Reaction of Organic Tin(II) Compound with Carbonyl Compound

Ikuko WAKESHIMA* and Ichiro KIJIMA
Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received October 22, 1980)

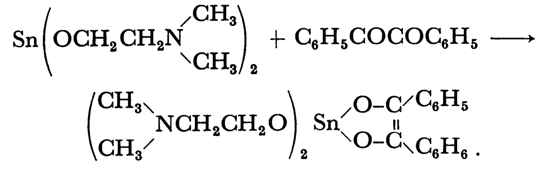
The reactions of organic tin(II) compounds bearing Sn–OC bonds with carbonyl compounds, C_6H_5COR ($R=C_6H_5CO$, C_6H_5, and H) and *p*-benzoquinone, have been investigated. The tin(II) compound reacted with benzil and *p*-benzoquinone to yield the corresponding oxidative addition products. However, the oxidative addition reaction did not occur in benzophenone and benzaldehyde.

We have reported the preparation of organic tin(II) compounds having a high volatility and an excellent solubility toward organic solvents.[1] The chemical behavior of the tin(II) compounds[2–5] has been studied by several research groups: for example, we reported on the reactions of the tin(II) compounds with alkyl halides and heterocumulenes.[2] We describe here a further study on the reactivity of tin(II) compounds, $Sn(OR)_2$, ($R=(CH_3)_2NCH_2CH_2-$, C_2H_5-, o-$C_2H_5OCOC_6H_4-$, $CH_3C{=}CHCOCH_3$, and $CH_3C{=}CHCO_2C_2H_5$), with carbonyl compounds such as benzil, benzophenone, benzaldehyde, and *p*-benzoquinone; the structural analogy of the tin(II) compound with a carbene is important here.

Results and Discussion

The reaction of bis(2-dimethylaminoethoxo)tin(II) (**1**) with benzil in refluxing THF for 6 h afforded yellow powders in 46% yield. The structure of the product was determined as bis(2-dimethylaminoethoxo)(1,2-diphenyl-1,2-ethenediolato)tin(IV), on the bases of the elemental analysis ($C_{22}H_{30}N_2O_4Sn$), the IR spectrum which has no band attributable to $\nu_{C=O}$ (1655 cm^{-1}), and the formation of 1,2-diphenylvinylene dibenzoate when the product was treated with benzoyl chloride. The structure was also supported by its hydrolyzate: on hydrolysis, the product gave benzoin, which appeared to be formed by a rapid tautomerization of the unsaturated glycol, 1,2-diphenyl-1,2-ethenediol.

These facts suggest that compound (**1**) can be oxidized by benzil to a tetravalent tin compound, as shown in Eq. 1:



$$Sn\left(OCH_2CH_2N\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2 + C_6H_5COCOC_6H_5 \longrightarrow \left(\begin{matrix}CH_3\\CH_3\end{matrix}NCH_2CH_2O\right)_2 Sn\begin{matrix}O-C\diagup C_6H_5\\ \| \\ O-C\diagdown C_6H_6\end{matrix} \quad (1)$$

The reaction proceeded more readily in THF and ethyl alcohol than in benzene (see Table 1).

The reaction of various organic tin(II) compounds with benzil was also examined in THF. The results, as summarized in Table 2, reveal that i) organic tin(II) compounds containing Sn–OC bond are more effective reducing agents for benzil than tin(II) chloride, which is a polymer of intermolecularly coordinated Cl→Sn bond; ii) in the organic tin(II) compounds, the oxidative addition reaction of **1** is the best for benzil, while that of diphenoxotin(II) (**4**) is the worst; iii) the reactivity of alkoxotin(II) compounds (**1** and **2**) is superior that of the conjugated chelate tin(II) compounds (**3**, **5**, and **6**); and finally; iv) the reaction of the monomeric tin(II) compounds (**1** and **3**) proceeds far more readily than that of the corresponding associated tin(II) compounds (**2** and **4**).

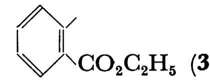
From these facts, it may be concluded that the migration of 5s electrons on the tin(II) atom in the intermediate (a), as indicated in Eq. 2, play an important role in the reaction with benzil and that, of the organic tin(II) compounds, the monomeric organic tin(II) compound bearing an electron releasing group behaves most effectively toward benzil.

TABLE 1. SOLVENT EFFECT ON THE REACTION[a)] OF BIS(2-DIMETHYLAMINOETHOXO)TIN(II) WITH BENZIL

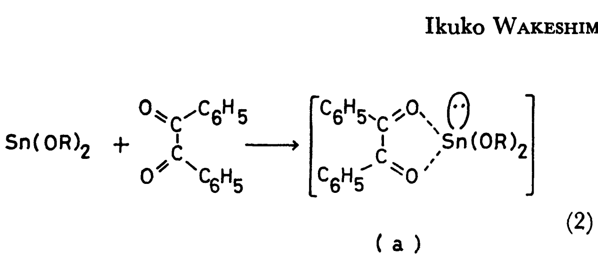
Solvents	Hydrolyzate	
	Yield/%[b)]	P[c)]
Benzene	90	1.03
Ethyl alcohol	91	1.62
Tetrahydrofuran	95	1.76

a) Reaction conditions: $[Sn(OR)_2]/[benzil]=1$, time: 6 h; temp: benzene 80 °C, ethyl alcohol 78 °C, THF 67—68 °C. b) Based on the weight of benzil used in the reaction. c) Proportion ([benzoin]/[benzil]) of benzoin the hydrolyzate.

TABLE 2. HYDROLYZATES OF PRODUCTS FROM THE REACTION[a)] OF VARIOUS ORGANIC TIN (II) COMPOUNDS WITH BENZIL IN THF

$Sn(OR)_2$	Hydrolyzates	
R	Yield/%[b)]	P[c)]
$(CH_3)_2NCH_2CH_2$-(**1**)	95	1.76
C_2H_5-(**2**)[d)]	87	0.72
 (**3**)	87	0.41
 (**4**)	80	0.09
$CH_3C{=}CHCOCH_3$ (**5**)	83	0.14
$CH_3C{=}CHCO_2C_2H_5$ (**6**)	81	0.15
$SnCl_2$	86	0.03

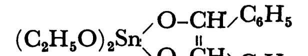
a) Reaction conditions: $[Sn(OR)_2]/[benzil]=1$, time; 6 h, temp; 67—68 °C. b) Based on the weight of benzil used in the reaction. c) Proportion ([benzoin]/[benzil]) of benzoin in the hydrolyzate. d)Associated in nature.



(2)

Compound **2** reacted unsatisfactorily with benzaldehyde in THF at 68—69 °C to give only traces of cinnamaldehyde and benzyl alcohol. Although the reaction was conducted under drastic conditions (no solvent, at 145±5 °C) for 3 h, there was no increase in the yields of cinnamaldehyde and benzyl alcohol. Therefore, it seems that the reaction of compound **2** with benzaldehyde proceeds neither through the oxidative addition reaction (Eq. 1) nor through the intermolecular oxidative coupling reaction (Eq. 3), but rather in a way similar to the Meerwein-Pondorf reaction, as shown in Eqs. 4 and 5:

$$Sn(OC_2H_5)_2 + 2\ C_6H_5CHO \xrightarrow{\times}$$



$$(C_2H_5O)_2Sn\begin{matrix}\diagup O\text{-}CH\diagup C_6H_5 \\ \| \\ \diagdown O\text{-}CH\diagdown C_6H_5\end{matrix} \qquad (3)$$

$$Sn(OC_2H_5)_2 + C_6H_5CHO \longrightarrow$$

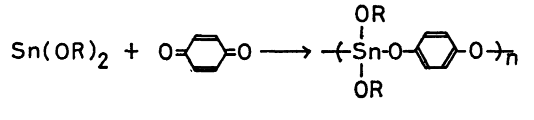
$$(C_2H_5O)Sn(OCH_2C_6H_5) + CH_3CHO \qquad (4)$$

$$C_6H_5CHO + CH_3CHO \xrightarrow[H_2O]{Sn(OC_2H_5)_2} C_6H_5CH{=}CHCHO. \qquad (5)$$

Compound **1** did not react at all with benzophenone in THF at 67 °C after 6 h.

The reaction of **1** and **5** with *p*-benzoquinone in benzene were investigated. As indicated in Table 3, it was found that each reaction readily gave the corresponding oxidative addition products in excellent yields.

The products were only soluble in common organic solvents with great dificulty and decomposed at high temperature. No chracteristic absorption band of *p*-benzoquinone presented itself. Therefore, the oxidative addition product is considered to be a polymer, as shown below:



(6)

$R = \text{-}CH_2CH_2N(CH_3)_2,\ CH_3\underset{|}{C}{=}CHCOCH_3.$

Although **5** was a less effective reducing agent for benzil, the reaction with *p*-benzoquinone took place easily to afford the oxidative addition compound. Therefore, it seems that the possibility of the oxidative addition reaction of organic tin(II) compounds depends greatly on the half-wave potentials of the carbonyl compounds: *p*-benzoquinone, benzil, benzaldehyde, and benzophenone have half-wave potentials of −0.146(2), −0.27(2), −0.94(1), and −0.94(1) SCE, respectively. The parenthesized-figure indicates the number of electrons involved in the reaction.

Experimental

All reactions were carried out in a nitrogen atmosphere dried with liquid nitrogen. The melting and boiling points are uncorrected. IR spectra were recorded with a Hitachi EPI-S2 spectrometer, and mass spectra were taken on Hitachi RMU-7 model double-focusing spectrometer. The CHN elemental analyses were carried out with a Yanagimoto MT-2 CHN corder. Gas chromatography was performed on a Yanagimoto model GCG-2, using SE-30 column.

Tin content was determined by chelate titration with M/100 EDTA aqueous solution. Benzil was determined by the redox titration with a chromous sulfate solution.[6] *p*-Benzoquinone was purified by sublimating a commercial extra-pure grade at 70—80 °C/20 mmHg (1 mmHg = 133.322 Pa) just prior to use. Benzaldehyde and benzophenone were purified by distillation before use.

Reaction of Organic Tin(II) Compounds with Benzil in a 1 : 1 Molar Ratio. Benzil (50 mmol) was added to a solution or a suspension of organic tin(II) compound (50 mmol) in 100 ml of solvent. After the mixture was refluxed for 6 h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was hydrolyzed with 100 ml of water (5 ml)–benzene (80 ml)–acetone(15 ml) solution. After separating the resulting solids by filtration, the solid was extracted with acetone in a Soxhlet extractor in order to obtain the benzoin. Subsequently, the mother liquor was combined with the extract and distilled *in vacuo* at a temperature below 155 °C (bath temperature) to isolate the hydrolyzate. Bp 118—138 °C/0.3 mmHg. The results are shown in Tables 1 and 2.

Isolation of Bis(2-dimethylaminoethoxo)(1,2-diphenyl-1,2-ethenediolato)tin(IV): Compound **1** (14.7 g, 50 mmol) and benzil (10.5 g, 50 mmol) were dissolved in 53 ml of THF. The mixture was heated at 68 °C for 6 h. Yellow powders precipitated during the reaction were filtered off, washed with THF, and dried: yield 12.0 g (47.5%). Found: C, 52.31; H, 6.01; N, 5.45; Sn, 23.05%. Calcd for $C_{22}H_{30}N_2O_4Sn$: C, 52.30; H, 5.94; N, 5.54; Sn, 23.62%. *m/e*: 505 (M^+). Mp 154 °C (dec).

Isolation of 1,2-Diphenylvinylene Dibenzoate: Benzoyl chloride (44.9 g, 106 mmol) was added drop by drop to the reaction mixture of **1** (7.3 g, 24.9 mmol) and benzil (5.2 g, 24.7 mmol) at 30—40 °C. After being warmed for 1 h, it was allowed to stand for 2 d at room temperature and then hydrolyzed with 100 ml of 9% hydrochloric acid. The resulting solids were

TABLE 3. REACTION WITH *p*-BENZOQUINONE

$Sn(OR)_2$ R	Reaction conditions		Products			
	Molar ratio [Quinone]/[Sn]	Time h	Yield %	Mp (dec) °C	Sn Found(Calcd) (%)	IR ν/cm^{-1}
$(CH_3)_2NCH_2CH_2$–	1	3	100	220	28.98 (29.45)	1220
$CH_3\underset{|}{C}{=}CHCOCH_3$	1	5	95	245	27.69 (27.93)	1210

isolated and extracted with diisopropyl ether. The ether solution was washed with 5% sodium carbonate aqueous solution, then with water, and evaporated to dryness. After removing the unreacted benzil under a reduced pressure, the residue was recrystallized from benzene–hexane (1/1 volume ratio) solution, giving 2.5 g of 1,2-diphenylvinylene dibenzoate with mp 156—158 °C (lit,[7] 158 °C); white powder. Found: C, 78.85; H, 4.68%. Calcd for $C_{28}H_{20}O_4$: C, 79.98, H, 4.79%. IR (KBr disk): $\nu_{C=O}$ 1720 cm^{-1}; ν_{C-O} 1082 cm^{-1}.

Reaction with p-*Benzoquinone.* A solution of 1.95 g (18 mmol) of *p*-benzoquinone in 37 ml of benzene was added drop by drop to **1** (5.31 g, 18 mmol) in benzene (20 ml) at 22—24 °C and then the solution was refluxed with stirring in an oil bath for 2 h. The precipitated solids were isolated by filtration, washed with benzene, and dried. Yield 7.25 g (100%).

The reaction of compound **5** was also carried out in a similar way.

Reaction with Benzaldehyde. Compound **2** (8.4 g, 40 mmol) and benzaldehyde (48.9 g, 461 mmol) were heated at 66 °C for 11 h. After filtrating the reaction mixture, traces of ethyl alcohol and cinnamaldehyde from the mother liquor were detected by gas chromatography. The residue in the filtrating flask was hydrolyzed with an aqueous diisopropyl ether. The solvent was removed by distillation; a trace of benzyl alcohol was found in the distillation flask.

The reaction under drastic conditions (no solvent, reaction temperature 145±5 °C, reaction time 3 h) was performed in a similar way. The presence of acetaldehyde, ethyl alcohol, cinnamaldehyde, and benzyl alcohol was confirmed by gas chromatography.

Reaction with Benzophenone. The mixture of **1** (16.2 g, 54.9 mmol) and benzophenone (10.3 g, 56.5 mmol) in 55 ml of THF was refluxed for 6 h. No decrease in Sn^{2+}% was observed. After removal of THF under a reduced pressure, the residue was hydrolyzed with 100 ml of water (15 ml)–benzene (80 ml)–acetone (15 ml) solution. The resultant solids were filtered off and then the mother liquor was evaporated to dryness. The solids were distilled *in vacuo*; 10 g of benzophenone (bp 153 °C/1 mmHg) was recovered.

The present work was partially supported by a Grant-in-Aid for Scientific Research No 555348 from the Ministry of Education, Science and Culture.

References

1) I. Wakeshima and I. Kijima, *Chem. Lett.*, **1972**, 325.

2) I. Wakeshima and I. Kijima, *J. Organomet. Chem.*, **76**, 37 (1974); I. Wakeshima, H. Suzuki, and I. Kijima, *Bull. Chem. Soc. Jpn.*, **48**, 1069 (1975); I. Wakeshima, Y. Saitoh, and I. Kijima, *ibid.*, **51**, 3549 (1978).

3) P. G. Harrison and J. J. Zuckerman, *Inorg. Nucl. Chem. Lett.*, **5**, 545 (1969); *J. Chem. Soc., D*, **1969**, 321.

4) A. B. Cornwell and P. G. Harrison, *J. Chem. Soc., Dalton Trans.*, **1975**, 1486, 2017.

5) K. D. Bos, R. J. Bulten, and J. G. Noltes, *J. Organomet. Chem.*, **99**, 397 (1975); *Inorg. Nucl. Chem. Lett.*, **9**, 961 (1973).

6) J. P. Tandon, *Z. Anal. Chem.*, **167**, 184 (1959).

7) W. E. Bachmann, *J. Am. Chem. Soc.*, **53**, 2762 (1931).