21 g. (28%) of styrene chlorohydrin, b. p. 98–134° (16 mm.), n^{25}_{D} 1.5496. Calculated on the same basis as employed previously, fraction I consisted of a 51% yield of phenylacetaldehyde contaminated with 10% of β-chlorostyrene.

Phenylacetaldehyde from Styrene Glycol.—In this case the catalyst was silica gel impregnated with phosphoric acid. A solution of 50 g. of styrene glycol in 75 cc. of alcohol was added over an eighty-minute period at a temperature of 200–225° and a 105–125 mm. pressure. Distillation of the product yielded 32 g. (74%) of phenylacetaldehyde, b. p. 92–96° (20 mm.), n^{25}_{D} 1.5242 ($n^{19.6}_{\mathrm{D}}$ 1.5255[15]).

Acetophenone from Styrene Chlorohydrin.—The vapor phase apparatus previously described was packed with activated alumina. At a temperature of 360–390° and a pressure of 115–125 mm., 25 g. of styrene chlorohydrin was dropped through during a ninety-five minute period. Distillation yielded 13 g. (67%) of acetophenone, b. p. 83–90° (16 mm.), n^{25}_{D} 1.5327 (n^{25}_{D} 1.5319[16]).

β-Chlorostyrene from Styrene Dichloride.—In this experiment the tube was packed with activated alumina and maintained at 360–400° and a pressure of 85–105 mm. During an eighty-minute period, 35 g. of styrene dichloride was added. Distillation yielded 25.5 g. (92%) of nearly pure β-chlorostyrene, b. p. 82–87° (16 mm.), n^{25}_{D} 1.5700 (n^{25}_{D} 1.5736[13]).

α-Chlorostyrene from Styrene Dichloride.—To a solution of 99 g. (2.5 moles) of sodium hydroxide in 377 cc. of ethyl alcohol and 124 cc. of water was added over a three-quarter hour period 333 g. (1.9 moles) of styrene dichloride. During the addition and for four hours thereafter the mixture was stirred at 50–60°. It was then diluted with water and the product removed by extraction with benzene. When this benzene solution was distilled, 234 g. (89%) of α-chlorostyrene was collected at 80–83° (21 mm.), n^{25}_{D} 1.5600 ($n^{24.5}_{\mathrm{D}}$ 1.5590[17]).

Acetophenone from α-Chlorostyrene.—A mixture of 20 g. of α-chlorostyrene and 100 g. of 80% sulfuric acid was agitated for four hours at 60°. After cooling, it was diluted with water and extracted with benzene. Distillation yielded 14 g. (81%) of acetophenone, b. p. 93–95° (19 mm.), n^{25}_{D} 1.5289.

β-Ethoxystyrene from β-Chlorostyrene.—A solution of 6 g. (0.26 mole) of sodium in 65 cc. of absolute alcohol and 34 g. (0.25 mole) of β-chlorostyrene was heated for five and one-half hours in an autoclave at 175–182°. The cooled bomb was opened and washed with benzene. When this solution was distilled, 24 g. (66%) of β-ethoxystyrene was collected at 96–108° (16 mm.), n^{25}_{D} 1.5440 ($n^{21.2}_{\mathrm{D}}$ 1.5502[18]), d^{25}_{25} 0.973 ($d^{21.4}_{4}$ 0.9714[18]).

Phenylacetaldehyde from β-Ethoxystyrene.—The tube was packed with silica skeleton. In the usual fashion 25 g. of β-ethoxystyrene was added over a forty-five minute period, while the temperature was maintained at 215–225° and the pressure at 135–150 mm. Distillation yielded 15 g. (74%) of phenylacetaldehyde, b. p. 85–95° (17 mm.), n^{25}_{D} 1.5263.

Summary

The vapor phase reactions of styrene chlorohydrin in the presence of steam have been examined.

In the presence of an acid catalyst dehydration to β-chlorostyrene occurs.

With a neutral catalyst, while there is some dehydration, the principal reaction is hydrolysis to styrene glycol which, in turn, loses water to form phenylacetaldehyde.

In the presence of a basic catalyst styrene chlorohydrin is dehydrohalogenated to acetophenone.

In contrast to liquid-phase dehydrohalogenation where α-chlorostyrene is produced, vapor-phase dehydrohalogenation of styrene dichloride yields β-chlorostyrene.

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[16] V. E. Lucas, private communication.

[17] Auwers, *Ber.*, **45**, 2795 (1912).

[18] Auwers, *ibid.*, **44**, 3520 (1911).

DAYTON, OHIO RECEIVED NOVEMBER 2, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds of the Alkaline Earth Group[1]

BY HENRY GILMAN AND LAUREN A. WOODS

The recent availability of organostrontium compounds[2] together with the presently described procedure for the preparation of diethylbarium made possible an examination of the relative reactivities of organometallic compounds of the alkaline earth group.[3]

Among the numerous procedures[4] which have been used to determine the relative reactivities of organometallic compounds, one of those used earlier in a related study with organoalkali compounds[5] appeared to be particularly suitable. In that study, reactions of phenylethynylalkali compounds were carried out with benzonitrile. The phenylethynylmetallic compounds were selected because of their generally low order of reactivity compared with other RM compounds. Benzonitrile was chosen as the reactant because the nitrilo group reacts slower than most organic functional groups which undergo reaction with RM compounds.[6] Slow-reacting combinations were desirable in order to measure with some accuracy the time required to use up the highly reactive organometallic compounds of the alkaline earth group when a definite excess of benzonitrile was used. Color Test I[7] was used to determine the disappearance of RM compound.

$$[\mathrm{C_6H_5{\equiv}C}]_2\mathrm{M} + \mathrm{C_6H_5CN} \xrightarrow{\text{(HOH)}} \mathrm{C_6H_5C{\equiv}C{-}COC_6H_5}$$

The present rate studies show the following

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[1] Paper LVII in the series "The Relative Reactivities of Organometallic Compounds"; the preceding paper is in THIS JOURNAL, **66**, 1515 (1944).

[2] Gilman, Meals, O'Donnell and Woods, THIS JOURNAL, **65**, 268 (1943).

[3] See Grüttner, Dissertation, Berlin, 1914, for the preparation of ethylbarium compounds from barium amalgam and ethyl iodide.

[4] A general account of some procedures is given in Gilman "Organic Chemistry," pp. 518–520 of Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1943.

[5] Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

[6] Entemann and Johnson, THIS JOURNAL, **55**, 2900 (1933).

[7] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

order of decreasing reactivities: R_2Ba, R_2Sr, R_2Ca, R_2Mg. An earlier study established that organoberyllium compounds were less reactive than the corresponding organomagnesium compounds.[8] The order of reactivity of these organometallic compounds can, like the corresponding organoalkali compounds,[9] be correlated with the ionization potentials of the corresponding metallic atoms. In a given group or sub-group, the lower the ionization potential of the metal the more reactive will be its simple[10] organometallic compounds. The ionization potentials[11] in volts of the metals under consideration are: Ba, 5.19; Sr, 5.67; Ca, 6.09; Mg, 7.61 and Be, 9.28. This correlation of reactivities with ionization potentials is more rigorous than that based on the order in the conventional periodic table. For example, the order of decreasing relative reactivities of the phenylmetallic compounds of the III-B metals on the basis of chemical reactivity is indium, gallium and thallium; and not gallium, indium, and thallium.[9] The ionization potentials in volts of these metals are: In, 5.76; Ga, 5.97; Tl, 6.07. Comparisons are to be restricted to a selected group or sub-group. For example, the ionization potential of calcium is 6.09 and that of thallium is 6.07, yet organocalcium compounds are significantly more reactive than organothallium compounds.

Although the organometallic compounds of the alkaline earth metals are of relatively high reactivity, they are less reactive than the corresponding organoalkali compounds. It is quite probable that a so-called free radical like C_2H_5Ba will be found to be more reactive than C_2H_5Li. For example, phenylthallium is decidedly more reactive than triphenylthallium.[12]

Incidental to the present studies it was observed that diethylzinc can accelerate markedly the reactivity of some RM compounds of both the alkali metals and alkaline earth metals. For example, the time required for the reaction of phenylethynylpotassium with benzonitrile is reduced from 4.5 hours to 0.2 hour in the presence of diethylzinc. Also, bis-(phenylethynyl)-magnesium gives a decidedly more pronounced color test in the presence of diethylzinc. It is uncertain at present whether rates of metalation are accelerated by diethylzinc. The function of diethylzinc is very probably associated with the marked effects of some compounds in the formation of coördination complexes.[13]

Experimental

Preparation of Diethylmetallic Compounds. Diethylbarium.—To a suspension of 8.3 g. (0.06 g. atom) of finely rasped barium metal in 5 cc. of benzene, contained in a three-necked flask, was added 22.2 g. (0.18 mole) of diethylzinc. The preparation and reactions were carried out in an atmosphere of dry nitrogen. The stirred mixture was slowly heated to 65–70° (bath temperature). The reaction set in very readily when the temperature was kept at 70°. As soon as a granular, pasty mass appeared (ten to twenty minutes), the bath was removed. After cooling the mixture to room temperature, 75–100 cc. of anhydrous ether was added and refluxing was carried on for one-half hour. The suspension was allowed to settle, and the clear supernatant solution was filtered through a dry asbestos mat. The solution was analyzed by two procedures. First, a 2-cc. aliquot was removed, hydrolyzed with distilled water, and the barium hydroxide titrated[14] with standard sulfuric acid using phenolphthalein as the indicator. Second, an aliquot was hydrolyzed and the barium determined gravimetrically as the sulfate. The values by these two methods agreed and the yield was 50%. Other preparations gave yields in the range of 50–63% even when using a ratio of two moles of diethylzinc to one gram atom of barium.

Diethylstrontium.—Essentially the same procedure was used as in the preparation of diethylbarium. The reaction mixture was heated slowly to 90° (bath temperature), over a period of two to three and a half hours. After heating a short time at 90°, the suspension changed to a black, granular, pasty mass. The extraction, preparation, and titration were carried out as previously described and the yield of the diethylstrontium-diethylzinc complex was 50.7%. In some subsequent preparations, yields in the range of 45–55% were obtained using a ratio of two moles of diethylzinc to 1 g. atom of strontium.

Diethylcalcium.—This compound which was previously described by Hein and co-workers[15] was prepared by us as follows. A mixture of 14.8 g. (0.12 mole) of diethylzinc, 2.4 g. (0.06 g. atom) of rasped calcium metal, and 4 cc. of benzene was heated slowly (over a period of fifty minutes), with stirring, to 102–105° (bath temperature). During the reaction a reddish suspension was produced, and after maintaining the temperature at 102–105° for one hour the bath was removed. The mixture first seemed quite pasty and then became more fluid. At this point the mixture was much less granular than either the diethylbarium or diethylstrontium preparations. Subsequent to the usual extraction and filtration, the titration value showed a yield of 52.8%.

Diethylmagnesium.—A halogen-free ether solution of diethylmagnesium was prepared from ethylmagnesium bromide in accordance with the method of Cope.[16]

Phenylethynylmetallic Compounds.—A solution of 2.05 g. (0.02 mole) of phenylacetylene in 10 cc. of ether was added, during ten minutes, to a stirred solution of 0.01 mole of the $(C_2H_5)_2M$-diethylzinc complex (M = Ba, Sr or Ca) in 30 cc. of ether cooled in an ice-salt bath. A yellowish suspension was formed with the barium and strontium compounds, but the calcium compound separated as an oil from the solution. The mixture was allowed to warm to room temperature, and was then stirred for three-fourths of an hour. The bis-(phenylethynyl)-magnesium was prepared by adding, with stirring, a solution of 2.04 g. (0.02 mole) of phenylacetylene in 10 cc. of ether to 0.01 mole of diethylmagnesium, but without the use of a cooling bath. On refluxing, a yellow suspension formed. To this mixture was added 3.4 g. (0.028 mole) of diethylzinc. This quantity was added on the basis of a zinc analysis of the residue of one of the reactions of bis-(phenylethynyl)-barium with benzonitrile.

Reactions with Benzonitrile.—To a suspension of 0.02 mole of the bis-(phenylethynyl)-metallic compound in 40 cc. of ether was added 3.09 g. (0.03 mole) of benzonitrile in 10 cc. of ether. Color tests I were made at regular intervals, and the times in hours required for a negative color

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[8] Gilman and Schulze, THIS JOURNAL, **49**, 2904 (1927).

[9] Gilman and Jones, *ibid.*, **62**, 2353 (1940).

[10] When only R groups and no salt-forming or acid radicals are attached to the metal.

[11] Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938, p. 14–15.

[12] Gilman and Jones. THIS JOURNAL, **62**, 2357 (1940).

[13] Gillman and Jones, *ibid.*, **62**, 1243 (1940).

[14] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

[15] Hein, Petzchner, Wagler and Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1924).

[16] Cope, THIS JOURNAL, **60**, 2215 (1938).

test were as follows: barium, 3.2, 2.8 and 2.5; strontium, 4.8 and 5.0; calcium, 10.5 and 11.3; and magnesium, 14.5 and 15.0.

Reactions of Phenylethynylalkali Compounds with Benzonitrile.—Phenylethynylpotassium and phenylethynyllithium were prepared in accordance with the procedure of Young.[5] Using the previously described conditions for reaction with benzonitrile and phenylethynylpotassium, the time required for a negative color test I was checked: namely, four and a half hours. Then, in another experiment, a clear solution was formed when 3.4 g. (0.028 mole) of diethylzinc was added to 0.2 mole of phenylethynylpotassium in 40 cc. of ether. To this stirred solution was added 3.09 g. (0.03 mole) of benzonitrile in 10 cc. of ether. Four experiments gave negative color tests in less than 0.2 hour as contrasted with 4.5 hours when diethylzinc was not present.

In comparable experiments it was found that in a reaction between phenylethynyllithium and benzonitrile the time for a negative color test was thirty-four hours in the absence of diethylzinc and 0.3 hour in the presence of diethylzinc. In another experiment concerned with the possibility of ether cleavage, the phenylethynyllithium was stirred in the presence of diethylzinc for eighteen hours. The solution gave as strong a color test at the end of this period as it did at the beginning. Then the benzonitrile solution was added and in 0.2 hour the color test was negative.

It should also be mentioned that phenylethynyllithium gives a more pronounced color test I in the presence of diethylzinc. More particularly, bis-(phenylethynyl)-magnesium ordinarily gives a very weak color test, but the color is markedly enhanced in the presence of diethylzinc.

Carbonation of Phenylethynylmetallic Compounds.—Incidental to the rate studies, the phenylethynylmetallic compounds were carbonated by slowly adding their suspensions to an excess of Dry Ice in ether. The yields of phenylpropiolic acid based on the reaction

$$R_2M + CO_2 \longrightarrow RCO_2MCO_2R$$

were as follows: barium, 73.6%; strontium, 42.1%; calcium, 36.0%; and magnesium, 20.6%.

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Summary

The present availability of organostrontium and organobarium compounds has made possible a determination of the relative reactivities of organometallic compounds of the alkaline earth metals. The decreasing order of relative reactivities is: R_2Ba, R_2Sr, R_2Ca, R_2Mg and R_2Be. This order, like that of some other series, parallels the ionization potentials of the metals.

Incidental to the rate studies, it has been observed that diethylzinc has a marked accelerating effect on some organometallic reactions. This effect is probably due to the formation of coördination complexes.

AMES, IOWA RECEIVED OCTOBER 25, 1944

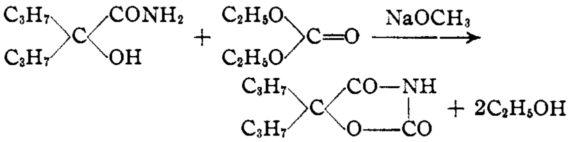
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE MALLINCKRODT CHEMICAL WORKS]

Alkyl Carbonates in Synthetic Chemistry. VI. Condensation with α-Hydroxy Amides. A New Method for Preparing 2,4-Oxazolidinediones[1]

BY V. H. WALLINGFORD, MELVIN A. THORPE AND ROGER W. STOUGHTON

In a recent publication[2] the known methods for the preparation of 2,4-oxazolidinediones were reviewed. The most satisfactory method was found to be that in which an ester of an α-hydroxy acid was condensed with urea in the presence of sodium ethylate. The α-hydroxy esters were prepared from the corresponding cyanohydrins by hydrolysis, first to the amide and then to the acid, with subsequent esterification in the usual manner. Difficulties were experienced in hydrolyzing some of these amides to the acids and the more highly hindered ones were so resistant to complete hydrolysis that it was found necessary to resort to tedious and less satisfactory methods in order to prepare the desired oxazolidinedione derivatives.

The present paper describes a new and much shorter synthesis of 2,4-oxazolidinediones which appears to be generally applicable. This method consists in the condensation of an amide of the appropriately substituted α-hydroxy acid with a dialkyl carbonate[3] in the presence of a metal alcoholate.[4] The reaction is illustrated by the equation



$$\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\!>\!C\!<\!\begin{matrix}CONH_2\\OH\end{matrix} + \begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\!>\!C{=}O \xrightarrow{NaOCH_3} \begin{matrix}C_3H_7\\C_3H_7\end{matrix}\!>\!C\!<\!\begin{matrix}CO-NH\\ \quad\ |\\ O-CO\end{matrix} + 2C_2H_5OH$$

This reaction has been found satisfactory for a wide variety of α-hydroxy amides and is especially useful in preparing oxazolidinediones from such extremely stable amides as di-isopropyl- and *t*-butylmethylglycolamide. While most of the condensations were carried out by refluxing the amide with diethyl carbonate in methanol solution in the presence of sodium methylate, it was found that other dialkyl carbonates, such as di-*n*-propyl and di-*n*-butyl carbonate, reacted with quite satisfactory yields. It was also found that other metal alcoholates, such as magnesium methylate, potassium *n*-butylate and sodium *n*-propylate could be satisfactorily substituted for sodium methylate, although slightly higher yields were obtained with the latter agent.

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(1) Presented before the Organic Division at the New York meeting of the American Chemical Society, September, 1944.

(2) Stoughton, THIS JOURNAL, **63**, 2376 (1941).

(3) For previous papers dealing with the application of alkyl carbonates in synthetic chemistry see THIS JOURNAL, **63**, 2056, 2252 (1941); **64**, 576, 578, 580 (1942).

(4) The process described in the present paper is the subject of U. S. Patent 2,338,220 (1944).