On the Metallo-Organic Compounds. X. Electroisomerism in Triethyltin.

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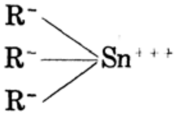
The triethyltin group may be prepared in various ways among which the two methods(1),(2)—(1) the reduction of triethyltin halide(1), or the hydroxide and (2) the oxidation of sodium diethyl stannide or disodium tetraethyl stannide—are shown in equations I and II, respectively. The triethyltin group prepared by the reduction process I and the triethyltin group prepared by the oxidation process II are highly interesting as regards their properties; although of like appearance (their tin content, M.W. in naphthalene and benzene, and refractive index)(1) their rate of oxidation appears to differ markedly.

$$\text{I.}\quad R_3SnX+Na^{+}+\varepsilon^{-}=R_3Sn+NaX$$

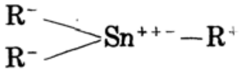
$$\text{II.}\quad R_2Sn^{-}Na^{+}+RX=R_2SnR+NaX\ .$$

The electronic constitutions of the triethyltin groups thus obtained are represented, therefore, as follows:

A.



B.



It is expected from the electronic constitutions that the compound B would be more unstable than the compound A. Such constitutional isomers will be called "electroisomers" by the present author. The stability of the compounds can be determined by their degree of conversion into triethyltin hydroxide or into diethyltin oxide through the formation of triethyltin oxide (b.p. 158°, 15 mm., uncor.,)(1) in the presene of oxygen and water. At present, under this condition the mechanism of the formation of diethyltin oxide is not known. However, perhaps it would conform with the following equation(3)

$$\text{III.}\quad R_3SnOH=R_2SnO+RH\ .$$

It cannot be strongly emphasized without further investigation from different points; however the existence of the so-called "electroisomers" is theoretically possible. Table 1, 2 and 3 (corresponding curves in Fig. 1.) illustrate the properties. The boiling points of both samples are approximately the same (152–154°, 17 mm (uncor.) for $(C_2H_5)_3Sn$ and 153–155°, 17 mm (uncor.) for $(C_2H_5)_2SnC_2H_5$).

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(1) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 290.
(2) T. Harada, this Bulletin, **4** (1929), 266.
(3) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **36** (1936), 501.

Table 1.

	A. $(C_2H_5)_3Sn$ 0.4 g. Subs. in 75 c.c. of 75% alc.	B. $(C_2H_5)_2Sn\ C_2H_5$ 0.4 g. Subs. in 75 c.c. of 75% alc.
Days	*p*H	*p*H
0	6.0	6.2
1	6.6	7.2
3	7.6	7.7
4	7.7	7.7
5	$(C_2H_5)_2SnO = 0.08$ g.	$(C_2H_5)_2SnO = 0.19$ g.

Table 2.

	A. $(C_2H_5)_3Sn$ 0.3 g. Subs. in 50 c.c. H_2O		B. $(C_2H_5)_2Sn\ C_2H_5$ 0.3 g. Subs. in 50 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	*p*H	c.c. of $\frac{1}{20}$ N HCl	*p*H
0	0.10	6.9	0.20	7.0
1	0.20	7.1	0.40	7.2
2	0.30	7.2	0.50	7.4
3	0.40	7.3	0.60	7.4
4	0.45	7.4	0.70	7.5
6	0.50	7.4	0.75	7.6
	$(C_2H_5)_2SnO = 0.03$ g.		$(C_2H_5)_2SnO = 0.08$ g.	

Table 3.

	A. $(C_2H_5)_3Sn$ 1.0 g. Subs. in 100 c.c. H_2O		B. $(C_2H_5)_2Sn\ C_2H_5$ 1.0 g. Subs. in 100 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	*p*H	c.c. of $\frac{1}{20}$ N HCl	*p*H
0	0.05	6.7	0.05	6.8
1	0.08	6.8	0.10	7.0
2	0.15	7.0	0.20	7.1
4	0.20	7.1	0.35	7.2
6	0.25	7.2	0.45	7.4
8	0.30	7.3	0.55	7.5
11	0.40	7.4	0.65	7.5
14	0.50	7.5	0.75	7.6
16	0.55	7.5	0.75	7.6
18	0.60	7.5	0.75	7.6
21	0.65	7.6	0.80	7.6
24	0.70	7.6	0.80	7.6
29	0.70	7.6	0.80	7.6
	$(C_2H_5)_2SnO = 0.10$ g.		$(C_2H_5)_2SnO = 0.27$ g.	

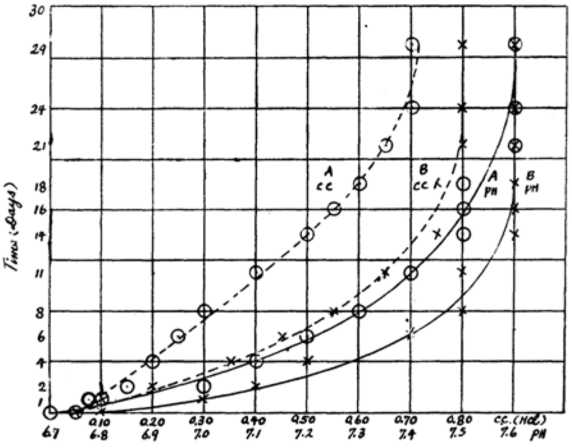

Fig. 1.

Experimental. One gram of sample A and B prepared by equations I and II respectively (and purified by distillation, and washing with alcohol and water)⁽¹⁾ were covered with 100 c.c. of water in Erlenmeyer flasks and agitated occasionally in a similar manner. One c.c. of each of the clear top aqueous solution was taken out and diluted with 10 c.c. of water, and finally was titrated with $\frac{1}{20}$ NHCl using methyl orange as indicator. Ten c.c. of the diluted solution were determined for pH simultaneously with phenol red as indicator. Insoluble $(C_2H_5)_2SnO$ on the other hand, was also formed by the above treatment. A similar experiment was also carried out with 0.4 g. of each of the sample but they were covered with 75 c.c. of 75% alcohol instead of water. The titration and the determination of pH were carried out similarly as above but for pH below 7.0, bromothymol blue was employed as indicator. In both cases, the total amount of diethyltin oxide precipitated from $(C_2H_5)_2SnC_2H_5$ was approximately three times that from $(C_2H_5)_3Sn$.

Summary.

The free triethyltin groups prepared by two methods, namely, the reduction of $(C_2H_5)_3SnX$ and the oxidation of $(C_2H_5)_2SnNa$ or $((C_2H_5)_2SnNa)_2$ appear to be identical. However, their rate of oxidation appears to differs markedly from one another. It is assumed that this is due to their electronic constitutional difference (electroisomeric) or in the methods of preparation.

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