Journal of Organometallic Chemistry, 66 (1974) 249—254

PHOTOELECTRON SPECTRA OF CYCLOPROPYLCARBINYLTRIMETHYLTIN AND ALLYLTRIMETHYLTIN

A COMPARISON OF σ-σ AND σ-π CONJUGATION

R.S. BROWN*, D.F. EATON, A. HOSOMI, T.G. TRAYLOR** and J.M. WRIGHT
Department of Chemistry, University of California, San Diego, La Jolla, California 92037 (U.S.A.)

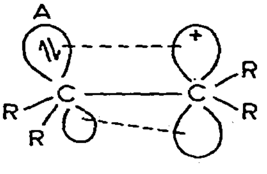
(Received June 25th, 1973)

Summary

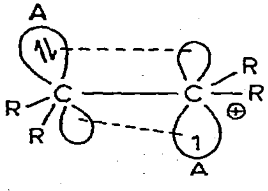
The UV photoelectron spectrum of cyclopropylcarbinyltrimethyltin (I) has been compared with the spectra of allyltrimethyltin (II) and isobutyltrimethyltin. A σ-σ conjugation in (I) resulting in a 1.6 eV interaction between the C—Sn bond and the cyclopropane orbitals and a 2.2 eV σ-π interaction in (II) have been demonstrated.

Introduction

The delocalization of electron-rich σ bonds into electron-deficient π systems (σ-π conjugation) has been extensively explored both experimentally [1 - 6] and theoretically [7 - 9]. The corresponding delocalization from one σ bond into an adjacent σ bond (σ-σ conjugation) [1] has received less attention.



σ-π Conjugation
(A)



σ-σ Conjugation
(B)

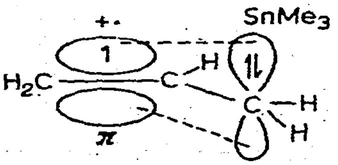
The decrease in ionization potentials with increasing size of straight chain hydrocarbons [10,11] suggested that electron-deficient σ bond systems were delocalized. The low ionization potentials of bicyclopropyl [12], and poly-

---

*Present address: Department of Chemistry, Columbia University, New York, N.Y. 10027 (U.S.A.)
** Author to whom correspondence should be addressed.

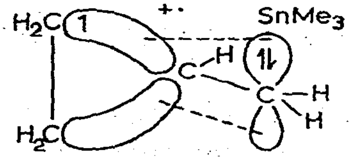
silanes [13], and the long wavelength absorption of 1,1'-bis-(bicyclo[1.1.0]-butane) [14] were further evidence for some kind of σ-σ conjugation. However, the magnitude of σ-σ conjugation and its relation to the type and geometry of the requisite σ bonds have not been determined.

We report here the photoelectron spectra of allyltrimethyltin, cyclopropylcarbinyltrimethyltin and several reference tin compounds to compare the vinyl and cyclopropyl groups in their interaction with a neighboring σ bond, in this case a C—Sn bond.



σ-π Conjugation

(C)



σ-σ Conjugation

(D)

Results and discussion

Except for tetramethyltin (Alfa), all compounds used in this study were prepared from Grignard or lithium reagents with trimethyltin chloride (II—IV, VII) or from an alkyl phosphinate (V) or phosphate (VI) and trimethyltinlithium (see Experimental).

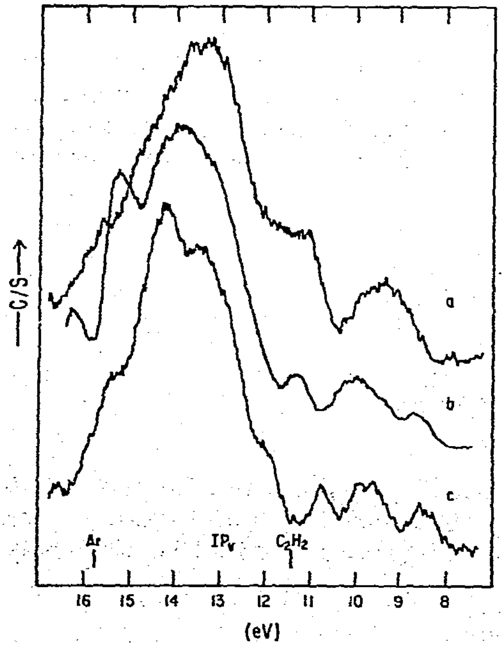


Fig. 1. Photoelectron spectra of isobutyltrimethyltin (a), cyclopropylcarbinyltrimethyltin (b) and allyltrimethyltin (c). Ordinates are arbitrarily displaced for clarity.

TABLE 1

VERTICAL IONIZATION POTENTIALS OF ORGANOTIN COMPOUNDS, $RSn(CH_3)_3$

R		IP_V		
		I	II	III
I	CH_3-	9.75	≈ 13	
II	n-Bu-	9.52[a]	11.31	
III	iso-Bu-	9.33[a]	11.06	
IV	Allyl-	8.70	9.76	10.87
V	Cyclopropyl-CH_2-	8.85	10.09	10.45
VI	4-Butenyl-	9.71[a]	11.74	
VII	5-Pentenyl-	9.72[a]	11.40	

[a] These compounds showed a very small shoulder at ≈9.1 eV.

Typical photoelectron spectra over the range of 8 to 16 eV are shown in Fig. 1. Vertical ionization potentials of these and other tin compounds are listed in Table 1.

The highest filled orbital in Me_4Sn, vertical ionization potential 9.75 eV [15], is indicated to be C—Sn bond orbital by the broad vibrational envelope. This level is raised by substituting a larger alkyl group for one of the methyls, thus removing the degeneracy of the C—Sn bond orbitals.

Using the experimental alkyltrimethyltin orbital levels and either propene or methylcyclopropane orbital energies as a basis set, we may ascertain the interaction of alternatively a vinyl or a cyclopropyl group with the carbon—tin σ bond. The correlation diagrams, illustrated in the manner of Heilbronner et al. [16], are shown in Figs. 2 and 3. The remarkable similarity of the correlations and the similarities of Figs. 1b and 1c are apparent. The energy of inter-

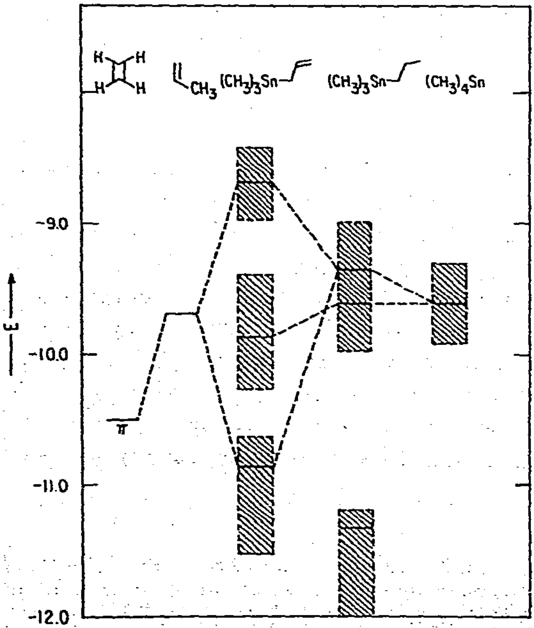


Fig. 2. Orbital correlation diagram for allyltrimethyltin.

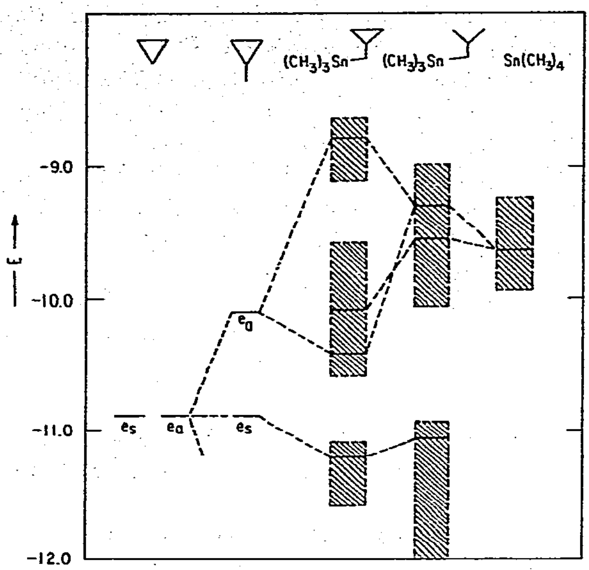


Fig. 3. Orbital correlation diagram for cyclopropylcarbinyltrimethyltin.

action of cyclopropane orbitals with the C—Sn σ bond (1.6 eV) may be compared with the σ-π interactions in allyltrimethyltin (2.2 eV) or vinylcyclopropane (2.6 eV) [16]. This shows that σ-σ conjugation between a bent and a polarized σ bond represented by B or D is substantial. Raising the energy level of the bent bonds by further distortion would undoubtedly cause the interaction in σ-σ conjugation to be comparable to that in σ-π conjugation*. Such large effects alter the reactivity of the cyclopropane ring and suggest some new stereospecific ring opening reactions which are under investigation.

Experimental

Photoelectron spectra were determined on an instrument constructed according to the method of Turner [20], with some modifications. The He (I) line was produced by microwave discharge. The 1.179" radius, 127° electrostatic analyzer was equipped with a Bendix Model 4028 Channeltron Electron Multiplier, a Princeton Applied Electronics Model 1120 Amplifier-Discriminator and 1105 - 10 Data Converter. The resolution was 35 - 45 meV. Spectra of norbornadiene [16,20,21], norbornene [16,21], norbornane [16,21], and chloroform [22], reproduced reported ionization potentials to within 0.03 eV. Spectra were recorded at sample pressures of ca. 0.05 mmHg using a 10^3 counts/sec maximum range at a scan rate of 0.33 eV/min over the range 18 - 8

---

* These results are consistent with the bond length studies in such compounds as butadiene [17], propylene [17], bicyclopropyl [18], and bis-1-apocamphyl [19], where the shortening of the central σ bond is attributed to hybridization changes in that bond. The highest filled orbital in these compounds is antibonding relative to the delocalized structure to an extent which cancels any π bonding across these central bonds.

eV. Spectra were standardized after each run with a mixture of argon and acetylene (15.76 and 11.40 eV bands, respectively).

Compounds

Materials for photoelectron spectroscopy were purified by gas liquid chromatography. NMR spectra were recorded in carbon tetrachloride solution on a Varian T-60 spectrometer; data are given in δ units from TMS. Combustion analyses were performed by Mikroanalytisches Laboratorium, Bonn.

Tetramethyltin (I) was a commercial sample (Alfa).

n-Butyltrimethyltin (II) [23] was prepared from n-butyllithium and trimethyltin chloride (Alfa): B.p. 52°/22 mm (lit. [23] 149/724 mm). NMR: 0.07 (s) 9H, 0.69 - 1.69 (m) 9 H.

iso-Butyltrimethyltin (III) [23] was prepared by the Grignard method: B.p. 53°/24 mm (lit. [23] 140°/726 mm). NMR: 0.1 (s) 9 H, 0.87 (d) 2 H, 0.96 (d) 6 H, 1.57 - 2.29 (m) 1H.

Allyltrimethyltin (IV), prepared according to Koton et al., [24] B.p. 128° (lit. [24] 128°) showed: NMR: 0.08 (s) 9 H, 1.73 (d) 2 H, 4.49 - 4.93 (m) 2 H, 5.4 - 6.3 (m) 1 H.

Cyclopropylcarbinyldiphenylphosphinate. To a stirred solution of cyclopropylcarbinyl alcohol (Aldrich, 1.08 g, 15 mmol) and pyridine (1.58 g, 20 mmol) in 20 ml dry ether was added 3.56 g (15 mmol) diphenylphosphinyl chloride [25] in 30 ml ether at room temperature over 30 min. The mixture was hydrolyzed at the end of 2 h and the organic portion washed successively with dilute hydrochloric acid, saturated bicarbonate, and water, dried and concentrated. The residue was chromatographed on alumina with chloroform eluent to give 1.6 g (40%) of a white solid (M.p. 78 - 79°). NMR: 0.17 - 1.44 (m) 5 H, 3.74 (d of d) 2 H, 7.07 - 7.9 (m) 10 H. Analysis: Found: C, 70.00; H, 6.34. $C_{16}H_{18}O_2P$ calcd.: C, 70.58; H, 6.29%.

Cyclopropylcarbinyltrimethyltin (V). To 0.272 g (1.0 mmol) phosphinate, prepared as above, in 10 ml dry tetrahydrofuran under argon was added 1.75 ml (1.2 mmol) of 0.687 *M* trimethyltinlithium in tetrahydrofuran. The mixture was stirred 4 h and hydrolyzed. Ether extraction, drying and concentration gave a residue which was short-path distilled to yield 0.180 g (82%) V; B.p. 58°/23 mm. NMR: 0.06 (s) 9 H, 0.08 - 0.21 (m) 7 H. Analysis: Found: C, 37.89; H, 7.39. $C_7H_{16}Sn$ calcd.: C, 38.19; H, 7.36%.

4-Butenyltrimethyltin (VI) [26] was prepared from diphenyl-4-butenylphosphate (analysis: Found: C, 63.13; H, 5.54. $C_{16}H_{17}O_4P$ calcd.: C, 63.16; H, 5.63%) in a manner similar to V. NMR: 0.05 (s) 9 H, 0.87 (t) 2 H, 2.0 - 2.5 (m) 2 H, 4.71 - 5.1 (m) 2 H, 5.4 - 6.2 (m) 1 H.

5-Pentenyltrimethyltin (VII) was prepared by the Grignard method. B.p. 65°/21 mm. NMR: 0.14 (s) 9 H, 0.7 - 1.1 (m) 2 H, 1.20 - 1.8 (m) 2H, 1.90 - 2.30 (m) 2 H, 4.77 - 5.20 (m) 2 H, 5.45 - 6.1 (m) 1 H. Analysis: Found: C, 42.07; H, 7.71. $C_8H_{18}Sn$ calcd.: C, 41.25; H, 7.79%.

Acknowledgement

The support of this work by the Air Force Office of Scientific Research, Grant AFOSR-69-1639, and the National Science Foundation, Grant GP36381X, is gratefully acknowledged.

References

1 T.G. Traylor, W. Hanstein, H.J. Berwin, N.A. Clinton, and R.S. Brown, J. Amer. Chem. Soc., 93 (1971) 5715 and references cited there; T.G. Traylor, H.J. Berwin, J. Jerkunica, and M.L. Hall, Pure Appl. Chem., 30 (1972) 599.

2 A.N. Nesmeyanov and I.F. Lutsenko, Dokl. Akad. Nauk SSSR, 59 (1948) 707.

3 F.R. Jensen and B.F. Smart, J. Amer. Chem. Soc., 91 (1969) 5686.

4 H. Sakurai, M. Kira, and M. Ochiai, Chem. Lett., 87 (1972).

5 A.R. Bassindale, C. Eaborn, D.R.M. Walton, and D.J. Young, J. Organometal. Chem., 20 (1969) 49.

6 C.G. Pitt, J. Organometal. Chem., 23 (1970) C35; C.G. Pitt and M. Bock, Chem. Commun., 28 (1972).

7 L. Radom, J.A. Pople, and P. v. R. Schleyer, J. Amer. Chem. Soc., 94 (1972) 5935; R. Hoffmann, L. Radom, J.A. Pople, P. v. R. Schleyer, W.J. Hehre, and L. Salem, J. Amer. Chem. Soc., 94 (1972) 6221

8 W.J. Hehre, J. Amer. Chem. Soc., 94 (1972) 6592.

9 L.D. Kispert, C. Engleman, C. Dyas, and C. Pittman, Jr., J. Amer. Chem. Soc., 93 (1971) 6948.

10 A. Streitwieser, Jr., Prog. Phys. Org. Chem., 1 (1963) 1.

11 D.W. Turner, Adv. Phys. Org. Chem., 4 (1966) 31; D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley-Interscience, New York, 1970.

12 N. Bodor, M.J.S. Dewar, and S.D. Worley, J. Amer. Chem. Soc., 92 (1970) 19.

13 C.G. Pitt, J. Amer. Chem. Soc., 91 (1968) 6613.

14 W.R. Moore and C.R. Costin, J. Amer. Chem. Soc., 93 (1971) 4910.

15 S. Evans, J.C. Green, P.J. Joachim, A.F. Orchard, D.W. Turner and J.D. Maier, J. Chem. Soc., Faraday Trans. II, 905 (1972).

16 P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schroder, Helv. Chim. Acta, 53 (1970) 1645.

17 M.J.S. Dewar, Hyperconjugation, The Ronald Press, N.Y., 1961, p. 51.

18 W. Lüttke, A. De Meijere, H. Wolff, H. Ludwig, and H.W. Schröffer, Angew. Chem. Int. Ed. Engl., 5 (1966) 123.

19 R.A. Alden, J. Kraut, and T.G. Traylor, J. Amer. Chem. Soc., 90 (1968) 74.

20 S. Evans, A.F. Orchard, and D.W. Turner, Int. J. Mass Spectrom. Ion Phys., 7 (1971) 261.

21 P. Bischof, J.A. Hashmall, E. Heilbronner, and V. Hornung, Helv. Chim. Acta. 52 (1969) 1745.

22 D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley-Interscience, New York, 1970, pp. 217, 235.

23 Z.M. Manulkin, J. Gen. Chem. USSR, 13 (1943) 42.

24 M.M. Koton, T.M. Kiseleva, and N.P. Zapevalova, Zh. Obshch. Khim., 30 (1960) 186.

25 G.M. Kosolapoff and R.H. Struck, J. Chem. Soc., 3950 (1959).

26 D. Seyferth, T.F. Jula, H. Dertouzos, and M. Pereyre, J. Organometal. Chem., 11 (1968) 63.