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Control of Product in the Reaction of Tributyltin ω-Haloalkoxide (n-$Bu_3SnO(CH_2)_nX$) with Diphenylketene

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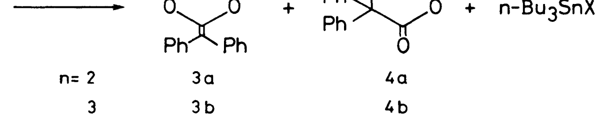
Synopsis. The reaction of tributyltin ω-haloalkoxide with diphenylketene gave cyclic ketene acetals and/or lactones, and the ratio of these products were controled by the number of methylene groups and by the addition of Lewis base in the reaction system. Moreover, the direct cycloaddition of diphenylketene with cyclic ethers proceeded in high yields, catalyzed by organotin halide-Lewis base complexes.

We have recently reported the novel use of tributyltin ω-haloalkoxides (**1**) (n-$Bu_3SnO(CH_2)_nX$, X=Cl, Br, I, n=2, 3),[1,2] yielding a variety of five- and six-membered heterocycles in the reactions with heterocumulenes such as isocyanates, isothiocyanates and carbodiimides.[1,2] In particular, it has been pointed out that the addition of Lewis bases significantly stimulated the formation of heterocyclic compounds. Moreover, new effective catalysts, the complexes of organotin halides with bases, have been developed on the basis of investigations on this reaction mechanism, conducting the direct cycloaddition of oxiranes with heterocumulenes under very mild conditions.[3] In the course of the study on this type of reaction in terms of diphenylketene (**2**) with **1**, we recognized some different features from the reactions of other heterocumulenes which have been already reported.[1,2] Thus, the types of the products were drastically changed by the number of methylene (n) of **1**, and moreover the addition of bases completely changed the product in the reaction with n-$Bu_3SnO(CH_2)_3X$ (**1b**). In addition, the direct cycloadditions of oxiranes or oxetane with **2** were performed.

The results of the reactions between tributyltin β-haloethoxides (n-$Bu_3SnO(CH_2)_2X$) (**1a**) with **2** are summarized in Table 1 (Entries 1—8). The types of products and the reactivity varied with temperature, additives and the kind of halogen. γ-Butyrolactone (**4a**) was obtained in only the reactions with iodide derivative (**1aa**) (Entries 1—3), and the 1,3-dioxolane **3a** was exclusively produced from the bromide (**1ab**) (Entry 4). Moreover, the ratio of **4a** to **3a** was increased with lowering the reaction temperature, however the reaction proceeded very slowly below 60 °C. The presence of Lewis bases allowed the reaction to proceed in high yields under significantly milder conditions, in addition, giving **3a** exclusively (Entries 6—8).

The effect of the number of methylene groups was very definitive as shown in the reaction with tributyltin γ-halopropoxides (n-$Bu_3SnO(CH_2)_3X$) (**1b**). In sharp contrast to the 1,3-dioxolane formation from the reaction of **1a**, δ-valerolactone (**4b**) was selectively obtained with **1b** (Entries 9 and 10). Moreover, the effect of base was more remarkable than in the reaction of **1a**, and the product was completely changed from the lactone **4b** to the 1,3-dioxane **3b** (Entry 11). This drastic change is very characteristic of the reaction of diphenylketene. Thus, no change of products by the addition of bases was observed in the reaction of **1b** with isocyanates or isothiocyanates.[1,2]

As Bloodworth et al. have reported,[4] these reactions are thought to proceed via stannyl ester type of adduct (**A**) as shown in Scheme 1. Products, **3** and **4**, may be



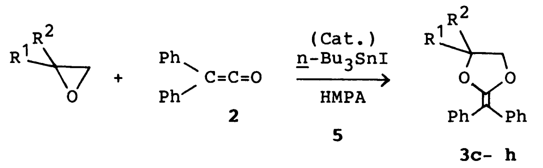
Scheme 1.

Table 1. Reactions of **1** with **2**[a)]

Entry	1	Base	Temp °C	Product	Isolated Yield/%[b)]
1	**1aa**	—	80	**3a**+**4a**	60 (40/60)[c)]
2	**1aa**	—	100	**3a**+**4a**	52 (50/50)[c)]
3	**1aa**	—	150	**3a**+**4a**	51 (85/15)[c)]
4	**1ab**	—	100	**3a**	43
5	**1ac**	—	120	**3a**	12
6	**1aa**	HMPA[d)]	60	**3a**	67
7	**1ab**	Et_3N[e)]	40	**3a**	78
8	**1ab**	Ph_3P[e)]	40	**3a**	93
9	**1ba**	—	120	**4b**	77
10	**1bb**	—	120	**4b**	57
11	**1ba**	HMPA[d)]	100	**3b**	52

a) **1** 5 mmol, **2** 4 mmol, Time 1 h, b) Based on **2**, c) **3a**/**4a** ratio; determined by ^{1}H NMR, d) 3 ml, e) 5 mmol.

Table 2. Cycloaddition of Oxiranes with 2[a)]



R¹	R²	Product	Yield/%[b)]
Me	H	**3c**	100
Et	H	**3d**	93
Me	Me	**3e**	73
CH_2Cl	H	**3f**	88
$PhOCH_2$	H	**3g**	82
Ph	H	**3h**	94

a) Oxirane 25 mmol, **2** 5 mmol, *n*-Bu$_3$SnI 1 mmol, HMPA 1 mmol, Temp 40°C, Time 1 h, b) Based on **2**.

formed by intramolecular *O*- and *C*-alkylations, respectively. As to the formation of **3**, stannyl enolate type of adduct (**B**) can be considered. However, IR spectrum showed the absorption at 1730 cm^{-1} (C=O) in the addition of **2** with **1a** or **1b**, where no cyclization occurred. And this absorption was also observed in the case using HMPA as a solvent. From these facts, we propose **A** as an intermediate rather than **B**.[5)] While it is unclear exactly why the remarkable alternation of products occurred, the significant effect of the number of methylene group seems to suggest an important role of the intramolecular coordination of the terminal halide to the tin atom. The characteristic reaction mode of diphenylketene may be rationalized by the lower ability of an intermolecular coordination of **A** in comparison with the adducts of **1** with an isocyanate. Namely, the nitrogen atom in the adduct of isocyanates, *n*-Bu$_3$SnN(R)COO(CH$_2$)$_n$X, can bring an intermolecular coordination toward another tin atom,[4)] whereas the carbon atom adjacent to Sn atom in **A** has no coordinative ability.

In the next stage, we tried to use *n*-Bu$_3$SnI-HMPA complex (**5**) as a catalyst for the cycloaddition of oxiranes with **2**. As shown in Table 2, cycloaddition proceeded under very mild conditions, and a variety of 1,3-dioxolanes, **3c**—**h**, were obtained in good to excellent yields. In this reaction system, the complex **5**, formally forms in situ, undergoes ring opening to give organotin *β*-iodoalkoxides.[6)] The activated halogen by the coordination of base to a tin atom of *n*-Bu$_3$SnI is effective for ring opening. Next, these tin alkoxides react with diphenylketene, and the 1,3-dioxolanes are formed, accompanied by the regeneration of the Sn-I bond. While, oxetane showed a lower reactivity than oxiranes, and heterocycles were scarcely obtained by using **5**. However, MeSnI$_3$-HMPA complex showed higher catalytic activity in direct cycloaddition reaction using oxetane and **2**, and heterocycles **3b** and **4b** were obtained in 18 and 40% yields, respectively. Although the yields are not so good as the case of oxiranes, this result is interesting because cycloaddition of heterocumulenes with oxetanes has been scarcely reported.[7)]

Experimental

Reaction of Tributyltin *ω*-Haloalkoxide (*n*-Bu$_3$SnO-(CH$_2$)$_n$X) (1) with Diphenylketene (2). All reactions were carried out under dry nitrogen. A typical procedure is described for the reaction of **1aa** with **2**. **1aa** (2.30 g, 5 mmol) and **2** (0.78 g, 4 mmol) were stirred in a 50 ml round-bottomed flask, then heat was evolved about 40 °C. The infrared spectrum showed disappearance of the characteristic absorption band of ν_{CCO} at 2100 cm^{-1}, and the presence of the new band at 1730 cm^{-1}. After 1 h at 80 °C, addition of excess amounts of hexane on cooling induced 0.57 g (60%) of white precipitates immediately, which were collected by filtration, washed with hexane and dried in vacuo. The precipitates were turned out to 2-diphenylmethylene-1,3-dioxolane (**3a**) (24% yield) and *α*,*α*-diphenyl-*γ*-butyrolactone (**4a**) (36% yield). The **3a**/**4a** ratio was determined by ^{1}H NMR spectra. When the reaction was carried out in a solvent, **1**, **2**, and a solvent were charged in this turn.

2-Diphenylmethylene-1,3-dioxolane (3a): Mp 148—149 °C (lit,[8)] mp 149—151 °C); IR (KBr) 1660 cm^{-1} (C=C); MS *m/z* 238 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=4.20 (s, 4H, CH$_2$), 7.00—7.40 (m, 10H, Ph).

2-Diphenylmethylene-1,3-dioxane (3b): Mp 80—81 °C; IR (KBr) 1640 cm^{-1} (C=C); MS *m/z* 252 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=1.95—2.25 (m, 2H, CH$_2$), 4.15 (t, 4H, OCH$_2$), 7.10—7.40 (s, 10H, Ph).

***α*,*α*-Diphenyl-*γ*-butyrolactone (4a):** Pure sample was isolated by column chromatography (Silica-gel, CHCl$_3$); Mp 80—81 °C (lit,[9)] mp 77—79 °C); IR (KBr) 1780 cm^{-1}; MS *m/z* 238 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=2.98 (t, 2H, CH$_2$), 4.22 (t, 2H, CH$_2$O), 7.32 (s, 10H, Ph).

***α*,*α*-Diphenyl-*δ*-valerolatone (4b):** Mp 116 °C (lit,[10)] mp 112 °C); IR (KBr) 1730 cm^{-1}; MS *m/z* 252 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=1.88 (m, 2H, CH$_2$), 2.62 (t, 2H, Ph$_2$CCH$_2$), 4.22 (t, 2H, CH$_2$O), 7.22 (s, 10H, Ph).

Cycloaddition of Diphenylketene (2) with Oxiranes or Oxetane: A typical procedure is described for the reaction of diphenylketene with 2-methyloxirane, catalyzed by *n*-Bu$_3$SnI-HMPA. To a solution of *n*-Bu$_3$SnI (0.42 g, 1 mmol) and HMPA (0.18 g, 1 mmol) in 2-methyloxirane (1.45 g, 25 mmol) was added **2** (0.97 g, 5 mmol) with stirring under dry nitrogen. The resulting mixture was stirred at 40 °C for 2 h and the yield was monitored by GLC. Diphenylketene was no longer detected, which was confirmed by the disappearance of IR absorption band of ketene (2100 cm^{-1}). Excess amounts of hexane was added on cooling to the reaction mixture, then 1.12 g (89%) of white precipitates were obtained immediately. This was collected by filtration, washed with hexane and dried in vacuo. The precipitates was 2-diphenylmethylene-4-methyl-1,3-dioxolane (**3c**). Compounds **3b**, **4b**, **3d**, and **3e** were isolated by a similar method. **3f**, **3g**, and **3h** were isolated by distillation from the reaction mixture.

2-Diphenylmethylene-4-methyl-1,3-dioxolane (3c): Mp 88—89 °C; IR (KBr) 1660 cm^{-1}; MS *m/z* 252 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=1.42 (d, 1H, CH$_3$), 3.82 (t, 1H, one of CH$_2$O), 4.38 (dd, 1H, one of CH$_2$O), 4.70 (m, 1H, OCH), 7.00—7.40 (m, 10H, Ph).

2-Diphenylmethylene-4-ethyl-1,3-dioxolane (3d): Mp 57—58 °C; IR (KBr) 1660 cm^{-1} (C=C); MS *m/z* 266 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=1.00 (t, 3H, CH$_3$), 1.50—1.90 (m, 2H, MeCH$_2$), 3.90 (t, 1H, one of OCH$_2$), 4.30 (t, 1H, one of OCH$_2$), 4.30—4.60 (m, 1H, OCH), 7.00—7.40 (m, 10H, Ph).

2-Diphenylmethylene-4,4-dimethyl-1,3-dioxolane (3e): Mp 98—100 °C; IR (KBr) 1660 cm^{-1} (C=C); MS *m/z* 266 (M$^+$); ^{1}H NMR (CDCl$_3$) δ=1.15 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$), 4.00 (d, 2H, CH$_2$O), 7.00—7.40 (m, 10H, Ph).

2-Diphenylmethylene-4-chloromethyl-1,3-dioxolane (3f): Bp 142 °C/10^{-3} mmHg (1 mmHg=133.322 Pa); IR (KBr) 1660 cm^{-1} (C=C); MS *m/z* 286.5 (M^+); ^1H NMR ($CDCl_3$) δ=3.60 (d, 2H, $ClCH_2$), 4.30 (t, 2H, CH_2O), 4.60—4.80 (m, 1H, OCH), 7.00—7.60 (m, 10H, Ph).

2-Diphenylmethylene-4-phenoxymethyl-1,3-dioxolane (3g): Bp 140 °C/10^{-3} mmHg (lit,[8] 220—260 °C/0.8 mmHg); IR (neat) 1660 cm^{-1} (C=C); MS *m/z* 344 (M^+); ^1H NMR ($CDCl_3$) δ=4.10 (d, 2H, $PhOCH_2$), 4.30 (dd, 2H, CH_2O), 4.70—5.00 (m, 1H, OCH), 6.70—7.40 (m, 15H, Ph).

2-Diphenylmethylene-4-phenyl-1,3-dioxolane (3h): Bp 132 °C/10^{-3} mmHg (lit,[8] bp 225—230 °C/0.8 mmHg); IR (neat) 1660 cm^{-1} (C=C); MS *m/z* 314 (M^+); ^1H NMR ($CDCl_3$) δ=4.10 (t, 1H, one of CH_2O), 4.60 (t, 1H, one of CH_2O), 5.50 (t, 1H, OCH), 7.00—7.40 (m, 15H, Ph).

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