[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PREPARATION OF ZINC ALKYLS AND THEIR USE IN THE SYNTHESIS OF HYDROCARBONS

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RECEIVED OCTOBER 23, 1928 PUBLISHED FEBRUARY 5, 1929

In attempting to prepare in considerable quantity the lower hydrocarbons of the type R_4C, several possible methods were investigated. Since the most promising method seemed to be by way of the Grignard reagent, this was tried first, but a number of difficulties were encountered. When a primary alkylmagnesium halide is allowed to react with a tertiary alkyl halide, the reaction is slow and incomplete, the yield is low due to the removal of halogen acid, and higher boiling products are formed from which it is difficult to separate the desired product. Furthermore, if the hydrocarbon has a high vapor pressure, it is difficult to separate it from the ether, which is always present even though a portion is distilled before carrying out the reaction with the alkyl halide. The same difficulties arise if a tertiary alkylmagnesium halide is treated with a compound such as diethyl sulfate, and in addition the yield of Grignard reagent is low (40–45% using the tertiary chlorides, 12–15% using tertiary bromides). Attempts to prepare these hydrocarbons by the Wurtz reaction from a mixture of tertiary and primary halides were entirely unsuccessful. These facts led to an investigation of the method by which these compounds were first prepared, namely, through the use of zinc alkyls. During the course of this work, several improvements in the preparation and manipulation of zinc alkyls have been made.

Preparation of Zinc Alkyls

There are four chief objections to the use of zinc alkyls for synthetic purposes. 1. They are spontaneously inflammable. 2. The preparation of the zinc–copper couple by reduction of a mixture of zinc dust and copper oxide cannot be performed on a large scale. 3. The process is expensive because of the necessity of using alkyl iodides rather than the bromides. 4. With the exception of zinc methyl and zinc ethyl, the yields are low. A fifth consideration that has done much to prevent their use is that for most purposes they can be replaced by the alkylmagnesium halides.

The objection to the use of zinc alkyls on the grounds of spontaneous inflammability was overcome by Blaise,[1] who worked with solutions of alkyl zinc iodides in toluene and in petroleum fractions. Here, however, it was necessary to use ethyl acetate to bring about the reaction, thus introducing a low boiling liquid, which is often objectionable. Furthermore, the exact quantities of alkyl zinc halide could be determined only by anal-

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[1] Blaise, *Bull. soc. chim.*, [4] 9, I (1911).

ysis. In the present investigation it was found that by dissolving the pure zinc alkyls in an equal weight of a solvent of the desired boiling point, for example, toluene, xylene or tetralin, the solutions could be readily handled in the open air and poured from one flask to another without danger of ignition. Moreover, in using the zinc alkyls, the presence of a solvent invariably gave better yields than when the reactions were carried out in the absence of a solvent.

Various methods of preparing the zinc for the reaction have been used. The best yields of zinc alkyls have been obtained with the zinc–copper couple of Gladstone and Tribe[2] as prepared by Lachman.[3] This method consists of mixing zinc dust with about 10% of its weight of powdered copper oxide and heating in a current of hydrogen to incipient fusion. It is rather difficult to heat to just the right temperature and almost impossible to carry the method out on a large scale. The product must be protected from the air to prevent oxidation. The present work shows, however, that equally good results can be obtained by using fine turnings of an alloy of zinc with from 5 to 8% of copper. This can be readily prepared in the laboratory from zinc and brass turnings in runs of a kilo or more and as much as five kilos made in four hours. Moreover, it will keep indefinitely in a dry, stoppered bottle.

It has been reported in the literature that alkyl bromides do not react to give either zinc alkyls according to the method of Lachman[3a] or alkyl zinc halides, according to the method of Blaise.[1] Job and Reich[4] state that ethyl bromide reacts with the zinc–copper couple in the presence of a catalyst prepared by causing aluminum to react with ethylene bromide. When using this catalyst, however, the reaction requires from six to eight hours for completion. Inasmuch as the reaction of alkyl iodides is very vigorous after it has started and requires continual watching and intermittent cooling, attempts were made to replace a portion of the iodide by the bromide. If an equimolecular mixture of alkyl iodide and bromide is used, the reaction starts easily, proceeds smoothly and if the product is distilled *in vacuo* the yields are equal to those obtained with iodide alone. A smaller proportion of iodide is necessary in preparing the higher zinc alkyls, such as zinc dibutyl, where one may use a mixture of one mole of butyl iodide to three moles of butyl bromide. It is entirely possible, even in the case of zinc ethyl, to start the reaction with the iodide and keep it going by the addition of the bromide, but this requires careful regulation and is not always successful.

The yields of zinc alkyls are greatly increased if the distillation from the crude reaction mixture is carried out under a vacuum. This was early

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[2] Gladstone and Tribe, *J. Chem. Soc.*, **26**, 445, 678, 961 (1873).

[3] (a) Lachman, *Am. Chem. J.*, 19, 410 (1897); (b) **24**, 31 (1900).

[4] Job and Reich, *Bull. soc. chim.*, **33**, 1424 (1923).

recognized by Gladstone and Tribe,[2] but for some reason, probably because zinc ethyl and zinc methyl are obtained in excellent yields from the iodide by ordinary distillation, they are the only ones who report such a procedure. The advantage of vacuum distillation is markedly brought out when bromides are used. When zinc ethyl is prepared using a mixture of ethyl iodide and ethyl bromide, ordinary distillation gives a yield of 68%, which is increased to 89% on vacuum distillation. It is even more noticeable in the case of the higher zinc alkyls. Thus ordinary distillation using mixed alkyl halides gives only 39% of zinc dipropyl, whereas on vacuum distillation the yield is 86%.

It is interesting to point out a possible course of the reaction using the mixed halides. In one experiment using a mixture of *iso*-amyl iodide and *iso*-amyl bromide, the reaction did not go to completion and since the run was of considerable size, the unused alkyl halides were recovered during the distillation. It was expected that since the iodide reacts most readily with the zinc, the unused halide would be the bromide. Actually the recovered halide was practically pure iodide. This might be explained by assuming that the alkyl iodide reacts with the zinc to give zinc alkyl iodide and this in turn reacts with the alkyl bromide to give more of the alkyl iodide.

$$\mathrm{Zn} + \mathrm{RI} \longrightarrow \mathrm{ZnIR}$$
$$\mathrm{ZnIR} + \mathrm{RBr} \longrightarrow \mathrm{RI} + \mathrm{ZnBrR}$$

This suggests that only a small quantity of iodide would be necessary to bring about the reaction. It was found, however, that a considerable concentration of iodide is necessary to keep the reaction going.

The zinc alkyls which were successfully prepared were zinc diethyl, zinc di-*n*-propyl, zinc di-*n*-butyl and zinc di-*iso*-amyl. Secondary halides such as *iso*-propyl and *iso*-butyl halides gave chiefly gaseous products, presumably the saturated and unsaturated hydrocarbons,[2] and only minute quantities of the zinc alkyl.[5] Cyclohexyl bromide was found to react with the zinc–copper couple at the boiling point of the bromide to give a mixture of cyclohexene and dicyclohexyl. Diethyl sulfate does not react with the couple.

Preparation of Hydrocarbons

Most textbooks of organic chemistry state that hydrocarbons may be prepared by the action of zinc alkyls on alkyl halides and give as a general reaction

$$\mathrm{ZnR_2} + 2\mathrm{R'X} \longrightarrow 2\mathrm{R{-}R'} + \mathrm{ZnX_2}$$

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[5] Bohm [*J. Russ. Phys.-Chem. Soc.*, **31**, 46 (1899); *Chem. Zentr.*, I, 1067 (1899)] claims a yield of 25% of zinc di-*iso*propyl, while Gladstone and Tribe (ref. 2) get only gaseous products. Garzarolli-Thurnlackh and Popper [*Ann.*, **223**, 168 (1884)] claim a yield of 35–41% of zinc di-*iso*butyl.

The only alkyl halides which we have found to react with the zinc alkyls are the tertiary alkyl halides. Primary and secondary halides and such compounds as diethyl sulfate and allyl bromide could not be made to react under the conditions of the experiment. Moreover, hydrocarbons reported in the literature as prepared by means of zinc alkyls are all prepared from the tertiary halides. Because of their ease of preparation, the chlorides only have been used in the present work.

It has been found that the yields are improved by carrying out the reaction in the presence of an inert solvent of such a boiling point that the product could be separated easily by distillation. Thus the yield of trimethylethylmethane was 18% without using a solvent and 45% using xylene as a solvent. To obtain a product as free from halogen as possible, the solution of alkyl halide is run into a slight excess of the zinc alkyl in the desired solvent.

The temperature used was the lowest that would permit the reaction to run smoothly. It is *absolutely essential* that only a small amount of the halide be added at first and the mixture warmed until the reaction starts. The mixture is then kept at this temperature throughout the reaction. If a considerable amount of the halide is added without the reaction starting, there is danger that the reaction will take place with explosive violence.[6] This would seem to indicate that the reaction is auto-catalytic and it would be interesting to attempt to find catalysts that would allow the reaction to start easily and possibly to proceed at lower temperatures.

In all cases the yields are low (25–51%) but it is believed that this method gives higher yields and purer products with less trouble than any other now available.

Experimental

General Procedure for Preparing Zinc Alkyls.—In a 1-liter round-bottomed flask fitted with a reflux condenser and a heavy stirrer is placed 130 g. (approx. 2 moles) of fine turnings of a zinc–copper alloy containing from 5 to 8% of copper. To this are added 0.5 mole of alkyl iodide and 0.5 mole of alkyl bromide and the mixture is gently refluxed with slow stirring. From twenty to forty minutes after refluxing begins the reaction starts, as is evidenced by the greatly increased rate of refluxing, and the source of heat should be removed. In case the reaction should become too vigorous, the flask is cooled with ice water but only to the point where the reaction is again under control. At the end of half an hour from the time the heat was removed the reaction is usually

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[6] In one instance the solution of zinc alkyl was cooled in an ice–salt bath and kept at a low temperature while the alkyl halide was added. No reaction seemed to take place at first, but shortly and without warning an explosion of such violence took place that it resembled a detonation. An enameled pan containing the ice–salt mixture was crumpled by the force of the explosion. On repeating the experiment on a smaller scale, the same violent reaction took place, though with less destructive force. If, however, the proper precautions are taken to start the reaction, it proceeds smoothly and without any danger whatsoever.

over. The flask is allowed to cool, transferred to a distilling head and condenser and distilled directly from the reaction flask under a pressure of less than 30 mm. of mercury. The apparatus need not be swept out with an inert gas before starting the distillation but at the end, when the vacuum is released, dry carbon dioxide is admitted to the apparatus instead of air. On redistillation *in vacuo* through a column, practically the entire product boils over a range of 3 to 5°. After weighing the product, an equal weight of the desired dry solvent is added and the solution is ready for use in subsequent reactions.

TABLE I

DATA ON ZINC DIALKYLS

Zinc alkyl	B. p., °C.	Yield, %
Zinc diethyl[a]	112–117 (atm.)	87–89
Zinc di-*n*-propyl[b]	39–40 (9 mm.)	85–86
Zinc di-*n*-butyl[c]	81–82 (9 mm.)	78–79
Zinc di-*iso*-amyl[a]	100–103 (12 mm.)	50–55

[a] Frankland, *Ann.*, **85**, 360 (1853). [b] Ref. 2. [c] *Anal.* Subs., 2.4121: 26.64 cc. of *N* HCl. Calcd. for $Zn(C_4H_9)_2$: Zn, 36.45. Found: 36.11.

General Procedure for Preparing Hydrocarbons.—To a 500-cc. three-necked flask fitted with a reflux condenser, thermometer, dropping funnel and stirrer is added 0.28 mole of zinc alkyl dissolved in an equal weight of inert solvent. In the dropping funnel is placed 0.5 mole of tertiary alkyl chloride, also dissolved in an equal weight of

TABLE II

REACTING SUBSTANCES AND PRODUCTS

No.	Reactants Zinc	 Chloride	 Solvent	Hydrocarbon produced	Yield, %
1	Diethyl	*Tert.*-butyl	Xylene	Trimethylethylmethane[a]	45
2	Di-*n*-propyl	*Tert.*-butyl	Xylene	Trimethylpropylmethane[b]	40
3	Di-*n*-butyl	*Tert.*-butyl	Tetralin	Trimethylbutylmethane	36
4	Di-*iso*-amyl	*Tert.*-butyl	Tetralin	Trimethyl-*iso*-amylmethane[c]	25[d]
5	Diethyl	*Tert.*-amyl	Xylene	Dimethyldiethylmethane[e]	51
6	Di-*n*-propyl	*Tert.*-amyl	Tetralin	Dimethylethylpropylmethane[f]	24
7	Di-*n*-butyl	*Tert.*-amyl	Tetralin	Dimethylethylbutylmethane	29

[a] Gorianow, *Ann.*, **165**, 107 (1873).

[b] Markownikow, *Ber.*, **33**, 1905 (1900).

[c] Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 957 (1913); *Chem. Zentr.*, II, 2131 (1913).

[d] In this case the yield is based on a fraction boiling at 115–125°. Other isomers were undoubtedly present in the *iso*-amyl iodide and bromide used and the fraction boiling at 121–123° was obtained only after several distillations.

[e] Friedel and Ladenburg, *Ann.*, **142**, 310 (1867).

[f] Späth, *Monatsh.*, **34**, 1965 (1913).

PHYSICAL CONSTANTS OF PRODUCTS

No.	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refr. Obs.	 Calcd.
1	49.5–50.5	0.6512	1.3675	29.6	28.5
2	80–81	.6778	1.3828	34.4	32.9
3	106–107	.6967	1.3931	39.0	37.4
4	121–123	.7091	1.3997	43.7	41.8
5	86–86.5	.6952	1.3908	34.2	32.9
6	111–112	.7116	1.3998	38.8	37.4
7	137–138	.7304	1.4095	43.3	41.8

solvent. A small amount of the chloride is run into the flask and the mixture is gradually heated until a sharp rise in temperature takes place, indicating that the reaction has started. (*Caution:* The reaction must get started before a large amount of the chloride has been added or an explosion may result.) More halide is then slowly added, keeping the mixture at the temperature at which the reaction started. At the end of the addition the mixture is decomposed with dilute hydrochloric acid, washed, dried and the hydrocarbon distilled from the solvent through a column. A second distillation gives a product boiling over a range of 1 to 2°. A considerable amount of gas or a low-boiling fraction is always obtained, either during the reaction or the distillation. This was not investigated but is probably a mixture of saturated and unsaturated hydrocarbons.

Summary

1. Improvements in the preparation and manipulation of zinc alkyls are given.

2. The zinc alkyls have been used to prepare a number of hydrocarbons of the type R_4C.

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THE CLEAVAGE OF DIETHYL ALPHA,ALPHA'-DIBROMO-ADIPATE BY SECONDARY AMINES[1]

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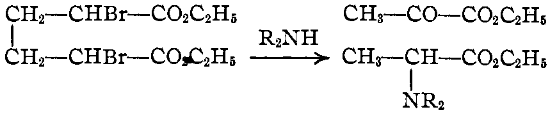
RECEIVED OCTOBER 31, 1928 PUBLISHED FEBRUARY 5, 1929

It has been shown by von Braun, Leistner and Münch[2] that diethyl α,α'-dibromo-adipate when treated with certain secondary amines is cleaved in such a way as to give ethyl pyruvate and an amino ester reported by them to be ethyl α-dialkylaminopropionate.



$$\begin{array}{l} CH_2\text{—}CHBr\text{—}CO_2C_2H_5 \\ | \\ CH_2\text{—}CHBr\text{—}CO_2C_2H_5 \end{array} \xrightarrow{R_2NH} \begin{array}{l} CH_3\text{—}CO\text{—}CO_2C_2H_5 \\ CH_3\text{—}\underset{\displaystyle NR_2}{\underset{|}{C}H}\text{—}CO_2C_2H_5 \end{array}$$

They reported that diethylamine, di-*n*-propylamine, copellidine and di-*iso*-amylamine produce the same type of cleavage, yielding in each case ethyl pyruvate and an α-dialkylaminopropionic ester. This list has subsequently been extended by von Braun, Jostes and Wagner[3] to include a number of similar amines of this class. Dimethylamine and piperidine, however, gave no cleavage but were found to react normally to give the corresponding tetra-alkyldiamino-adipic esters.

[1] This work was presented before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 9, 1928.

[2] Von Braun, Leistner and Münch, *Ber.*, **59B**, 1950 (1926).

[3] Von Braun, Jostes and Wagner, *ibid.*, **61B**, 1423 (1928).