Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

INVESTIGATIONS ON ORGANOZINC COMPOUNDS
XIV. ORGANOZINC-CATALYZED POLYMERIZATION OF LACTONES. THE INTERACTION BETWEEN ETHYLZINC METHOXIDE AND (ETHYLZINC)DIPHENYLAMINE AND β-PROPIOLACTONE*

J. G. NOLTES, F. VERBEEK AND H. G. J. OVERMARS
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)
J. BOERSMA
Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)

(Received April 14th, 1970)

SUMMARY

Ethylzinc methoxide brings about selective acyl–oxygen cleavage of the ring of β-propiolactone to give ethylzinc 2-(methoxycarbonyl)ethoxide. The latter compound, which is pentameric in benzene, has been characterized, as well as the alkyl–oxygen cleavage product ethylzinc 3-methoxypropionate. The isolation of the 2-(methoxycarbonyl)ethyl ester of 3-hydroxypropionic acid suggests that the EtZnOMe-catalyzed polymerization of β-propiolactone proceeds by successive insertion of monomer units into the Zn–O bond of the complex between the catalyst and the growing polymer through acyl–oxygen cleavage of the lactone ring.

(Ethylzinc)diphenylamine similarly reacts selectively with acyl–oxygen cleavage to give ethylzinc 2-(diphenylcarbamoyl)ethoxide in the 1/1 reaction. This compound readily decomposes with formation of *N*,*N*-diphenylacrylamide.

INTRODUCTION

In the course of our study of organozinc compounds with the general formula RZnX[2] several types of catalysts for the polymerization of lactones have been discovered[3]. In order to shed light on the polymerization mechanism we have studied more closely the interaction of a few simple model compounds RZnX with β-propiolactone. In view of the interest in the ring opening of β-propiolactone by organometallic amines[4,5] and alkoxides[6] we report our results on the 1/1 interaction of β-propiolactone with ethylzinc methoxide (EtZnOMe) and (ethylzinc)diphenylamine ($EtZnNPh_2$). Details of the polymerization reactions will be reported elsewhere.

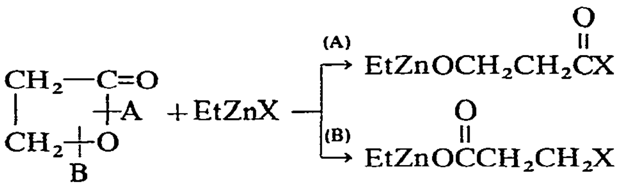
RESULTS AND DISCUSSION

As is evident from the characteristic changes in the IR and NMR spectra, β-propiolactone readily reacts with an equimolecular amount of ethylzinc methoxide

---

* For part XIII see ref. 1.

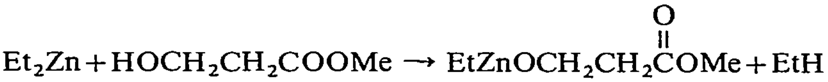
or (ethylzinc)diphenylamine with opening of the lactone ring. Interaction of compounds RZnX with reactive dipolar molecules has been observed to involve the zinc–hetero atom rather than the zinc–carbon bond (X = OR[7], NR$_2$[7], PR$_2$[8]). Similarly, in the present reactions the zinc–hetero atom bond is involved, since the NMR spectrum of the reaction product in each case shows that the ethyl groups have remained bound to zinc [$\delta(CH_3) \approx 1.5$ ppm (triplet); $\delta(CH_2) \approx 0.5$ ppm (quartet)]. Ring opening of β-propiolactone may proceed either by acyl–oxygen bond cleavage (A), which leads to an alkylzinc alkoxide, or by alkyl–oxygen cleavage (B), which gives an alkylzinc carboxylate:



(X = OMe, NPh$_2$)

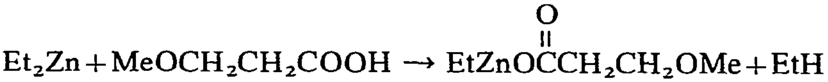
Ishii *et al.* have shown that both Me$_3$SiNR$_2$[4] and Me$_3$GeNR$_2$[5] react with β-propiolactone with alkyl-oxygen cleavage, but that Me$_3$SnNR$_2$[5] brings about acyl–oxygen cleavage. Acyl–oxygen cleavage dominates with Me$_3$SnOMe, but the selectivity decreases with increasing polarity of the solvent[6].

When EtZnOMe was treated with an equimolar amount of β-propiolactone in benzene at 75°, the lactone had completely reacted after 3 h as shown by the absence of the IR absorption at 1848 cm^{-1} which is characteristic of the lactone ring. The NMR spectrum clearly showed that a mixture of products had been formed. To establish the IR and NMR characteristics for the 1/1 reaction products resulting from acyl–oxygen (A) and alkyl–oxygen (B) cleavage of the lactone ring, respectively, compounds (I) (A) and (II) (B) were prepared by acidolysis of diethylzinc with methyl 3-hydroxypropionate and 3-methoxypropionic acid, respectively:



$$Et_2Zn + HOCH_2CH_2COOMe \rightarrow EtZnOCH_2CH_2\overset{\overset{O}{\|}}{C}OMe + EtH$$

(I)



$$Et_2Zn + MeOCH_2CH_2COOH \rightarrow EtZnO\overset{\overset{O}{\|}}{C}CH_2CH_2OMe + EtH$$

(II)

Relevant NMR and IR data are given in Table 1.

The IR spectrum of the EtZnOMe/propiolactone reaction mixture showed a strong, broad ester absorption centered at 1736 cm^{-1} [*cf.* the absorption at 1736 cm^{-1} in (I)], but a carboxylate absorption around 1600 cm^{-1} [*cf.* the band at 1595 cm^{-1} in (II)] was notably absent, indicating that reaction had occurred via acyl–oxygen cleavage. Since it was not possible to isolate a well-defined organozinc compound from the reaction mixture, this mixture was hydrolyzed. The organic fraction which was obtained appeared to consist of mainly two products which were isolated in about equal amounts. The more volatile component was identified as methyl 3-hydroxy-

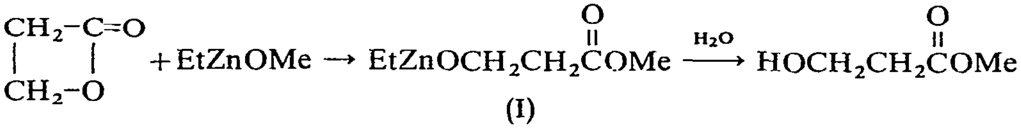
TABLE 1

NMR AND IR DATA FOR THE ACYL–OXYGEN (I) AND ALKYL–OXYGEN (II) CLEAVAGE PRODUCT OF THE ETHYLZINC METHOXIDE/β-PROPIOLACTONE REACTION

Compound	NMR, δ (ppm)[a]					IR, ν(COO) (cm^{-1})[b]
	a	b	c	d	e	
(I) $\overset{a}{CH_3}\overset{b}{CH_2}ZnO\overset{c}{CH_2}\overset{d}{CH_2}\overset{\overset{O}{\|}}{C}O\overset{e}{CH_3}$	1.43	0.45	4.08	2.54	3.37	1736, 1170
(II) $\overset{a}{CH_3}\overset{b}{CH_2}ZnO\overset{\overset{O}{\|}}{C}\overset{c}{CH_2}\overset{d}{CH_2}O\overset{e}{CH_3}$	1.58	0.65	2.58	3.38	3.05	1595, 1420

[a] Downfield from TMS internal standard; benzene solution. [b] Benzene solution.

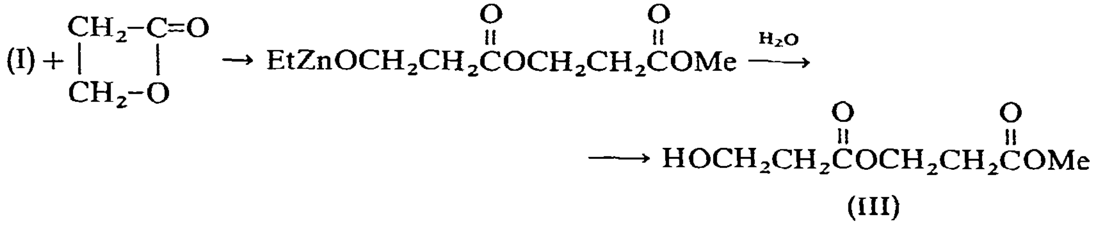
propionate, which shows that ethylzinc methoxide has brought about acyl–oxygen cleavage of the lactone ring:



$$\begin{matrix} CH_2-C{=}O \\ | \qquad | \\ CH_2-O \end{matrix} + EtZnOMe \rightarrow \underset{(I)}{EtZnOCH_2CH_2\overset{\overset{O}{\|}}{C}OMe} \xrightarrow{H_2O} HOCH_2CH_2\overset{\overset{O}{\|}}{C}OMe$$

No formation of 3-methoxypropionic acid could be detected, which demonstrates the selectivity of this reaction.

The second component was shown by NMR spectroscopy and C,H-analysis to be the 2-(methoxycarbonyl)ethyl ester of 3-hydroxypropionic acid (III). The formation of this ester can be rationalized in terms of A-type insertion of a second β-propiolactone molecule in the Zn–O bond of the primary 1/1 insertion product:



$$(I) + \begin{matrix} CH_2-C{=}O \\ | \qquad | \\ CH_2-O \end{matrix} \rightarrow EtZnOCH_2CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{\overset{O}{\|}}{C}OMe \xrightarrow{H_2O}$$

$$\longrightarrow \underset{(III)}{HOCH_2CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{\overset{O}{\|}}{C}OMe}$$

The isolation of the ester (III) would seem to indicate that the EtZnOMe-catalyzed polymerization of β-propiolactone proceeds by successive insertion of monomer units into the Zn–O bond of the catalyst-growing polymer complex through acyl–oxygen cleavage of the lactone ring*.

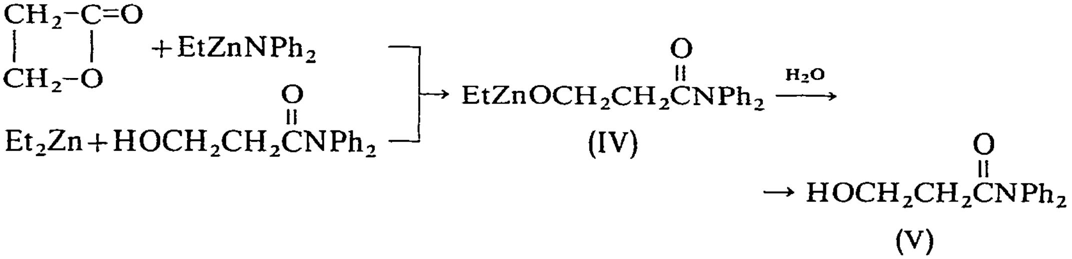
The normal position of the carbonyl absorption in (I) indicates that the ester group is not involved in coordination to the zinc atom. This is also borne out by the nearly identical chemical shift of the methoxycarbonyl protons in (I) (3.37 ppm) and methyl 3-hydroxypropionate (3.46 ppm). Surprisingly, (I) has been found to be

---

* Separate experiments (1/3 molar ratio of EtZnOMe and β-propiolactone) in which the non-volatile hydrolysis products were subjected to gas chromatography after trimethylsilylation afforded evidence for the formation of the 1/3 insertion product.

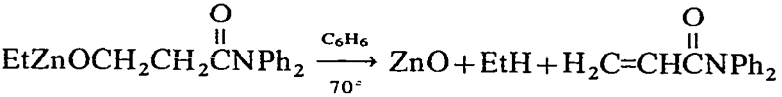
pentameric in benzene. Pentameric RZnX compounds are rare, and so far only two examples, *viz.* RZnS-t-Bu (R = Me and Et) have been reported[9,10].

(Ethylzinc)diphenylamine reacts much faster with β-propiolactone than does ethylzinc methoxide, the 1/1 reaction in benzene solution being complete after 90 min at room temperature (disappearance of the 1848 cm^{-1} lactone absorption from the IR spectrum which displays two new absorptions at 1679 and 1639 cm^{-1}). The NMR spectrum showed in addition to the ethylzinc and diphenylamino proton signals, two broad bands centered at 2.55 and 4.28 ppm. Attempts to isolate a crystalline product from this reaction were unsuccessful, so the reaction product was hydrolyzed. The organic compound isolated was identified as *N*,*N*-diphenyl-3-hydroxypropionamide (V), indicating that, like EtZnOMe, the compound $EtZnNPh_2$ brings about acyl–oxygen cleavage of the lactone ring to form (IV):



$$\left.\begin{array}{l}\begin{array}{l}\mathrm{CH_2{-}C{=}O}\\ |\qquad\ \ |\\ \mathrm{CH_2{-}O}\end{array} + \mathrm{EtZnNPh_2}\\ \mathrm{Et_2Zn + HOCH_2CH_2\overset{O}{\overset{\|}{C}}NPh_2}\end{array}\right] \rightarrow \underset{\text{(IV)}}{\mathrm{EtZnOCH_2CH_2\overset{O}{\overset{\|}{C}}NPh_2}} \xrightarrow{H_2O} \underset{\text{(V)}}{\mathrm{HOCH_2CH_2\overset{O}{\overset{\|}{C}}NPh_2}}$$

Compound (IV), prepared by acidolysis of diethylzinc with (V), showed two carbonyl absorptions at 1675 cm^{-1} and 1639 cm^{-1} in the IR and broadened triplets at 2.56 ppm (CH_2CO) and 4.28 ppm (OCH_2) for the ethylene protons in the NMR spectrum. Both the IR and the NMR spectrum of (IV) are in good agreement with those recorded for the crude $EtZnNPh_2$/β-propiolactone 1/1 reaction product, which indicates the exclusive formation of (IV) in the latter reaction. The presence of two carbonyl absorptions in the IR spectrum of (IV) [(V) shows $\nu(C{=}O)$ at 1656 cm^{-1}] suggests the presence of coordinated and non-coordinated carbonyl groups in (IV). The broadness of the ethylene proton signals in the NMR spectrum of (IV) seems to confirm this (*cf.* the presence of broadened ethylene proton signals in the NMR spectrum of $EtZnOCH_2CH_2NMe_2$[11]). Attempts to obtain an accurate molecular weight for (IV) were unsuccessful (erratic values of $\bar{n}$ between 3 and 4), as were attempts to study its NMR spectrum at elevated temperatures. Interestingly, (IV) was found to decompose readily with the formation of *N*,*N*-diphenylacrylamide when its benzene solution was warmed to 70°:



$$\mathrm{EtZnOCH_2CH_2\overset{O}{\overset{\|}{C}}NPh_2} \xrightarrow[70^\circ]{C_6H_6} \mathrm{ZnO + EtH + H_2C{=}CH\overset{O}{\overset{\|}{C}}NPh_2}$$

Organozinc alkoxides in general possess excellent thermal stability[9], and thus the thermal lability of (IV), which contrasts with that of (I) (unchanged after heating for 2 h at 80° in benzene solution), is unexpected.

EXPERIMENTAL

General

Reactions involving organozinc compounds were carried out in an atmosphere of dry nitrogen. IR spectra were recorded with a Grubb–Parsons Spectromaster spectrometer. NMR spectra were recorded at 100 MHz using a Varian HA-100 spectrometer. Molecular weights were measured by cryometry in benzene solution.

Commercial β-propiolactone was distilled using a spinning band column. Ethylzinc methoxide[12], (ethylzinc)diphenylamine[13], methyl 3-hydroxypropionate[14], and 3-methoxypropionic acid[14] were prepared as previously described.

Reaction of ethylzinc methoxide with β-propiolactone

To a solution of 5.50 g (44 mmoles) of ethylzinc methoxide in 40 ml of benzene 3.16 g (44 mmoles) of β-propiolactone was added dropwise. After 3 h at 75° the IR spectrum of the solution showed no lactone absorption at 1848 cm^{-1}. The NMR spectrum showed the presence of five methoxy proton signals.

The reaction mixture was hydrolyzed by stirring for 30 min with 1.5 ml of water at room temperature. The solid formed was separated by filtration and washed with diethyl ether. The combined filtrates were dried over anhydrous $MgSO_4$. Evaporation of the solvents afforded 2.2 g of a colourless liquid which was subjected to fractional distillation *in vacuo* (bath temperature 40°). In this way 1.1 g of a liquid with b.p. 30–31°/0.6 mm was isolated, and this was shown by its NMR spectrum and n_D^{20} (found: 1.4223; lit.[13]: 1.4225) to be methyl 3-hydroxypropionate. The remaining viscous liquid (1.1 g), which could not be crystallized, analysed for the 2-(methoxycarbonyl)ethyl ester of 3-hydroxypropionic acid. (Found: C, 47.90; H, 6.81. $C_7H_{12}O_5$ calcd.: C, 47.72; H, 6.87%.) The peaks present in the NMR spectrum recorded at 70° (δ and peak area given) at 4.26 (33), 3.76 (32), 3.47 (47), 3.00 (16) and at 2.44 ppm (66) were assigned to CH_2 (d), CH_2 (b), OCH_3 (f), OH (a) and CH_2 (c) + CH_2 (e), respectively, in $H^aOCH^b_2CH^c_2C(O)OCH^d_2CH^e_2C(O)OCH^f_3$ (III).

Ethylzinc 2-(methoxycarbonyl)ethoxide (I)

Upon dropwise addition of 3.40 g (34 mmoles) of methyl 3-hydroxypropionate to a solution of 4.18 g (34 mmoles) of diethylzinc in 25 ml of benzene (room temperature), 770 ml of ethane (theory: 760 ml) were evolved. After evaporation of the solvent *in vacuo*, a colourless oily liquid was obtained which could not be crystallized. (Found: Zn, 33.12; mol.wt., 976, 982 and 983 at 2.2, 4.1 and 6.0 wt.%. $C_{30}H_{60}O_{15}Zn_5$ calcd.: Zn, 33.09%; mol.wt., 987.) For IR and NMR data see Table 1.

Ethylzinc 3-methoxypropionate (II)

The theoretical amount of ethane was evolved upon dropwise addition of 2.00 g (20 mmoles) of 3-methoxypropionic acid to a solution of 2.46 g (20 mmoles) of diethylzinc in 20 ml of benzene (room temperature). After evaporation of the solvent the product was taken up in pentane. After standing for several weeks at −12°, 1.0 g of a white crystalline solid with m.p. 75–76° had separated. (Found: Zn, 33.07. $C_6H_{12}O_3Zn$ calcd.: 33.09%.) For IR and NMR data see Table 1.

Reaction of (ethylzinc)diphenylamine with β-propiolactone

To a solution of 1.20 g (46 mmoles) of (ethylzinc)diphenylamine in 10 ml of benzene, 0.33 g (46 mmoles) of β-propiolactone in 5 ml of benzene was added dropwise. After 90 min stirring at room temperature the lactone absorption at 1848 cm^{-1} had disappeared from the IR spectrum.

The reaction mixture was hydrolyzed at room temperature. Work-up in the usual way afforded a colourless solid with m.p. 110–111.5° (from carbon tetrachloride) identified as *N,N*-diphenyl-3-hydroxypropionamide (n.c.). (Found: C, 74.79; H, 6.39. $C_{15}H_{15}NO_2$ calcd.: C, 74.66; H, 6.26%.) NMR (benzene solution, 20°): $\delta(CH_2CO)$ 2.48, $\delta(CH_2O)$ 3.83, $\delta(OH)$ 3.02 ppm. IR (benzene solution): $\nu(CO)$ 1656 cm^{-1}.

Ethylzinc 2-(diphenylcarbamoyl)ethoxide (IV)

The theoretical amount of ethane was evolved upon adding a solution of 1.20 g (5 mmoles) of *N,N*-diphenyl-3-hydroxypropionamide in 10 ml of benzene to 0.61 g (5 mmoles) of diethylzinc in 5 ml of benzene (30 min at 20°; 15 min at 40°). After evaporation of the solvent, the oily residue was stirred with 15 ml of hexane, which caused the gradual crystallization of 1.35 g (81%) of colourless crystals with m.p. 87–89° (with evolution of gas). (Found: Zn, 19.53. $C_{17}H_{19}NO_2Zn$ calcd.: Zn, 19.54%.) NMR (benzene solution, 20°): $\delta(CH_2CO)$ 2.56 (broad triplet), $\delta(CH_2O)$ 4.28 ppm (broad triplet). IR (benzene solution): $\nu(C{=}O)$ at 1675 and 1639 cm^{-1}.

The NMR spectrum of a 10 wt.% solution of (IV) in benzene solution after heating at 70° for 2 h failed to show the triplets at 4.28 and 2.56 ppm, but showed new signals in the olefinic region characteristic of *N,N*-diphenylacrylamide[15] (10% solution of $H^aH^bC{=}CH^cCONPh_2$ in CCl_4: δH_a 5.45, δH_b 6.03, δH_c 6.11 ppm; J_{ab} 2.08, J_{ac} 10.22 and J_{bc} 16.60 Hz).

ACKNOWLEDGEMENTS

This work was sponsored by the International Lead Zinc Research Organization, Inc., New York (Director: Dr. S. F. Radtke).

REFERENCES

1 J. Boersma and J. G. Noltes, *J. Organometal. Chem.*, 21 (1970) P32.
2 J. Boersma and J. G. Noltes, *J. Organometal. Chem.*, 17 (1969) 1 and references cited therein.
3 H. G. J. Overmars and J. G. Noltes, unpublished results.
4 K. Itoh, S. Sakai and Y. Ishii, *J. Org. Chem.*, 31 (1966) 3948.
5 K. Itoh, S. Sakai and Y. Ishii, *Tetrahedron Lett.*, (1966) 4941.
6 K. Itoh, S. Kobayashi, S. Sakai and Y. Ishii, *J. Organometal. Chem.*, 10 (1967) 451.
7 J. G. Noltes, *Recl. Trav. Chim. Pays-Bas*, 84 (1965) 126.
8 J. G. Noltes, *Recl. Trav. Chim. Pays-Bas*, 84 (1965) 782.
9 G. E. Coates and D. Ridley, *J. Chem. Soc.*, (1965) 1870.
10 G. E. Coates, in W. O. Milligan (Ed.), *Proceedings Robert A. Welch Foundation Conferences on Chemical Research, XI, Organometallic Chemistry*, Houston, 1965, p. 49.
11 G. E. Coates and D. Ridley, *J. Chem. Soc. A*, (1966) 1064.
12 M. Ishimori, T. Tomoshige and T. Tsuruta, *Kogyo Kagaku Zasshi*, 70 (1967) 548; *Chem. Abstr.*, 68 (1968) 3916.
13 J. G. Noltes and J. Boersma, *J. Organometal. Chem.*, 16 (1969) 345.
14 T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory and W. L. Beears, *J. Amer. Chem. Soc.*, 70 (1948) 1004.
15 W. Reppe, *Justus Liebigs Ann. Chem.*, 582 (1953) 1.