Journal of Organometallic Chemistry, 63 (1973) 133–138
© Elsevier Sequoia S A , Lausanne – Printed in The Netherlands

STERICALLY HINDERED GROUP IVB ORGANOMETALLICS

X*. PREPARATION AND SOME PROPERTIES OF BIPHENYLYLSILICON AND -TIN COMPOUNDS

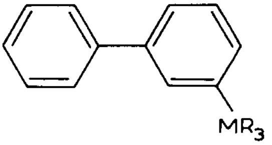
HANS ZIMMER** and MARIA ANGELES BARCELON
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (*U S A*)
WILLIAM R JONES Jr
NASA, Lewis Research Center, Lubrication Branch, Cleveland, Ohio 44135 (*U S A*)

(Received March 30th, 1973)

SUMMARY

A representative number of *meta*- and *para*-trialkylsilicon and trialkyltin substituted biphenyls have been synthesized and their thermostability determined. The silicon compounds were found to be more heat resistant than the corresponding tin compounds. No significant difference in the thermostability between the *meta*- and *para*-substituted compounds seems to exist.

Our investigations of the preparation and some of the chemical and physical properties of sterically hindered Group IVB organometallic compounds have been extended to include the biphenylyl group. One of the goals of the present study was to synthesize resistant high-temperature organosilicon and organotin compounds, and test their suitability as lubricants. Besides thermal stability, therefore, these compounds had to be liquids over an extended temperature range. It was thought that compounds of the general structure



would come close to possessing the desired properties. Staab[2] found the *meta*-linked oligophenylenes to exhibit remarkable thermal stability. The investigation of the *meta*-biphenylyl derivatives was therefore chosen in preference to the *para*-biphenylyl derivatives. A representative number of *para*-substituted biphenyls were also synthesized and included in this study. Though a few biphenylyltin and silicon

---

* For part IX see ref 1

** To whom inquiries should be adressed

compounds have been prepared[3-5], no systematic investigation of the biphenylyl group as substituent in silicon and tin organics has been made

RESULTS

Synthesis

The compounds used in this study were prepared by allowing the magnesium or lithium derivative of *m*- or *p*-bromobiphenyl to react with the appropriate triorganotin or triorganosilicon chloride. Attempts to substitute the bromobiphenyl with the corresponding chlorobiphenyl were unsuccessful. The synthesis of the desired compounds posed similar problems as have been reported by earlier investigators[6]. For no apparent reason certain compounds could only be obtained via the corresponding lithium reagents, while with others, the desired product could be prepared only if the appropriate Grignard compound was employed. Generally, once the metal (Li or Mg) was chosen, the *meta* derivatives could be prepared and purified with less difficulty than the *para* derivatives; this is true for the tin as well as the silicon series. The work-up and preparation of pure material was often rather tedious due to the presence of by-products, such as biphenyl, various coupling products, and in the case of the tin organics, the hexaalkylditins. Most of the compounds could be obtained in a pure state only by repeated vacuum distillation. The fractions were monitored by VPC and NMR-spectroscopic methods. Only cuts which showed chemical shifts in the aromatic as well as aliphatic region were collected and further purified. Attempts to obtain the desired compounds by treating the *m*- or *p*-biphenylyltin trichloride with the appropriate alkyllithium compounds were abandoned when it was found that the preparation and purification of biphenylyltin trichloride according to a Kocheshkov reaction led to a mixture of tetrabiphenylyltin, mono-, di-, and trichlorides, which was exceedingly difficult to separate.

Thermostability

As an indication for the thermal stability of the biphenylyltrialkylsilicon and tin compounds, their decomposition temperature (T_D) was measured[7]. A common method of determining the thermal stability of organic compounds is by measuring time rate of vapor pressure rise with increasing temperature. The T_D is determined from a plot of the logarithm of the vapor pressure as a function of the reciprocal of absolute temperature. The temperature at which the vapor pressure curve deviates from linearity is taken as the decomposition temperature. The T_D may also be determined from isothermal rates of pressure rise. Several rates are measured and the logarithm of rate of pressure rise is plotted as a function of the reciprocal of absolute temperature. The decomposition temperature is taken to be that temperature at which the rate of pressure rise is 50 mm per hour[8]. This latter procedure was used to determine T_D of the compounds prepared in this study (Tables 1 and 2).

Inspection of the data reveals that in every case the silicon compounds are thermally more stable than the corresponding tin compounds. Generally, there is a difference in T_D's of 40–50° in favor of the silicon compounds. In the tin series, there seems to be no difference in the thermal stability between the *meta*- and *para*-biphenylyl derivatives. A possible explanation of this behavior might be that the thermostability of the compounds is determined by the Sn–C bond strength of the tin–carbon bond

TABLE 1

BIPHENYLYL-SUBSTITUTED TIN COMPOUNDS

Compounds[a]	*Method of synthesis*	T_D	*Yield (%)*	*B p(°C/mm) or m p(°C)*	*Analysis*[b], *found (calcd) (%)* *C*	*H*
m-BphSnMe$_3$	B	230	87	105/0.005	56.65 (56.83)	5.73 (5.73)
p-BphSnMe$_3$[c]	B		40	50	57.02 (56.83)	5.84 (5.73)
m-BphSnPr$_3$	B	236	46	145–55/0.06	62.23 (62.87)	7.7 (7.53)
p-BphSnPr$_3$	B	240	60	155–65/0.01	62.66 (62.87)	7.25 (7.53)
m-BphSnBu$_3$	B	236	75	159–62/0.03	64.78 (65.03)	7.95 (8.18)
p-BphSnBu$_3$	B	240	46	175–85/0.01	65.29 (65.03)	8.40 (8.18)
m-BphSn(CH$_2$CMe$_3$)$_3$	AB	283	72	88.5–89	66.6 (66.81)	8.77 (8.72)
m-BphSn(n-C$_6$H$_{13}$)$_3$	AB	236	26	180–95/0.005	68.34 (68.31)	9.24 (9.17)
m-BphSn(n-C$_7$H$_{15}$)$_3$	AB	260	53	214–20/0.02	69.75 (69.59)	9.35 (9.55)
m-BphSn(CH$_2$CHEtBu)$_3$	AB	260	30	200–09/0.01	71.3 (70.7)	9.92 (9.88)
m-BphSn(n-C$_8$H$_{17}$)$_3$	AB		34	238–46/0.03	70.71 (70.7)	10.06 (9.88)
p-BphSnPh$_3$	B	297	33	120–23	71.37 (71.6)	4.82 (4.81)
(*m*-Pr$_3$SnC$_6$H$_4$)$_2$	B	214	42	130/0.06	55.57 (55.59)	7.74 (7.77)

[a] Bph = $C_6H_5C_6H_4$. [b] NMR spectra of all compounds were taken to corroborate the elemental analyses. [c] Previously reported in ref 5

between the biphenylyl group and the trialkyltin moiety, and differences in the stability of the resulting biphenylyl radicals are not determining factors. Though only a few examples are available for comparison in the silicon series, a similar trend seems to exist here.

The data further reveal that all the biphenylyltrialkyltin compounds with alkyl groups of little steric requirements (methyl to n-butyl) have practically identical T_D's. It is noteworthy that the trineopentyltin homolog, in agreement with our previous findings[9], is by a considerable margin the most heat resistant among the tin compounds. The T_D of the *m,m'*-bis(tri-n-propyltin)biphenyl is rather unexpectedly low.

The T_D's of the silicon derivatives seem to increase with increasing chain length of the alkyl group, with the tri-n-octylsilicon derivative being stable to about 350°.

Since the trends in thermostability with both elements were similar, the most heat-resistant compound of this type should be *m*-(trineopentylsilyl)biphenyl. Considerable efforts were made to synthesize this compound. However, probably due to steric hindrance, we were unable to make the necessary trineopentylchloro- or

TABLE 2

BIPHENYLYL-SUBSTITUTED SILICON COMPOUNDS

Compound[a]	*Method of synthesis*	T_D	*Yield* (%)	*B p(°C/mm) or m p (°C)*	*Analysis*[b], *found (calcd)(%)* C	H
m-BphSiMe$_3$[c]	B	278	76	78–82/0 03	79 42	8 11
					(79 58)	(8 02)
p-BphSiMe$_3$[d]	C	311	34	45	79 39	7 85
					(79 58)	(8 02)
m-BphSiEt$_3$	B	296	56	117–25/0 07	80.79	8 93
					(80 52)	(9.01)
p-BphSiEt$_3$[d]	C		46	125/0 02	80 70	8 7
					(80 52)	(9 01)
m-BphSiPr$_3$	C	276	75	125–31/0 02	81 20	9 77
					(81 21)	(9 73)
m-BphSiBu$_3$	B	295	78	159–60/0 04	81 58	10 38
					(81 74)	(10 29)
p-BphSiBu$_3$[e]	C	300	36	162–64/0 01	80 91	9 98
					(81.74)	(10 29)
m-BphSi(n-C$_6$H$_{13}$)$_3$	B	300	31	185–90/0 02	82 20	10 84
					(82 49)	(11.07)
m-BphSi(n-C$_8$H$_{17}$)$_3$	B	358	71	215–20/0 005	83 07	11 51
					(82 99)	(11 61)

[a] Bph = $C_6H_5C_6H_4$ [b] NMR spectra of all compounds were taken to corroborate elemental analysis [c] Ref 4 [d] Ref 3 [e] NMR spectrum showed the right proportion of aliphatic to aromatic protons, therefore the compound was not redistilled for further purification

-bromosilane. There are several reports in which the failure of the synthesis of R_4Si compounds with four large and bulky groups was believed due to steric hindrance around the silicon atom[10].

EXPERIMENTAL

Synthesis

The biphenylyl–silicon and –tin compounds were prepared by the reaction of either a Grignard reagent derived from biphenyl, or of a lithiobiphenyl compound, with the trialkylhalo derivative of tin or silicon. No attempt was made to optimize the yields and all boiling points as well as melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. The following detailed descriptions should serve as examples for the methods used for the preparation of the compounds.

Triheptyltin chloride (*Scheme A*) To a mixture of 75 ml of dry tetrahydrofuran (THF) and 5.86 g (0.24 g-atom) of magnesium turnings was added 10 g (0.08 mole) of heptyl chloride The mixture was stirred and gently warmed until it was evident that the reaction had started. More THF was then added and the rest of the heptyl chloride, 22.07 g (0.16 mole) in 25 ml of THF, was added dropwise. The reaction mixture was refluxed until most of the magnesium turnings had disappeared. The heating was then discontinued and a solution of 15 63 g (0.06 mole) of stannic chloride in benzene was added at room temperature The reaction mixture was stirred and refluxed overnight and decomposed by adding a saturated ammonium chloride solution to the mixture The organic layer was separated, washed, and dried over anhydrous magnesium sulfate. The oil obtained was dissolved in ether, saturated with anhydrous gaseous HCl and allowed to stand for two days Excess acid and solvent were removed and the remaining mixture was fractionally distilled to give 22 7 g of triheptyltin chloride (83% yield) (Found: C, 56.19; H, 10.00 $C_{21}H_{45}ClSn$ calcd : C, 55.83; H, 10.04%.

The preparation of *trineopentyltin chloride*[9] from tetraneopentyltin was accomplished by a Kocheshkov reaction in benzene by heating a mixture of 3/1 mole ratio of the tetraorganotin and stannic chloride at reflux (80°) for 48 h

m-Biphenylyltriheptyltin (*Scheme B*) A Grignard solution was prepared from 0 97 g (0.04 g-atom) of magnesium and 9 32 g (0 04 mole) of *m*-bromobiphenyl in 150 ml of THF. To this mixture a solution of 13.55 g (0 03 mole) of triheptyltin chloride in THF was gradually added and then refluxed for 1 h. The solvent was changed to xylene and the mixture was heated at reflux overnight. After the usual work-up, the resulting heavy liquid was fractionated under reduced pressure, to give 9.7 g (53%) of *m*-biphenylyltriheptyltin boiling between 214 and 220° at 0.02 mm.

m-Biphenylyltripropylsilane (*Scheme C*) A mixture of 1 13 g (0.08 g-atom) of lithium wire, cut into small pieces, and 50 ml of anhydrous ether was stirred under argon and reacted with 18.77 g (0.08 mole) *m*-bromobiphenyl. After almost all the lithium had disappeared, 12.48 g (0.06 mole) of tripropylchlorosilane in ether was gradually added. The ether solvent was then replaced with benzene and the resulting mixture refluxed for 12 h.

The reaction mixture was hydrolyzed with dilute sulfuric acid and the organic layer was separated and dried over anhydrous magnesium sulfate. Fractional distallation gave 15 g (75%) of *m*-biphenyltripropylsilane distilling between 125 to 131° at 0.02 mm.

Thermostability

The tensimeter used for determining the T_D's in this study consists of two units: the sample oven with an associated temperature programmer and the electronics module containing the recorder. The function of a tensimeter is to heat a liquid sample and plot either the vapor pressure, or the isothermal rate of increase of vapor pressure (due to thermal decomposition), as a function of temperature.

Procedure. Three to four mls. of test fluid are placed in the sample cell. The cell is attached to the cell assembly and the fluid is degassed and refluxed under vacuum. The cell assembly is then placed in the oven The sample is heated to an initial temperature about 50° below the suspected decomposition temperature. After a 5-minute stabilization period, the increase in vapor pressure, if any, is recorded as a vertical bar during a fixed time interval. Then the programmer raises the sample temperature by a preset amount, usually 5°, and the previous process is repeated. The plot one obtains essentially is a plot of the logarithm of the isothermal rate of vapor pressure increase as a function of reciprocal absolute temperature A straight line is drawn connecting the tops of the recorded bars at the higher temperatures. The intersection with the temperature reference axis is the thermal decomposition temperature, T_D. This temperature axis corresponds to a pressure rise of 50 mm per hour, which is the definition of the T_D. Generally, it is possible to dupicate the T_D's within ±5° for pure compounds.

ACKNOWLEDGEMENT

This research was generously supported by NASA-Grants, NGR 36-004-043 and NGR 36-004-056.

REFERENCES

1 H Zimmer and A V Bayless, *Tetrahedron Lett*, (1970) 459
2 H A Staab and C Wuensche, *Chem Ber*, 101 (1968) 887
3 A D Petrov and T I Chernysheva, *Doklady Akad Nauk SSSR*, 84 (1952) 515
4 H Gilman and G Lichtenwalter, *J Org Chem*, 21 (1956) 1307
5 M D Curtis and A L Allred, *J Amer Chem Soc*, 87 (1965) 2554
6 L W Breed, *J Org Chem*, 25 (1960) 1198
7 I B John, E. A McElhill and J. O Smith, *Ind Eng. Chem. Prod. Res. Develop*, 1 (1962) 2
8 W R Jones and W F Hady, *NASA TN D*-6251 (1971)
9 H Zimmer, O. Homberg and M Jayawant, *J Org Chem*, 31 (1966) 3857
10 C Eaborn, *Organosilicon Compounds*, Academic Press, 1960, New York