The Carboxylation of 3-Phenyl-2,4-oxazolidinedione

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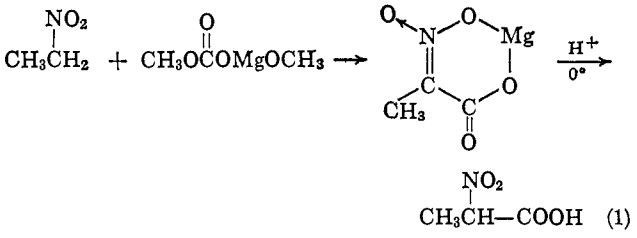
The reaction between magnesium methyl carbonate (MMC) and 3-phenyl-2,4-oxazolidinedione has been shown to give the magnesium chelate of 3-phenyl-5-carboxy-2,4-oxazolidinedione. The magnesium salt was hydrolyzed and the acid, 3-phenyl-2,4-oxazolidinedione-5-carboxylic acid, was isolated. Alternatively, the magnesium salt may be alkylated to produce 5-alkyl-substituted 2,4-oxazolidinediones or acylated with acid anhydrides to produce the corresponding 5-acyl-2,4-oxazolidinediones.

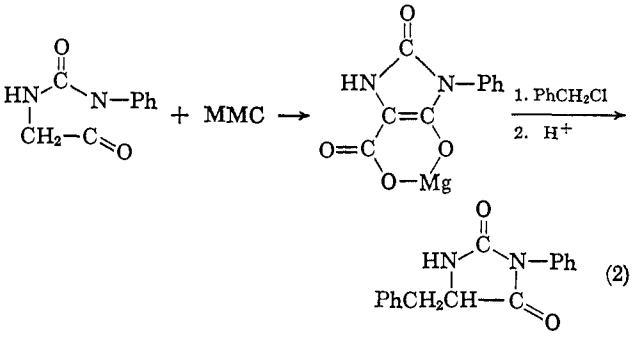
Introduction

Magnesium methyl carbonate (MMC) has previously been shown to carboxylate such diverse materials as hydantoins,[1] ketones,[2] and primary nitroalkanes.[3] This carboxylation reaction is of interest because the initial product can be hydrolyzed to give the free carboxylic acid as shown in eq. 1 for nitroethane[3] or,



(1)

alternatively, the chelated intermediate can be alkylated without isolation. This sequence is particularly useful because methinyl carbons are not alkylated, a common difficulty in other alkylation methods. An illustration is shown in eq. 2 using 3-phenylhydantoin.[1] Of equal interest, perhaps, is the similarity to the biological



(2)

carboxylation[4] and acylation[5] reactions involved in fatty acid synthesis. To some extent this sequence can be described in the same terms as the carboxylation reactions given above.[6]

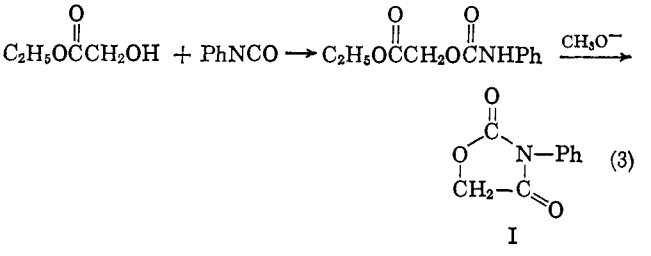
(1) H. Finkbeiner, *J. Am. Chem. Soc.*, **86**, 961 (1964).
(2) M. Stiles, *ibid.*, **81**, 2598 (1959).
(3) H. Finkbeiner and M. Stiles, *ibid.*, **85**, 616 (1963).
(4) F. Lynen, J. Knappe, E. Lorch, G. Jutting, and E. Ringelmann, *Angew. Chem.*, **71**, 481 (1959).
(5) S. J. Wakil, *J. Am. Chem. Soc.*, **80**, 6465 (1958).
(6) J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes and Acetogenins," W. A. Benjamin Inc., New York, N. Y., 1964; M. Stiles, *Trans. N. Y. Acad. Sci.*, **88**, 332 (1960).

Work was undertaken to explore the possibility of carboxylating glycolic acid derivatives since it could be useful to demonstrate a synthetic carboxylation of esters in drawing analogies with the biological carboxylation. This work had three objectives: the demonstration of the carboxylation of glycolic acid derivatives, a comparison with previous carboxylation work, and possible use of the carboxylation–alkylation technique for the preparation of α-hydroxy acids.

2,4-Oxazolidinedione. Wheeler and Hoffman[7] showed that aromatic aldehydes undergo a base-catalyzed condensation with hydantoins to produce five arylidenehydantoins, demonstrating the acidity of protons at the 5-position. However, only the more reactive aromatic aldehydes condense with 2-thiooxazolidine-2,4-dione and not at all with 2,4-oxazolidinedione.[8] On this basis, oxazolidinedione would be most comparable to ordinary aliphatic esters and would be best of the three compounds for carboxylation experiments.

Results and Discussion

Carboxylation of 3-Phenyl-2,4-oxazolidinedione. The compound chosen for this work was 3-phenyl-2,4-oxazolidinedione (I). It was prepared by condensing phenyl isocyanate with ethyl glycolate, followed by base-catalyzed ring closure, as shown in eq. 3, using a modification of the procedure given by Lambling.[9]



(3)

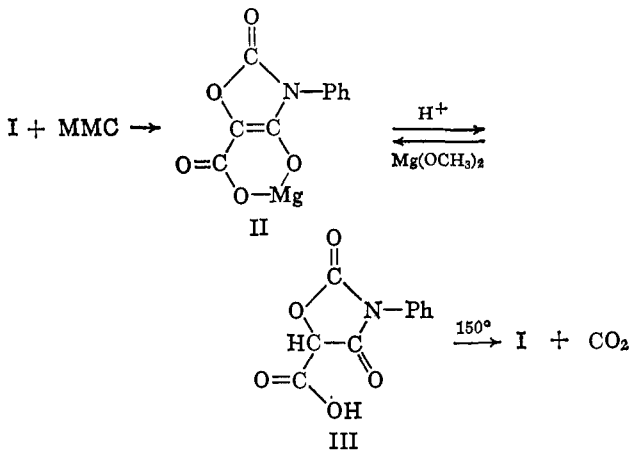
I

3-Phenyl-2,4-oxazolidinedione was dissolved in magnesium methyl carbonate (MMC) and heated to 80° for 30 min. The ultraviolet spectrum of a sample dissolved in methanol showed a peak at 271 mμ which disappeared after the addition of hydrochloric acid. The reaction mixture was hydrolyzed and compounds III (m.p. 146–149° dec.) and IV (m.p. 216–218°) were obtained.

Compound III gave an intense peak at 271 mμ (ϵ 16,150) when dissolved in methanolic magnesium methoxide, coincident with the peak shown by the reaction mixture. A sample heated to the decomposition temperature (150°) for a few minutes and subsequently crystallized had a new melting point of 116–118° and proved to be starting material. Compound III is an acid (pK_a = 2.83) with an equivalent weight of 222.

(7) H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, **45**, 368 (1911).
(8) N. K. Ushenko and T. E. Gorizdra, *Ukr. Khim. Zh.*, **16**, 545 (1950).
(9) E. Lambling, *Bull. soc. chim.*, [3] **27**, 441 (1902).

Chart I



These data are consistent with reactions shown in Chart I.

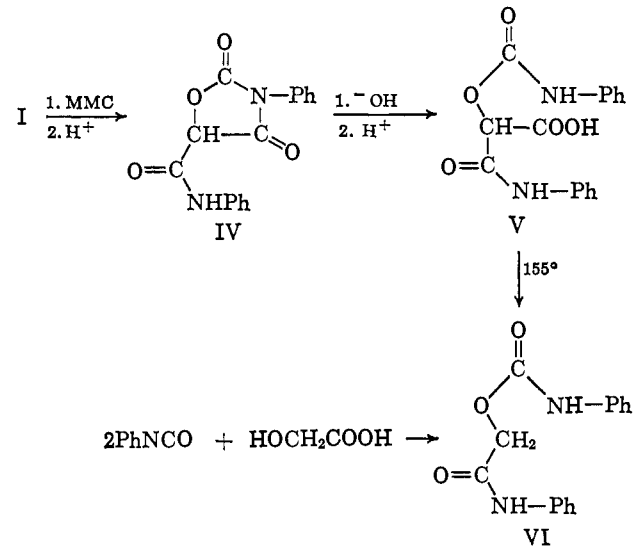
Compound IV was a minor constituent in the initial reaction. However, it became the only isolated product when the reaction time was extended to 3 hr. Accompanying the change in product was a decrease in the absorption peak at 271 mμ and the appearance of a new peak centered at 312 mμ. The formula of IV proved to be $C_{16}H_{12}N_2O_4$ and the molecular weight 295. A proton magnetic resonance spectrum (perdeuterioacetone) showed a singlet at 348 c.p.s. and two sets of aromatic protons, a singlet at 449 c.p.s. and a complex pattern. The ratio of aliphatic to aromatic protons was 1:10. In methanolic sodium methoxide, compound IV gave a peak at 312 mμ (ε 27,350). In methanol it gave two peaks, one at 242 mμ (ε 23,400) and another at 308 mμ (ε 840). These spectral changes are consistent with the presence of an ionizable proton. However, an attempted titration did not show a recognizable end point. A hydrolysis was carried out using 1 equiv. of sodium hydroxide, assuming that the original compound of molecular weight 295 would lead to a monobasic product. This hydrolysis gave a new material, compound V, $C_{16}H_{14}N_2O_5$ (m.p. 151–153° dec.; equiv. wt., 318). Decarboxylation of compound V was effected by heating at 155° for 5 min. and produced compound VI ($C_{15}H_{14}N_2O_3$) which proved to be identical with the phenylurethan of α-hydroxyacetanilide; thus, compound IV is 3-phenyl-5-phenylcarbamyl-2,4-oxazolidinedione. Chart II summarizes these reactions.

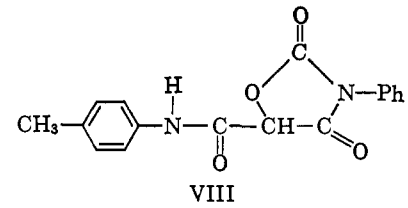
If compound VI is heated over its melting point for a few minutes, aniline is eliminated[10] and 3-phenyl-2,4-oxazolidinedione, the original starting material in this case, is formed.

The formation of II may come about by cleavage of I to form phenyl isocyanate and glycolate followed by addition of the phenyl isocyanate to the magnesium complex II. Bayer[11a] referred to this type of compound as an "isocyanatabspalter" and gives a number of examples. Work by Mukaiyama and Hoshino[11b] also has shown that urethans and ureas are in equilibrium with the corresponding isocyanates and alcohols or amines, respectively.

When phenyl isocyanate was added to the reaction product of 3-phenyl-2,4-oxazolidinedione and magnesium methyl carbonate, an 80% increase in the yield of 3-phenyl-5-phenylcarbamoyl-2,4-oxazolidinedione (IV) was obtained. Similarly, when *p*-tolyl isocyanate was substituted for phenyl isocyanate, the product obtained was 3-phenyl-5-*p*-tolylcarbamoyl-2,4-oxazolidinedione (VIII). Further evidence for the presence of

Chart II





VIII

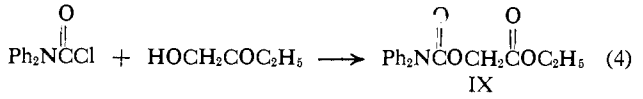
phenyl isocyanate during the course of the reaction of magnesium methyl carbonate and 3-phenyl-2,4-oxazolidinedione was obtained when methyl N-phenylcarbamate was isolated from a reaction mixture. Presumably this arose from the reaction of methanol (present to a small extent in the magnesium methyl carbonate) with phenyl isocyanate. However, methyl N-phenylcarbamate had no effect on the yield of IV when added to the reaction mixture, eliminating the possibility that IV arose by reaction of the magnesium complex II with the carbamate.

Carboxylation of Other Glycolic Acid Derivatives. The initial product from the reaction of phenyl isocyanate with ethyl glycolate is the phenylurethan, $C_6H_5NHCOOCH_2COOC_2H_5$. Since the methylene group of this material should behave somewhat like that in an ordinary ester, it was treated with magnesium methyl carbonate. Periodic sampling and examination of the ultraviolet spectrum showed the formation of a chromophore with a maximum at 271 mμ. However, after work-up and isolation, the product was shown to be 3-phenyl-5-carboxy-2,4-oxazolidinedione. Apparently ring closure occurs prior to carboxylation.

The same product was obtained when the phenylurethan of α-hydroxyacetanilide was used. In order to determine whether the ring closure was a necessary prelude to carboxylation, a carbamate was prepared in which the nitrogen was fully substituted. Diphenylcarbamyl chloride was heated with ethyl glycolate and

(10) E. Lambling, *Bull. soc. chim.*, [3] **29**, 122 (1903).
(11) (a) O. Bayer, *Angew. Chem.*, **59**, 265 (1947); (b) T. Mukaiyama and Y. Hoshino, *J. Am. Chem. Soc.*, **78**, 1946 (1956).

the diphenylurethan of ethyl glycolate (IX) shown in reaction 4 was obtained. When the diphenylurethan

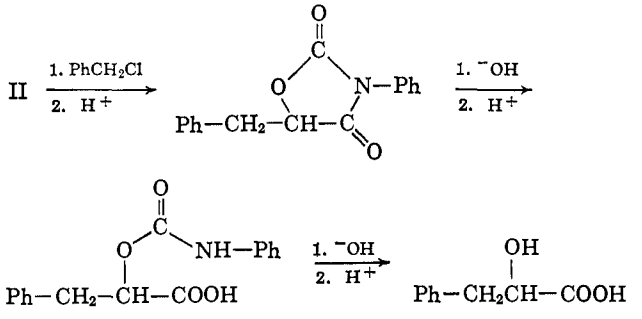


IX was heated with magnesium methyl carbonate in the usual fashion, no spectral changes were observed. Work-up gave only starting material and the corresponding methyl ester, which probably arose from ester interchange with the methoxide of the magnesium methyl carbonate.

These results can be interpreted to mean that formation of magnesium complex II introduces a double bond into the five-membered ring producing a 2-keto-4-oxazoline, a pseudo-aromatic system. The sum of the free energy decrease from this "aromatization" of the oxazole ring and from the formation of the magnesium salt may provide the driving force for the carboxylation.

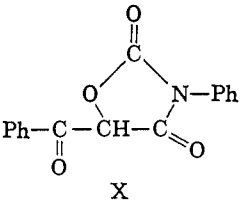
Reactions of the Magnesium Salt of 3-Phenyl-5-carboxy-2,4-oxazolidinedione. Direct alkylation of II was shown to be possible as was demonstrated previously for ketones[2] and hydantoin.[1] When benzyl chloride was added to the reaction mixture of 3-phenyl-2,4-oxazolidinedione and magnesium methyl carbonate, an exothermic reaction took place and work-up gave a 93% yield of 3-phenyl-5-benzyl-2,4-oxazolidinedione. The product was identified by stepwise hydrolysis, first to the phenylurethan of β-phenyllactic acid and then to β-phenyllactic acid. Comparison of the n.m.r. and infrared spectra of the β-phenyllactic acid with an authentic sample established its identity. These reactions are summarized in Chart III.

Chart III

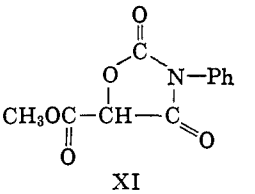


Analogous experiments using *n*-butyl bromide, α-phenylethyl bromide, and β-phenylethyl bromide led to 5-butyl-, 5-α-phenethyl-, and 5-β-phenethyl-3-phenyl-2,4-oxazolidinedione, respectively. Yields were in the 30–70% range and no attempt was made to separate the diastereomers produced in the reaction with α-phenethyl bromide.

Acylation of II with benzoic anhydride gave 3-phenyl-5-benzoyl-2,4-oxazolidinedione (X) as the product, and with dimethyl pyrocarbonate gave 3-phenyl-5-carbomethoxy-2,4-oxazolidinedione (XI). As expected, the 5-benzoyl compound reacted with ferric chloride to produce a deep green color. A solution in 0.001 *N* sodium methoxide had an ultraviolet absorption maximum at 325 mμ (ε 17,680). Similarly, 3-phenyl-5-carbomethoxy-2,4-oxazolidinedione had an absorption maximum at 282 mμ (ε 20,600) in 0.001 *N* sodium



X



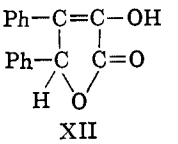
XI

methoxide and at 285 mμ (ε 22,800) in 0.01 *N* magnesium methoxide.

Condensation of II with benzaldehyde led to a product $C_{16}H_{12}O_3$ (m.p. 209–211°, mol. wt. 260). The infrared spectrum showed at least one kind of carbonyl (1730 cm.$^{-1}$), a hydroxyl, and probably two different aromatic groups. A complex aromatic region at about 425 c.p.s., a singlet at 363 c.p.s., and a broad peak (presumably hydroxy) are found in the n.m.r. spectrum. These characteristics are consistent with β-phenylcinnamoylformic acid.

Erlenmeyer and Knight[12a] prepared this compound from the condensation of benzaldehyde with phenylpyruvic acid and established that it exists as α-hydroxy-β,γ-diphenylbutyrolactone (XII). Holmberg[12b] carried out a condensation of 3-phenyl-2-thiooxazolidine-2,4-dione with benzaldehyde in alcoholic base and obtained the same product.

At present, no explanation is available for the radical difference between this reaction and the analogous reaction between benzaldehyde and the magnesium salt of 3-phenyl-5-carboxyhydantoin. In the latter case, the reaction leads cleanly and with good yield to either 5-benzylidene or 5-(phenylhydroxymethyl)-3-phenylhydantoin, depending on the work-up procedure.



XII

Experimental Section

Phenylurethan of Ethyl Glycolate. Ethyl glycolate (110 g.) was added to 150 ml. of dimethylformamide, and the mixture was cooled to 5°. Phenyl isocyanate (115 g.) was added slowly, keeping the temperature below 15°. After addition was complete (~2 hr.), the mixture was warmed to 80° for 3 hr. The reaction mixture was poured onto 2 kg. of ice; the product was filtered off when completely solidified and dissolved in benzene. After removing the occluded water, drying over magnesium sulfate, and decolorizing, *n*-hexane was added at 60° to almost the cloud point. A total of 188 g. (88%) of the urethan was obtained, m.p. 64–65°, lit.[13] m.p. 64–65°.

3-Phenyl-2,4-oxazolidinedione (I). A solution of 112 g. (0.5 mole) of the phenylurethan of ethyl glycolate and 1.0 g. of sodium methoxide in 500 ml. of toluene was heated to reflux in a distillation apparatus equipped with a short fractionating column. The distillation was continued as long as the ethanol–toluene azeotrope was formed. On cooling, 62.5 g. (71% yield) of 3-phenyl-2,4-oxazolidinedione separated and was re-

(12) (a) C. Erlenmeyer and O. N. Knight, *Ber.*, 27, 2224 (1894); (b) B. Holmberg, *J. prakt. chem.*, [2] 84, 634 (1911).

(13) R. F. Rekker, A. C. Faber, D. H. E. Tom, H. Verleur, and W. Th. Nauta, *Rec. trav. chim.*, 70, 113 (1951).

crystallized from ethanol–water, m.p. 118–120°, lit.[9] m.p. 121–122°. *Anal.* Calcd. for $C_9H_7NO_3$: C, 61.02; H, 3.98; N, 7.91. Found: C, 61.3; H, 4.1; N, 8.1.

Carboxylation of 3-Phenyl-2,4-oxazolidinedione. The carboxylation reaction was carried out by adding 6.0 g. of 3-phenyl-2,4-oxazolidinedione to 50 ml. of 2 *M* magnesium methyl carbonate[3] which had been heated to 80°. A slow stream (3–5 cc./min.) of nitrogen was passed over the surface of the stirred reaction mixture. After 30 min., the reaction mixture was cooled to room temperature and poured onto a slurry of 30 ml. of hydrochloric acid and 130 g. of ice. The solid, 3-phenyl-5-phenylcarbamyl-2,4-oxazolidinedione, was washed with ether, and the filtrate extracted five times with 75-ml. portions of ether. The ether extracts were combined and dried over magnesium sulfate; the ether was removed at room temperature under vacuum. The product, 3-phenyl-5-carboxy-2,4-oxazolidine-2,4-dione, crystallized on standing. Yields of these two products varied as the reaction time was changed.

3-Phenyl-5-phenylcarbamyl-2,4-oxazolidinedione (IV). The ether-insoluble product IV was recrystallized from carbon tetrachloride, m.p. 216–218°. *Anal.* Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45; mol. wt., 296. Found: C, 64.7; H, 4.2; N, 9.8; mol. wt., 298.

3-Phenyl-5-carboxy-2,4-oxazolidinedione. The ether-soluble product from the carboxylation reaction was dissolved in a small amount of acetone. After adding carbon tetrachloride to the cloud point, it was refrigerated overnight and the product crystallized, m.p. 146–149° dec.[14] *Anal.* Calcd. for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33; neut. equiv., 221. Found: C, 54.2; H, 3.4; N, 6.3; neut. equiv., 222.

Hydrolysis of 3-Phenyl-5-phenylcarbamyl-2,4-oxazolidinedione. A mixture of 13 ml. of 0.1 *N* sodium hydroxide, 25 ml. of water, and 384 mg. of 3-phenyl-5-phenylcarbamyl-2,4-oxazolidinedione was refluxed for 30 min. After cooling to room temperature, it was filtered to remove the unreacted starting material. The filtrate was acidified and refrigerated to crystallize the product, the phenylurethan of tartronic monoanilide (V), yield 267 mg. (66%), m.p. 151–152°. *Anal.* Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91; neut. equiv., 314. Found: C, 61.2; H, 4.3; N, 9.2; neut. equiv., 318. The product was decarboxylated easily at a temperature of 155° to produce the phenylurethan of α-hydroxyacetanilide.

Carboxylation of the Phenylurethan of Ethyl Glycolate. A solution of 4.0 g. of the phenylurethan of ethyl glycolate in 50 ml. of 2 *M* magnesium methyl carbonate was heated at 85° for 2 hr. Hydrolysis with ice and hydrochloric acid gave the same pair of products obtained from the carboxylation of 3-phenyl-2,4-oxazolidinedione.

Reaction of Isocyanates with 3-Phenyl-2,4-oxazolidinedione and Magnesium Methyl Carbonate. (*a*) *Phenyl Isocyanate.* A solution of 5.2 g. of 3-phenyl-2,4-oxazolidinedione and 50 ml. of magnesium methyl carbonate was heated under a slow stream of nitrogen at 85° for 1 hr. Phenyl isocyanate (3.5 g.) was added and the temperature spontaneously rose to 104°. After 1.5 hr., the reaction mixture was hydrolyzed in ice and hydrochloric acid; the product was filtered off and recrystallized from acetone–water. A 62% (5.4 g.) yield of 3-phenyl-5-phenylcarbamyl-2,4-oxazolidinedione (IV) was obtained.

(*b*) *p-Tolyl Isocyanate.* The above reaction was repeated except *p*-tolyl isocyanate was substituted for the phenyl isocyanate. Two recrystallizations were necessary to remove the small amount of IV also formed. A 48% (4.4 g.) yield of 3-phenyl-5-*p*-tolylcarbamyl-2,4-oxazolidinedione (m.p. 207–209°) was obtained. *Anal.* Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.80; H, 4.55; N, 9.03; mol. wt., 310. Found: C, 65.6; H, 4.5; N, 9.0; mol. wt., 313.

Preparation of 3-Phenyl-5-benzyl-2,4-oxazolidinedione. Magnesium methyl carbonate (50 ml. of a 2 *M* solution) and 5.0 g. 3-phenyl-2,4-oxazolidinedione were heated under a slow stream of nitrogen at 85° for 30 min. Benzyl chloride, (4.0 g.) was added and the temperature spontaneously rose to 93°. After 3 hr., at 85–90°, the reaction mixture was poured, with vigorous stirring, into 150 g. of ice and 30 ml. of hydrochloric acid. The product (7.0 g., 93%) was filtered off after the original semisolid crystallized. It was recrystallized from ethanol, m.p. 151–153°, lit.[15] m.p. 152–153°. *Anal.* Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.5; H, 4.9; N, 5.3.

3-Phenyl-5-butyl-2,4-oxazolidinedione. The other 5-alkyl-substituted oxazolidinediones were prepared by the procedure given for 5-benzyl except heating was continued for 5 hr. after the alkylating agent was added. *n*-Butyl bromide gave a 58% yield of 3-phenyl-5-*n*-butyl-2,4-oxazolidinedione, m.p. 63–66°. *Anal.* Calcd. for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00; mol. wt., 233. Found: C, 66.5; H, 6.2; N, 6.1; mol. wt., 225.

In the case of α-phenethyl bromide and β-phenethyl bromide, the alkylation product was hydrolyzed directly to the α-hydroxy acids. The diastereomers of α-hydroxy-β-phenylbutyric acid were not separated and the isolated oil was identified entirely on the basis of a correct n.m.r. spectrum. α-Hydroxy-γ-phenylbutyric acid, obtained by alkylation of the oxazolidinedione with β-phenethyl bromide and subsequent alkaline hydrolysis, had a melting point of 102–104°, lit.[16] m.p. 103–104°, and the expected n.m.r. spectrum. *Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; mol. wt., 180. Found: C, 66.4; H, 6.6; mol. wt., 172.

3-Phenyl-5-carbomethoxy-2,4-oxazolidinedione (XI). A solution of 4 g. of 3-phenyl-2,4-oxazolidinedione in 50 ml. of 2 *M* magnesium methyl carbonate was heated at 80° for 1 hr. After cooling to 50°, 4 g. of methyl pyrocarbonate[17] was added and the reaction mixture was kept at 50° for an additional 3 hr. The reaction mixture was hydrolyzed by pouring it onto 150 g. of ice and 30 ml. of concentrated hydrochloric

(14) A crude determination of the comparative rates of decarboxylation of various α-hydroxymalonic acid derivatives was carried out using n.m.r. The reactions were run at pH 8 in water at 80°. Tartronic acid had a half-life of approximately 17 hr.; the phenylurethan of tartronic monoanilide (V), a half-life of about 10 hr.; and 3-phenyl-5-carboxy-2,4-oxazolidinedione (III), a half-life of less than 5 min.

(15) H. Aspelund, *Acta Acad. Aboensis, Math. Phys.*, **13**, 22 (1942).
(16) P. Cordier, *Bull. soc. chim. France*, 564 (1956).
(17) V. I. Kovalenko, *Zh. Obshch. Khim.*, **22**, 1546 (1952).

Table I. Ultraviolet Spectra of 5-Substituted 3-Phenyl-2,4-oxazolidinediones

Substituent	Solvent: Methanol λ, mμ	Methanol ε	10^{-3} M $NaOCH_3$ λ, mμ	10^{-3} M $NaOCH_3$ ε	10^{-3} M HCl λ, mμ	10^{-3} M HCl ε	10^{-2} M $Mg(OCH_3)_2$ λ, mμ	10^{-2} M $Mg(OCH_3)_2$ ε	10^{-1} M NaOH[a] λ, mμ	10^{-1} M NaOH[a] ε
Carboxy	218	9,130	233	10,820	258	348	271	16,150	270	773
									233	14,900
Carbomethoxy	229	7,920	282	20,600	255	1,408	285	22,800		
	283	2,520								
Benzoyl			325	17,680						
Phenylcarbamyl	308	3,585[b]	312	27,350	244	15,480				
	242	17,000[b]								
	308	840[c]								
	242	23,400[c]								

[a] In water. [b] The spectrum changed with time, possibly owing to the presence of enol in the original sample. [c] Final values.

acid. The solid was removed by filtration and the filtrate was extracted with three 75-ml. portions of ether. After drying over magnesium sulfate, the ether was removed; the residue was combined with the precipitate and recrystallized from methanol, m.p. 104–107°, yield 2.8 g. (53%). *Anal.* Calcd. for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.95; mol. wt., 235. Found: C, 55.6; H, 3.8; N, 5.9; mol. wt., 228. The n.m.r. spectrum showed aromatic, methyl, and methinyl protons in the ratio of 5:3:1.

3-Phenyl-5-benzoyl-2,4-oxazolidinedione (X). The benzoylation of oxazolidinedione was carried out as given for the preparation of 3-phenyl-5-carbomethoxy-2,4-oxazolidinedione except benzoic anhydride was substituted for the methyl pyrocarbonate. The product was recrystallized from carbon tetrachloride, m.p. 111–114°, yield 2.7 g. (42.5%). *Anal.* Calcd. for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.98; mol. wt. 281. Found: C, 67.7; H, 3.8; N, 5.2; mol. wt., 284.

Ultraviolet Spectra of Oxazolidinedione Derivatives. Spectra were taken at 25° using a Cary Model 14 spectrophotometer. The data are shown in Table I.

2-Keto-3,4-diphenylbutyrolactone (XII). 3-Phenyl-2,4-oxazolidinedione (3 g.) and 50 ml. of 2 *M* magnesium methyl carbonate were heated under a slow nitrogen stream at 85° for 1 hr. Benzaldehyde (4 ml.) was added and the heating continued for 3 hr. The reaction mixture was poured onto ice and hydrochloric acid, the precipitate filtered off, and the aqueous phase extracted with ether. After drying, the ether was removed; the residue was combined with the original precipitate and recrystallized from benzene, yield 2.4 g. (56%), m.p. 209–211°, lit.[11a] m.p. 210°. *Anal.* Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79; mol. wt., 252. Found: C, 76.3; H, 5.0; mol. wt., 260.

Preparation of Ethyl Diphenylcarbamyloxyacetate (VIII). Diphenylcarbamyl chloride (46 g.) and ethyl glycolate (21 g.) were dissolved in 100 ml. of pyridine. After the initial reaction had subsided, the mixture was heated to 65° for 3 hr. It was poured onto 250 g. of ice and the solid filtered off. Recrystallization from ether–hexane gave 41 g. (66%) of product, m.p. 72–74°. *Anal.* Calcd. for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72; N, 4.68; mol. wt., 299. Found: C, 68.3; H, 6.0; N, 5.0; mol. wt., 299.

Carboxylation and alkylation were carried out as given for 3-phenyl-5-benzyl-2,4-oxazolidinedione. The only product isolated was the methyl ester of the starting material, m.p. 88–90°. *Anal.* Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91; mol. wt., 285. Found: C, 67.6; H, 5.4; N, 5.1; mol. wt., 280.

Preparation of the Phenylurethan of Glycolic Acid and Anilide. Glycolic acid (14 g.) was dissolved in 50 ml. of dimethylformamide, and 40 g. of phenyl isocyanate was added over a 2-hr. period. When the addition was complete, the temperature was raised to 55° for 3 hr. The product was precipitated by pouring the reaction mixture into 150 g. of an ice–water slurry. The semisolid was separated and dissolved in methanol. Water was added to the cloud point and the mixture was placed in the refrigerator to crystallize. Recrystallization from benzene–ethanol gave phenylcarbamyloxyacetanilide, m.p., 154–156°, lit.[18] m.p. 145–147°.

A second product crystallized from the aqueous phase on standing. This was recrystallized from benzene–ethanol and was shown to be phenylcarbamyloxyacetic acid, m.p. 140–142°, lit.[11b] m.p. 141–142°. *Anal.* Calcd. for $C_9H_9NO_4$: C, 55.38; H, 4.65; N, 7.18; mol. wt., 195. Found: C, 55.2; H, 4.6; N, 7.0; mol. wt., 193.

Hydrolysis of 3-Phenyl-5-benzyl-2,4-oxazolidinedione. A slurry of 3-phenyl-5-benzyl-2,4-oxazolidinedione (2.4 g.) and potassium hydroxide (0.8 g.) in 50 ml. of water was refluxed for 1.5 hr. The hot solution was acidified with hydrochloric acid and cooled to room temperature. The product, α-phenylcarbamyloxyhydrocinnamic acid was filtered off and recrystallized from ethanol–water, m.p. 151–153°, lit.[19] m.p. 156–157°. *Anal.* Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.7; H, 5.3; N, 4.8.

The α-phenylcarbamyloxyhydrocinnamic acid was hydrolyzed to α-hydroxyhydrocinnamic acid by refluxing with excess 1.0 *N* sodium hydroxide for 1.5 hr. The reaction mixture was acidified with hydrochloric acid and evaporated to dryness; the solid was extracted with ether. After drying over magnesium sulfate, the ether was removed and the product recrystallized from benzene–hexane, m.p. 94–96°, lit.[20] m.p. 96–97°. *Anal.* Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.4; H, 6.0.

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