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.

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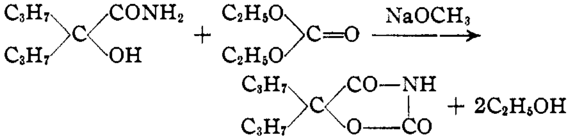
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE MALLINCKRODT CHEMICAL WORKS]

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



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).

TABLE I

REACTION OF ALKYL CARBONATES WITH α-HYDROXY AMIDES

Amide	Temp., °C.	Time, hours	Yield, %	2,4-Oxazolidinedione
Glycolamide	50–55	1	95	2,4-Oxazolidinedione
Lactamide	50–55	1	78	5-Methyl-
α-Hydroxyenanthamide	68–70	3	82	5-*n*-Amyl-[d]
α-Hydroxy-α-*n*-propylvaleramide	50–55	3	96	4,5-Di-*n*-propyl-
α-Hydroxy-α-*n*-propylvaleramide	50–58	2	72	5,5-Di-*n*-propyl-[a]
α-Hydroxy-α-*n*-propylvaleramide	67–68	60	88	5,5-Di-*n*-propyl-[b]
α-Hydroxy-α-isopropylisovaleramide	68–70	4	85	5,5-Diisopropyl-
α-Ethyl-α-hydroxycaprylamide	68–70	4	80	5-Ethyl-5-*n*-hexyl-[f]
β-Ethyl-α-hydroxyenanthamide	68–70	5.5	78	5-(1-Ethylamyl)-[e]
α-Hydroxy-α,β,β-trimethylbutyramide	68–70	3	77	5-*t*-Butyl-5-methyl-
α-Benzyl-α-hydroxybutyramide	68–70	6	79	5-Benzyl-5-ethyl-[g]
Mandelamide	50–52	0.5	86	5-Phenyl-
α-Ethylmandelamide	85–87	9.5	82	5-Ethyl-5-phenyl-[c]
Benzilamide	68–70	4	90	5,5-Diphenyl-

[a] Prepared from *n*-propyl carbonate with sodium propylate in *n*-propyl alcohol. [b] Magnesium methylate used as condensing agent. [c] Prepared from *n*-butyl carbonate with potassium *n*-butylate in *n*-butyl alcohol. [d] New compound. White plates from a benzene–petroleum ether mixture, m. p. 75–76°. *Anal.* Calcd. for $C_8H_{13}NO_3$: N, 8.18. Found: N, 8.34. [e] New compound. Colorless oil, b. p. 144–146° at 2.5 mm. *Anal.* Calcd. for $C_{10}H_{17}NO_3$: N, 7.03. Found: N, 6.92. [f] New compound. Colorless crystals from petroleum ether, b. p. 149–151° at 3 mm., m. p. 31–32°. *Anal.* Calcd. for $C_{11}H_{19}NO_3$: N, 6.57. Found: N, 6.49. [g] New compound. Colorless plates from carbon tetrachloride, m. p. 90–91°. *Anal.* Calcd. for $C_{12}H_{13}NO_3$: N, 6.39. Found: N, 6.41.

Experimental

Glycolamides.—These amides, other than those readily available, were prepared from the corresponding aldehyde or ketone by the addition of hydrogen cyanide and subsequent hydrolysis of the cyanohydrin to the amide with sulfuric acid. The procedure followed was essentially that described in the previous paper.[2]

2,4-Oxazolidinediones.—The general method used for obtaining oxazolidinediones from the corresponding glycolamides and diethyl carbonate is given below.

Sodium (1.05 g. atom) was dissolved in dry methyl alcohol (8–10 moles) in a three-necked flask fitted with a thermometer, reflux condenser and a mercury-sealed stirrer. After the solution had cooled to 35°, the α-hydroxy amide (1 mole) was added in solution in diethyl carbonate (1.15 moles) and when necessary, sufficient methyl alcohol (3–8 moles) to bring about complete solution of the amide. The resulting reaction mixture was then heated to the refluxing temperature (55–70°) until the reaction was considered complete (one to eight hours). At the end of the reaction period the alcohol was distilled off, the cooled residue dissolved in water, and the solution extracted with ether to remove traces of unreacted starting material. On acidification of the aqueous layer, the oxazolidinedione separated. If the oxazolidinedione solidified the product was filtered off and dried. In the preparations involving low melting or water soluble derivatives, the acidified aqueous solution was extracted with isopropyl ether. The ether extract was dried and the ether removed by distillation. The residual oxazolidinedione often crystallized without further purification. When necessary, furthur purification was obtained by vacuum distillation or by recrystallization from suitable solvents. The yields varied from 77 to 95% of the theoretical.

Other metals such as magnesium and potassium were substituted for the sodium, using the same general procedure. Also di-*n*-propyl carbonate in *n*-propyl alcohol and di-*n*-butyl carbonate in *n*-butyl alcohol were used in place of diethyl carbonate in methyl alcohol.

Table I summarizes the preparation of twelve typical oxazolidinedione derivatives by this general method using different metal alcoholates and alkyl carbonates. The temperatures and times given in the table are not necessarily optimum but are those actually used.

Summary

A method has been described for the condensation of alkyl carbonates with amides of substituted α-hydroxy acids by means of metal alcoholates to give 5-substituted-2,4-oxazolidinediones. The method has been used for the preparation of twelve oxazolidinediones of which four are new compounds.

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