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3,641,081

PROCESS FOR PREPARING DIALKYLZINC
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12 Claims

ABSTRACT OF THE DISCLOSURE

A direct process for preparing dialkylzinc compounds, wherein zinc alloyed with sodium, potassium or lithium is reacted with alkylbromide in the absence of moisture to produce a dialkylzinc compound.

This invention relates to a direct process for preparing dialkylzinc compounds.

Diorganic compounds are generally prepared by two methods. The first method reacts a zinc halide with a reactive organometallic, such as lithium or magnesium, in an ether solvent. The second method involves a direct synthesis starting from metallic zinc or zinc alloys with alkyl iodides. Mixtures of alkyl bromides and iodides have also previously been used in combination with zinc-copper alloy.

The first method is disadvantageous in that it requires two separate steps to be performed. In the first step the lithium or magnesium reagent must be formed, and in the second step the actual formation of the organozinc compound takes place. An additional disadvantage is the presence in the reaction of flammable solvents. The separation of the solvents from the product is not always easily achieved, especially with the utilization of lower alkyls.

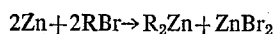
The second method is more attractive in that only one step is required and the use of solvents is not necessary, although recent attempts to find improved conditions have utilized solvents with high dielectric constants, such as dimethylformamide. The use of solvents, however, makes it impossible to separate solvent from the product.

It has been suggested that the reaction of ethyl iodide and the fusion product of zinc with a large proportion of sodium will result in a diethylzinc compound. The iodide material, however, is expensive, and the presence of free sodium in the zinc alloy is hazardous and difficult to work with.

Since metallic zinc alone does not react with alkyl iodide or bromide to produce more than minimal amounts of the dialkylzinc even under ideal conditions, attempts have been made to use a zinc-copper alloy or fusion product. Unless extreme precautions are taken, however, the reaction may not start for several hours. If after the start of the reaction the reaction mixture is cooled too low, the reaction may stop entirely and is difficult to begin again. More importantly, it is recognized that the yields are then much lower. An additional disadvantage is the necessity of using expensive copper and alkyl iodides as starting materials.

It is therefore an object of this invention to provide a method for preparing dialkylzinc compounds by direct synthesis, and more particularly to provide such a process utilizing less expensive starting materials.

According to the invention it has been found that zinc alloyed with sodium, potassium, or lithium will react with alkylbromide to synthesize dialkylzinc compounds. The reaction is believed to follow the general formula:



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The reactions are performed by refluxing a mixture of the finely divided zinc alloy and the alkylbromide. The reaction should be carried out in the absence of moisture and therefore an inert atmosphere is preferred, such as nitrogen, argon, or carbon dioxide. The reactions may be carried out at atmospheric pressure, unless the starting materials are too volatile, in which case pressure should be applied as with MeBr and EtBr.

It is preferred to use an excess of the zinc alloy since this increases the speed and the yield of the reaction. A molar ratio of zinc to alkylbromide of between 2:1 and 1:1 has been found satisfactory. It is unnecessary to perform the reaction in the presence of a solvent, since it is usually very difficult, if not impossible, to separate the product from the solvent.

The reaction usually begins a few minutes after the starting materials have made contact with each other, especially if substantially all traces of moisture have been removed from the atmosphere and the apparatus. Heating of the reaction mixture may be necessary to begin the reaction, but if the reaction is exothermal refluxing temperature is maintained without the application of external heat. In the event that the reaction is not exothermal, external heating may be applied to maintain the reflux temperature. It has been found that a temperature in the range of 40–180° C. is satisfactory. A temperature range of 100°–140° C. is preferred.

The reaction is considered complete when refluxing stops. The flask is connected with a distilling head and the contents of the flask are distilled under reduced pressure. Distillation of the product mixture vaporizes the dialkylzinc compound which is captured as a distillation product.

The zinc alloys which have proved themselves reliable for purposes of the invention are the lithium, potassium and sodium alloys. The alloys may be formed by fusing the metals together in a steel crucible under an inert atmosphere, for example, argon. The cooled melt is machined to fine particle size. Usually turnings may be used, but if the alloy is very brittle a sandlike material is obtained upon machining. The shot method may also be utilized to prepare the alloys on an industrial scale.

The maximum amount of sodium which can be alloyed with zinc is one atom of sodium per twelve atoms of zinc. This corresponds with an alloy containing three wt. per cent sodium, the balance being zinc.

Table I contains data showing the yield of dialkylzinc in relation to the percentage of sodium in the alloy.

TABLE I

Wt. percent Na in alloy	Alkyl-bromide	Yield R ₂ Zn, percent	Details
3	n-PrBr	67	100 min. reflux.
3	i-PrBr	39	Reaction complete after 10 min. reflux.
55	3	72	Exothermal reaction complete in 10 min.
1	n-BuBr	58	60 min. reflux. No gas formation.
3	n-C ₈ H ₁₇ -Br	80	Exothermal reaction 10 min. complete.
3	iso-C ₈ H ₁₇ Br	46	Kept at 120° for 15 min.
3.0	BuBr	72	
2.0	BuBr	67	
1.0	BuBr	58	
0.5	BuBr	50	

It is apparent that the yield of dialkylzinc decreases as the sodium content of the alloy decreases. The 2% sodium/zinc alloy gives, however, no significantly lower yields than the 3% sodium/zinc alloy. The zinc alloy containing as little as 1% sodium also gives good results with the alkylbromide. Upon further lowering of the sodium content in the zinc alloy, the yields of dialkylzinc gradually decrease to those obtained using pure zinc. In view of the higher yields obtainable with the 2% and 3% sodium zinc alloy,

it is preferred that the percentage of sodium lie between 2 and 3 wt. percent.

Zinc alloyed with potassium is obtained by fusing zinc and potassium under an inert atmosphere, such as nitrogen, and machining in the usual way. The alloy is very reactive and should be kept in an inert atmosphere.

The maximum amount of potassium in the zinc/potassium alloy is approximately 5 wt. percent, which corresponds to a molar ratio of 12 moles zinc to 1 mole potassium. The reaction with the alkylbromide is carried out in the same manner as with the zinc/sodium alloy. Once begun, the reaction continues spontaneously upon addition of the bromide.

A comparison of the yield in dialkylzinc as a function of the percent of potassium in the zinc alloy is shown in Table II.

TABLE II

Wt. percent K in alloy	Alkyl-bromide	Yield percent	Details
5.0-----	BuBr	58	Starts spontaneously. Finally kept at 140° for 60 min.
5.0-----	BuBr	58	
2.0-----	BuBr	55	
0.5-----	BuBr	47	

It is evident that the potassium content of the alloy may be reduced without loss of activity. The zinc/potassium alloys are easily handled and machined to small particle size. As appears from the results in Table II, the 2% potassium/zinc alloy is well suited for the direct synthesis of zinc dialkyls, although the yields in general are somewhat lower than for the zinc/sodium alloys. The recommended range would be 0.5–5.0 wt. percent potassium with 1.5 to 2.0 wt. percent potassium preferred.

Reactions with the zinc/potassium alloys started without any appreciable induction period and were easily controlled.

In formulating the zinc/lithium alloys it was found important to control closely the homogeneity of the alloy. A well-defined alloy containing 2.0 wt. percent lithium was reacted with butylbromide to produce a yield of 52% dibutylzinc compound. Experiments conducted with a 20% lithium/zinc alloy produced side reactions and the yield of dialkylzinc isolated was invariably lower. For example, with a 20% lithium/zinc alloy the reaction with butylbromide yielded 23% dibutylzinc.

It was found that a useful lithium range is 1 to 10 wt. percent lithium in the zinc alloy, with a preferred content of approximately 2 wt. percent lithium.

Ternary alloys may be used to provide good yields of dialkylzinc compounds. The amalgamation of the zinc/sodium alloy by treating the 3% sodium/zinc alloy with HgCl_2 in tetrahydrofuran provides approximately the same yield as using the zinc/sodium alloy without the HgCl_2 . An alloy composed of 2.6% sodium, 1.1% mercury and the rest zinc was reacted with butylbromide and yielded 52% dibutylzinc.

An alloy composed of 2.3% sodium, 0.8% lithium, and the rest zinc was reacted with butylbromide and yielded 60% dibutylzinc.

The synthesis according to the invention may be carried out with both normal and branched chain alkylbromides. Since longer chain dialkylzincs, for example, where R is greater than C_8 , have limited thermal stability, a direct synthesis involving thermal cracking of primarily formed RZnBr to give $\text{R}_2\text{Zn} + \text{ZnBr}_2$ is not practical. At the other end of the scale, the boiling point of methylbromide is low and requires reaction under higher pressure conditions than atmospheric pressure.

The alkyl group may be unsaturated, but the double bond should be more than two carbon atoms removed from the zinc atom. Both $\text{Zn}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ and $\text{Zn}(\text{CH}_2\text{CH}=\text{CHCH}_3)_2$ are thermally unstable. Compounds with a $\text{C}\equiv\text{C}$ group can be prepared if the $\text{C}\equiv\text{C}$ group is internal. Compounds with a terminal $\text{C}\equiv\text{CH}$

group decompose due to the acidity of the terminal hydrogen.

The following examples illustrate the process of the invention and are not intended to limit in any way the scope of the invention.

EXAMPLE 1

n-Bu₂Zn from Zn/Na alloy (3% Na) and n-BuBr

In 500 ml. flask was placed 30.1 g. finely divided Zn-3.0 Na alloy (0.44 g. at.), 30.2 g. n-butylbromide (0.22 mole) and a crystal of iodine. Upon gradually warming the mixture a slightly exothermal reaction took place. The oil bath was heated to 160° in 30 min. No reflux occurred indicating termination of the reaction. n-Bu₂Zn was isolated by distillation under reduced pressure. B.P. 88°/12 mm. Yield 14.4 g. of colorless liquid (72% of theory).

EXAMPLE 2

(n-C₅H₁₁)₂Zn from Zn/Na alloy (3% Na) and n-C₅H₁₁Br

In 500 ml. flask: 20.4 g. Zn-3.0 Na (0.30 g. at.), 22.7 g. n-pentylbromide (0.16 mole) and a crystal of I₂. The mixture was gradually warmed to 100° when an exothermal reaction occurred which was completed in about 10 minutes. The product isolated by distillation under reduced pressure (B.P. 99–100°/11 mm.) consisted of nearly pure di-n-pentylzinc (gas chromatographic analysis of the products obtained after hydrolysis of a small sample in ether showed the presence of n-pentane and only traces of n-pentylbromide).

EXAMPLE 3

(Iso-C₅H₁₁)₂Zn from Zn/Na alloy (3% Na) and iso-C₅H₁₁Br

In 500 ml. flask: 15.5 g. Zn-3.0 Na (0.23 g. at.), 17.2 g. (0.11 mole) of iso-amylobromide and a crystal of I₂. The temperature of the mixture was raised by gradually heating the oil bath to 120°. An exothermal reaction started which was completely in circa 15 min. The product (5.95 g.) isolated upon heating (oil bath temp. 120°) the reaction product in vacuo (2 mm. Hg) contained some 2,7-dimethyloctane (the Wurtz coupling product of iso-amylobromide) as appeared from a gas chromatographic analysis of the hydrolysis products). The yield of di-iso-amylyl zinc after refractionation, B.P. 64–68°/2 mm.) was 5.48 g. (46% of theory).

EXAMPLE 4

n-Bu₂Zn from Zn/K alloy (5% K) and n-BuBr

Upon dropwise addition of n-BuBr to 40.6 g. Zn-5.0 K (0.30 g. at. Zn) an exothermal reaction started. The dropwise addition was continued until 32 ml. BuBr (0.30 mole) had been added. At the same time the temperature of the oil bath was gradually raised to 150° and kept at that temperature for 60 min. Volatile products were then removed in vacuo. In this way 13.2 g. of n-Bu₂Zn were obtained.

EXAMPLE 5

n-Bu₂Zn from ZnK alloy (2% K) and n-BuBr

A mixture of 29.0 g. of finely divided Zn-2.0 K alloy (0.44 g. at. Zn) and 5.0 ml. of n-BuBr was gradually warmed up (to oil bath temp. of ~140°). When reaction had started 18 ml. of n-BuBr (0.22 mole n-BuBr in total) was added dropwise. After a further 30 min. heating period 10.8 g. n-Bu₂Zn (55% of theory) was isolated by distillation in vacuo.

EXAMPLE 6

n-Bu₂Zn from Zn/Li alloy (2.0% Li) and n-BuBr

The reaction of 45.4 g. Zn-2.0 Li (0.68 g. at. Zn) and 36 ml. of n-BuBr (0.34 mole) carried out as in Example 5 afforded 15.8 g. of n-Bu₂Zn (52% of theory).

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EXAMPLE 7

Di-n-buten-3-ylzinc from Zn/Na alloy (2% Na) and 4-bromobutene-1

A mixture of 29.8 g. Zn-2.0 Na (0.44 g. at. Zn), 29.7 g. (0.22 mole) of 4-bromobutene-1 and a few crystals of I_2 were gradually warmed up till an exothermal reaction occurred. When the reaction had subsided heating (oil bath ~ 140) was continued for 30 min. Upon distillation in vacuo 10.5 g. of $(CH=CHCH_2CH_2)_2Zn$ were isolated. Yield 54%.

I claim:

1. A process for preparing dialkylzinc compounds comprising:

(a) reacting in a moisture-free atmosphere:

(i) an alloy of zinc having at least one metal selected from the group consisting of sodium, potassium, and lithium, the amount of metal in the alloy being about 1 to about 3 weight percent sodium, about 0.5 to about 5.0 weight percent potassium and about 1 to about 10 weight percent lithium, with the remaining percentage being zinc, with

(ii) a reagent consisting essentially of alkylbromide in a molar ratio of at least 1 to 1, zinc to alkylbromide, wherein the alkyl radical is selected from the group consisting of saturated and unsaturated alkyl radicals containing from 1 to 8 carbon atoms; and

(b) refluxing the mixture of said alloy and alkylbromide reagent at a temperature of between $40^\circ C.$ and about $180^\circ C.$ until the refluxing ceases.

2. A process as described in claim 1, wherein the refluxed mixture is distilled under reduced pressure in the absence of moisture to separate the volatile dialkylzinc compound from the involatile residue.

3. A process as described in claim 1, wherein the zinc alloy is in particulate form.

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4. A process as described in claim 1, wherein the zinc alloy contains approximately 2-3 wt. percent sodium.

5. A process as described in claim 1, wherein the zinc alloy contains approximately 1-2 wt. percent potassium.

6. A process as described in claim 1, wherein the zinc alloy contains approximately 2 wt. percent lithium.

7. A process as described in claim 1, wherein the zinc alloy contains both sodium and lithium in addition to zinc.

8. A process as described in claim 1, wherein the alkylbromide is selected from the group consisting of methylbromide and ethylbromide, and the alkylbromide is refluxed under a pressure above that of atmospheric pressure.

9. A process as described in claim 1, wherein the refluxing temperature is approximately $100^\circ C.$ to $140^\circ C.$

10. A process as described in claim 1, wherein the molar ratio of the zinc alloy to the alkylbromide in the mixture is from 2:1 to 1:1.

11. A process as described in claim 1, wherein dialkylzinc is added to the reaction mixture to remove traces of moisture.

12. A process as described in claim 1, wherein the zinc alloy contains approximately 1.1 wt. percent mercury.

References Cited

- Reith et al., *Annalen*, vol. 123, pp. 245-48 (1862).
 Alexeyeff et al., *Compt. rendu.*, vol. 58, pp. 171-73 (1864).
 Nesmeyanov et al., *Methods of Elemento-Organic Chemistry*, North-Holland Publ. Co., Amsterdam, vol. 3, pp. 8 to 14, 24 and 25 (1967).

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,641,081 Dated February 8, 1972

Inventor(s) Schrade F. Radtke

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 48, before "material" insert --starting--;

Column 5, line 10, "(CH=CHCH₂CH₂)₂Zn" should be --
(CH₂=CHCH₂CH₂)₂Zn--.

Signed and sealed this 1st day of August 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
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Commissioner of Patents