

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)

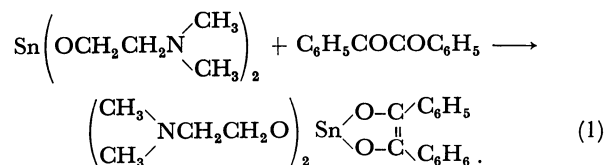
The reactions of organic tin(II) compounds bearing Sn–OC bonds with carbonyl compounds, C_6H_5COR ($R=C_6H_5CO$, C_6H_5 , and H) and *p*-benzoquinone, have been investigated. The tin(II) compound reacted with benzil and *p*-benzoquinone to yield the corresponding oxidative addition products. However, 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_5 - $OCOC_6H_4-$, $CH_3C\equiv CHCOCH_3$, and $CH_3C\equiv CHCO_2C_2H_5$), 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-dimethylaminoethoxy)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-dimethylaminoethoxy)(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:



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 $Cl \rightarrow Sn$ 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

TABLE 1. SOLVENT EFFECT ON THE REACTION^{a)} OF BIS(2-DIMETHYLAMINOETHOXY)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 R	Hydrolyzates	
	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
$CH_3C\equiv CHCOCH_3$ (5)	83	0.14
$CH_3C\equiv CHCO_2C_2H_5$ (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.

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.

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) ₂ NCH ₂ CH ₂ -	1	3	100	220	28.98 (29.45)	1220
CH ₃ 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.

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