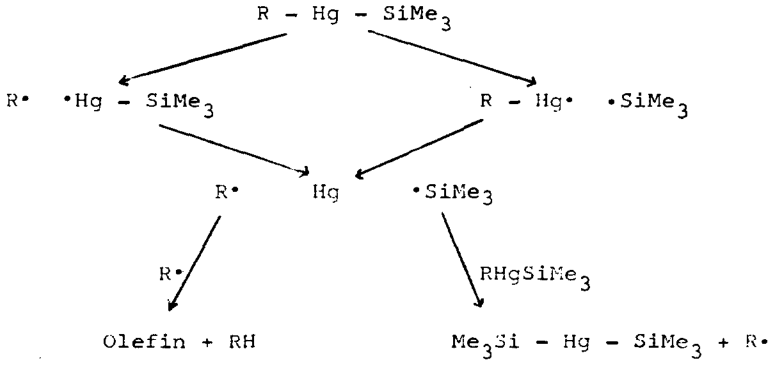
SCHEME I

* denotes polazization of the indicated protons; polarization of hexamethylethane, though suspected, could not with certainty be established.

Further evidence for Scheme I is given by the following observations: firstly, the tert-butyl phenyl nitroxyl radical ^{t}BuPhNO [7] is formed during thermal and photochemical decomposition of $^{t}BuHgSnR_3$ (R=Me,Et) in the presence of nitrosobenzene; secondly the decomposition of $^{t}BuHgSnEt_3$ in the presence of hexamethylditin leads to the formation, possibly by an S_H2 displacement reaction, of $Me_3SnSnEt_3$ in good yield, as shown by gas chromatography:

$$Et_3Sn\cdot + Me_3Sn-SnMe_3 \rightleftharpoons Et_3Sn-SnMe_3 + Me_3Sn\cdot \qquad 3)$$

Thirdly, the decomposition of the alkyl(trimethylsilyl)mercurials $RHgSiMe_3$ (prepared according to the method of Vyazankin et al. [8]) on irradiation with a daylight lamp (Philips HPL 125) leads to the formation of the alkyl radical R· in yields ≥ 90 o/o (identified as its recombination products e. g. C_2H_6 and C_2H_4 from $C_2H_5\cdot$) together with mercury (50 o/o) and bis (trimethylsilyl) mercury (≥ 90 o/o based on Me_3Si). Scheme II shows the suggested steps in this reaction, which is analogous to the decomposition of the stannyl mercurials. Formation of Me_3SiR, suggested by other workers [9], was not observed.



SCHEME II

Another possible route to $Me_3SiHgSiMe_3$ involves the recombination of two Me_3SiHg radicals, followed by elimination of mercury:

$$2\ Me_3SiHg^{\bullet} \longrightarrow Me_3SiHgHgSiMe_3 \qquad 4)$$

$$Me_3SiHgHgSiMe_3 \longrightarrow Me_3SiHgSiMe_3 + Hg \qquad 5)$$

Here too the capture of tert-butyl free radicals by nitrosobenzene has been observed, while the decomposition of $^tBuHgSiMe_3$ in the presence of hexamethylditin leads to the formation of trimethyl(trimethylsilyl)tin.

Further studies are planned using other mercurials which can give stable free radicals (e. g. benzyl) in order to determine the scope of such free radical processes in the field of Group IV derivatives of mercury.

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