

PHOTOCHEMISTRY OF ORGANOMETALLIC COMPOUNDS. I.
PHOTOLYSIS OF 1,1-DIPHENYL-1-STANNACYCLOHEPTA-2,6-DIENE

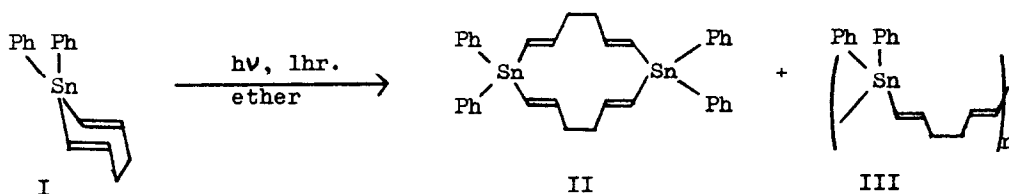
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The photochemistry of organometallic compounds is an area that has received only scant attentions up to date. This might be due to a facile destruction of a metal-carbon bond by the irradiation and the metal deposits at the wall of the reaction vessel to bring difficulties to carry out the reaction.⁽¹⁾ Recently, however, Brook et al.⁽²⁾ and Seyferth et al.⁽³⁾ have reported some photoisomerizations of organosilyl and organotin compounds where the metal remains in its oxidation state during the reaction. We have also found a new photoreaction of organotin derivative in which the metal retains its electronic configuration through out the reaction.

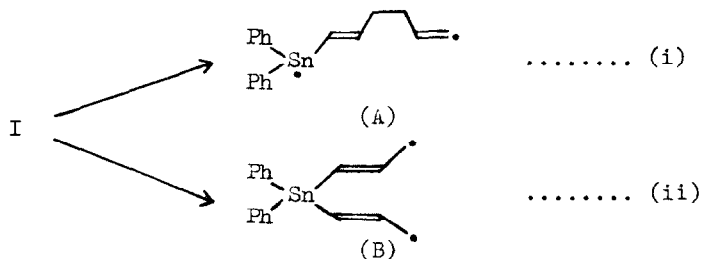
The irradiation of an ethereal solution of 1,1-diphenyl-1-stannacyclohepta-2,6-diene (I)* resulted in a smooth conversion into 1,1,8,8-tetraphenyl-1,8-distannacyclotetradeca-2,6,9,13-tetraene (II, mp 145-146°, 34 %) and polymer



* This compound was assigned to be trans-trans isomer based on IR and the vicinal coupling constants of the vinyl protons in nmr.

(III, amorphous solid, 56%). It is noteworthy to mention that this tin compound is very stable thermally but its photochemical change have taken place with great ease.

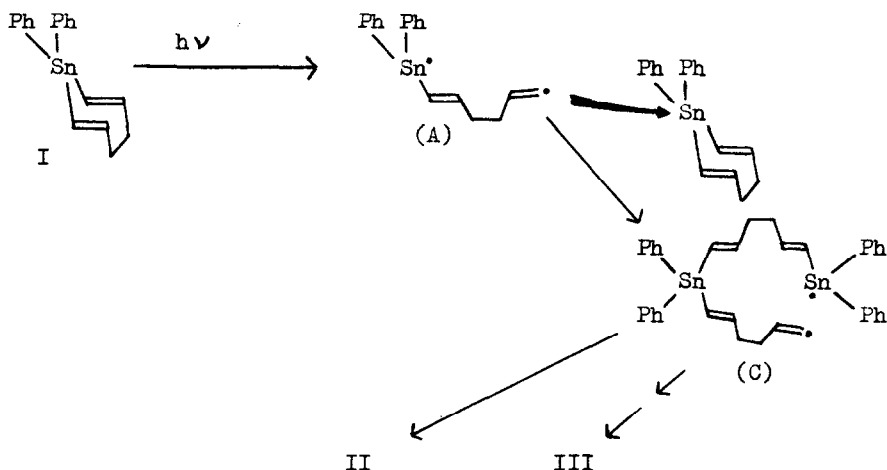
The structures of the dimer (II) and polymer (III) were deduced from the elemental analysis, molecular weight, IR, UV, and nmr spectra. The structure of organic chains in them was confirmed further by the treatments of II and III with bromine. Bromine is known not only to add the double bond but also cleave the tin-carbon bond so that the isomeric hexabromohexanes are expected.⁽⁴⁾ Now, the treatments of II and III with bromine gave a 1:1 mixture of meso- (mp 142-144°) and dl-1,1,2,5,6,6-hexabromo-*n*-hexane (mp 72.5-74°) in quantitative yields in both cases. Careful examinations by nmr indicated that the six bromines were clearly substituted at 1, 2, 5, and 6 positions of *n*-hexane and none at 3 or 4 position. This bromination results strongly show that the organic chains in II and III are purely consisted of *n*-hexa-1,5-diene; i.e., no branching of the chain has taken place in the present photoreaction.



Now, a remarkable result in the reaction was the sole formation of head to tail dimer and polymer which could suggest that the transformation took an ionic process. However, it might not be the case because the polarity of the solvent had no effect at all on the reaction rate. The reaction underwent with equal ease in ether, in 2-propanol, and in benzene. Another strong indication that the reaction might take radical process was that the same polymer as III was obtained in a dark reaction when I was refluxed in benzene with 2,2'-azobisisobutyronitrile. The fact that the quantum yield of this photoreaction being 4.2⁽⁵⁾ was also explicable in terms of the radical chain mechanism. Consequently, it is safe to conclude that the photoreaction undertakes

a radical process.

Well, there might be two paths for the radical process; (i) the bond fission at the tin-carbon bond giving intermediate biradical A, and (ii) the C₄-C₅ bond breaking process yielding a biradical B stabilized by allylic resonances. From three reasons described below, we suggest that the reaction undertakes the path (i). First, if the reaction has taken the route (ii), the chain should have branchings because of the allylic rearrangement at the biradical stage. However, the experimental results clearly show that the branching has not been detected. Secondly, there was observed the existence of non-cyclized n-hexa-1,5-dienyl group in the photoproduct of I in ethanol. This group can only be produced by the tin-carbon bond fission. Finally, the quantum yield (4.2) indicates that 4.2 molecules of I have reacted on the absorption of each one photon and this is only in accord with the route (i); the quantum yield expected in the route (ii) should be 1.0 or below.



When the light was filtered so that the light of 2537 Å irradiated the solution, the same reaction as above underwent smoothly, but the filtration by a Pyrex filter brought about no reaction at all. The UV studies on organotin compounds have shown that the vinyltin group has a maximum only at 2100 Å or below,⁽⁶⁾ but the phenyltin group absorbs the light in 2537 Å region.⁽⁷⁾ Since it has been known that the mutual interaction between the

unsaturated functions on the tin atom is negligible,**^(7,8) the photon is absorbed by the phenyl groups in I and the photoexcited I underwent the bond fission at tin-vinyl bond. The tin-vinyl bond is known to be weaker than the tin-phenyl bond⁽⁹⁾ and hence it is leaved preferentially. The resulted bi-radical A is consisted of a tin radical and a vinyl radical in that the latter attacks the second II at the tin atom to give the dimeric biradical. This couples to give II or attacks the third I in the same manner as above leading to the formation of the polymeric product. This seems to be a first example of the radical substitution reaction on the tin atom.

**This was also actually the case in the present compound. The UV spectrum of I was almost superimposable to that of tetraphenyltin.

REFERENCES

- (1) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, J. Am. Chem. Soc., 88, 3021 (1966); D. Seyferth and A. B. Aunin, ibid., 89, 1468 (1967).
- (2) A. G. Brook and J. M. Duff, ibid., 89, 454 (1967).
- (3) D. Seyferth and L. G. Vaughan, J. Organometal. Chem., 1, 138 (1963).
- (4) R. K. Inghan, S. D. Rosenberg and H. Gilman, Chem. Rev., 60, 459 (1960).
- (5) Quantum yield was mesured by the methode of the liquid phase chemical actinometer (potassium ferrioxalate).
J. G. Calvert and J. N. Pitts, Jr., Photochemistry, John Wiley and Sons, Inc., New York, London, 1967.
- (6) P. P. Shorygin, V. A. Petukhov and L. G. Stolyarova, Dokl. Akad. Nauk. SSSR., 154, (2) 441 (1964)
- (7) V. S. Griffiths and G. A. W. Derwish, J. Mol. Spectroscopy, 3, 165 (1959).
- (8) D. R. Eaton and W. R. McClellan, Inorg. Chem., 6, 2134 (1967).
- (9) A. L. Yergey and F. W. Lampe, J. Amer. Chem. Soc., 87, 4204 (1965).