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

α-HALOBENZYLZINC HALIDES

L. Y. GOH AND S. H. GOH
Department of Chemistry, University of Malaya, Kuala Lumpur (Malaysia)

(Received January 13th, 1970)

SUMMARY

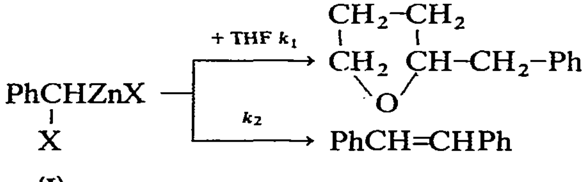
α-Halobenzylzinc halides ($C_6H_5CHXZnX$) in tetrahydrofuran decompose via two routes, *viz.*: insertion into tetrahydrofuran and formation of stilbenes. The stability of $C_6H_5CHXZnX$, studied by iodometric titration, was shown to decrease in the order: $X = I > Br > Cl$.

INTRODUCTION

Except for iodomethylzinc iodide[1] α-haloorganozinc intermediates have received little attention although they are of considerable importance in the synthesis of cyclopropanes[2]. Because of the similarity between their reactions and those of carbenes, intermediates of this type have been referred to as carbenoids[3]. Zinc carbenoids are intermediate in stability between the stable α-haloorganomercurials[4] and the α-haloorganolithium compounds, which have been characterised only at low temperatures[5].

RESULTS AND DISCUSSION

The formation of α-chlorobenzylzinc chloride has been detected during the reaction of phenyldiazomethane with zinc chloride in ether by use of a stopped-flow and continuous-flow apparatus[2c]. We discuss below the comparative stabilities of the organozinc chlorides, bromides, and iodides. When phenyldiazomethane was treated with an excess of zinc halide in tetrahydrofuran (THF), α-halobenzylzinc halide was formed, and slowly decomposed, via two major routes, *viz.* insertion into tetrahydrofuran (k_1) and formation of stilbenes (k_2).



(1)

(2)

(I)

Intermolecular insertions by carbenoid species are not common[6], but in this instance the insertion probably occurs via a transition state involving THF which is strongly complexed to the zinc ion, so that in this sense the insertion may be considered intramolecular. If this is the case the insertion into THF will depend on the ability of THF to complex to the metal ion, on the nature of the ion as well as that of the leaving group X. The results shown in Table 1 are in agreement with this. The decreasing yield of insertion product by changing X from chloride to bromide or iodide indicates that THF is complexed more strongly in the organozinc chloride. Steric factors may also be involved.

TABLE 1

INSERTION INTO TETRAHYDROFURAN

MX_2	Percentage yield[a]
$ZnCl_2$	33
$ZnBr_2$	27
ZnI_2	18
$CoCl_2$	13
Others[b]	0–2

[a] Based on $PhCHN_2$ used. [b] Include LiCl, LiBr, $LiClO_4$, $FeCl_3$, $AlCl_3$, $AlBr_3$

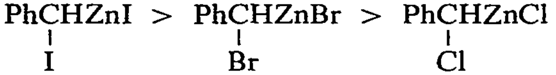
The stabilities of compounds of type (I) were studied by iodometric titration, and a summary of the results is given in Table 2. Under given reaction conditions it was found that the stability decreases in the following order:

TABLE 2

THE DECOMPOSITION OF PhCHXZnX IN TETRAHYDROFURAN

ZnX_2	Molar ratio $ZnX_2/PhCHN_2$	Temperature (°C)	$[PhCHN_2]$	Initial molar concentration of PhCHXZnX[a]	Half-life (h)
$ZnCl_2$	12.2/1	$-8\pm1°$	0.0195	0.0070	2.1
$ZnBr_2$	10.6/1	$-8\pm1°$	0.0195	0.0087	7
	13.8/1	$0\pm0.05°$	0.0195	0.011	1.9
ZnI_2	10.5/1	$0\pm0.05°$	0.0195	0.0135	26

[a] Estimated by iodometric titration as soon as the reaction of $PhCHN_2$ was complete.



$$\underset{\mathrm{I}}{\mathrm{PhCH}}\mathrm{ZnI} > \underset{\mathrm{Br}}{\mathrm{PhCH}}\mathrm{ZnBr} > \underset{\mathrm{Cl}}{\mathrm{PhCH}}\mathrm{ZnCl}$$

This order of stability is in contrast with that observed by Wittig[1b] that ICH_2ZnI is less stable than $ClCH_2ZnCl$. However it is not difficult to explain the present results since the reactivity of species (I) is dependent on two pathways, (1) and (2). The relative yields of insertion product agrees with the observed order of stability. Furthermore it is reasonable that the bimolecular pathway, (2), will be subject to steric effects and accounts for the greater stability of PhCHIZnI. On the other hand, if all the reactions were due to the unimolecular decomposition of (I) to a free carbene ($Ph\ddot{C}H$), then the stability of (I) may be expected to be the reverse of the observed order as iodide is a better leaving group[7]. Previous evidence[2c] as well as the present results rule out the possibility that a free carbene is involved in these reactions.

EXPERIMENTAL

General

Anhydrous metal halides were dried by sublimation or heating at 0.05 mm pressure.

Analyses were carried out on a Varian Aerograph 200 gas chromatograph. The NMR spectrum was recorded on a Varian A-60 instrument.

Reaction of phenyldiazomethane with tetrahydrofuran in the presence of zinc chloride

Phenyldiazomethane (0.0038 mole) in tetrahydrofuran (ca. 10 ml) was added dropwise under nitrogen to a solution of zinc chloride (1.6 g, 0.0117 mole) in tetrahydrofuran (10 ml). After the addition the reaction mixture was stirred for a further 20 min and then subjected to rotary evaporation to ca. 5 ml. Water (30 ml) was added and the solution extracted with petroleum ether, b.p. 40–60°, (5 × 10 ml). The combined extracts after drying over sodium hydroxide pellets were rotary evaporated to about 5 ml and then made up to 10 ml in a volumetric flask with petroleum ether, b.p. 60–80°. Gas–liquid chromatography showed the yield to be 33%. Short-path distillation (bath temperature 120–140°/2 mm) of the crude product gave 0.2 g of 2-benzyltetrahydrofuran. (Found; C, 81.3; H, 8.8; $C_{11}H_{14}O$ calcd.: C, 81.4; H, 8.7%.) NMR (CCl_4): τ 2.9 (5H) singlet, τ 6.0–6.5 (3H) multiplet, τ 7.1 (1H) doublet (13.5 Hz) of a doublet (6 Hz), τ 7.4 (1H) doublet (13.5 Hz) of a doublet (6.5 Hz), τ 8.0–8.5 (4H) multiplet.

Similar reactions were carried out using other metal halides. When the reaction was slow (Li salts, $FeCl_3$), the addition of phenyldiazomethane was carried out at the refluxing temperature of tetrahydrofuran. The results are given in Table 1.

Kinetics of decomposition of PhCHXZnX in tetrahydrofuran

In a typical procedure, freshly-sublimed zinc bromide (6.05 g, 0.0269 mole) was dissolved in anhydrous tetrahydrofuran (90 ml) under nitrogen and the solution was thermostatted at 0±0.05°. Phenyldiazomethane (0.00195 mole) in tetrahydrofuran (10 ml) was injected, and the red colour of phenyldiazomethane faded completely within a few minutes. A 10 ml aliquot of the reaction mixture was quickly withdrawn by a syringe and quenched in a known volume of iodine solution in toluene (15 ml, 0.011 *M*) and the excess of iodine was titrated with aqueous sodium thiosulphate (0.010 *M*). Further aliquots were taken at timed intervals up to two half-lives. Approximately first-order plots were obtained.

A summary of the rate data is given in Table 2.

ACKNOWLEDGEMENT

We thank Dr. D. G. Williamson of University of Aberdeen for the NMR spectrum and Mr. Chiam Yeow Boon for technical assistance.

REFERENCES

1 (a) E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.*, 86 (1964) 1337; (b) G. Wittig and F. Wingler, *Justus Liebigs Ann. Chem.*, 656 (1962) 18; (c) G. Wittig and K. Schwarzenbach, *Justus Liebigs Ann. Chem.*, 650 (1962) 1.

2 (a) H. E. SIMMONS, E. P. BLANCHARD AND R. D. SMITH, *J. Amer. Chem. Soc.*, 86 (1964) 1347; (b) G. WITTIG AND F. WINGLER, *Chem. Ber.*, 97 (1964) 2146: (c) S. H. GOH, L. E. CLOSS AND G. L. CLOSS, *J. Org. Chem.*, 34 (1969) 25.

3 (a) G. L. CLOSS AND R. A. MOSS, *J. Amer. Chem. Soc.*, 86 (1964) 4042; (b) G. KOBRICH, *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 41.

4 (a) D. SEYFERTH AND J. M. BURLITCH, *J. Amer. Chem. Soc.*, 85 (1963) 2667. (b) D. SEYFERTH AND H. DERTOUZOS, *J. Organometal. Chem.*, 11 (1968) 263.

5 D. F. HOEG, D. I. LUSK AND A. L. CRUMBLISS, *J. Amer. Chem. Soc.*, 87 (1965) 4147.

6 W. KIRMSE, *Carbene Chemistry*, Academic Press, New York, 1964.

7 J. HINE, *Divalent Carbon*, The Ronald Press, New York, 1964.