

ter hydrochlorides when heated to 60–80° give the corresponding amides and alkyl halides.

When examined in aqueous solutions at 25° and pH 7.9, acetyl-L-phenylalanine glycolamide ester was rapidly hydrolyzed, to acetyl-L-phenylalanine and glycolamide, by  $\alpha$ -chymotrypsin.

#### EXPERIMENTAL<sup>3,4</sup>

*Acetyl-DL-phenylalanine cyanomethyl ester.* The reaction of 14.4 g. of acetyl-DL-phenylalanine with 9.08 g. of redistilled chloroacetonitrile in the presence of triethylamine according to the procedure of Schwyzer *et al.*<sup>1</sup> gave 11.0 g. (64%) of crude cyanomethyl ester. The crude ester was recrystallized twice from a mixture of anhydrous ethanol and hexane to give acetyl-DL-phenylalanine cyanomethyl ester, colorless needles, m.p. 94–95°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub> (246): C, 63.4; H, 5.7; N, 11.4. Found: C, 63.5; H, 5.7; N, 11.4.

Reaction of the cyanomethyl ester with benzylamine<sup>1</sup> gave acetyl-DL-phenylalaninebenzylamide, m.p. 161.5–162.9°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub> (282): N, 9.5. Found: N, 9.5.

*Acetyl-DL-phenylalanine glycolamide ester.* A solution of 2.46 g. of acetyl-DL-phenylalanine cyanomethyl ester in 75 ml. of benzene and 3.3 ml. of 3 M methanol in benzene was saturated with dry hydrogen chloride. The solution was allowed to stand at room temperature for 15 min., the benzene removed by distillation at atmospheric pressure, and the colorless residue dissolved in 350 ml. of hot ethyl acetate. This solution was cooled to give 1.69 g. (64%) of the glycolamide ester which was recrystallized from ethyl acetate to give acetyl-DL-phenylalanine glycolamide ester, m.p. 160.5–161.5°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub> (264): C, 59.1; H, 6.1; N, 10.6. Found: C, 59.1; H, 6.1; N, 10.7.

*Acetyl-L-phenylalanine cyanomethyl ester.* Acetyl-L-phenylalanine, 7.2 g., when treated with 4.5 g. of redistilled chloroacetonitrile, as described for the DL-compound, gave 4.4 g. (52%) of crude cyanomethyl ester. Recrystallization of the crude ester from a mixture of anhydrous ethanol and hexane gave acetyl-L-phenylalanine cyanomethyl ester, colorless needles, m.p. 124.5–125.5°,  $[\alpha]_D^{25}$  –11.2 ± 0.4 (c, 3.0% in acetone).

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub> (246): C, 63.4; H, 5.7; N, 11.4. Found: C, 63.6; H, 5.8; N, 11.4.

*Acetyl-L-phenylalanine glycolamide ester.* The reaction of 2.46 g. of acetyl-L-phenylalanine cyanomethyl ester with methanol and hydrogen chloride, under the conditions employed for the DL-compound, gave 1.6 g. (61%) of crude glycolamide ester. Recrystallization of the crude ester from a mixture of anhydrous ethanol and hexane gave acetyl-L-phenylalanine glycolamide ester, colorless needles, m.p. alanine glycolamide ester, colorless needles, m.p. 120.5–121.5°,  $[\alpha]_D^{25}$  +2.2 ± 0.2° (c, 2.3% in absolute ethanol).

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub> (264): C, 59.1; H, 6.1; N, 10.6. Found: C, 59.1; H, 6.1; N, 10.6.

A mixture of the above compound and the DL-compound, m.p. 160.5–161.5 melted at 132–162°.

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AND CRELLIN LABORATORIES OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIF.

(3) Melting points are corrected.

(4) Microanalyses by Dr. A. Elek.

## Improved Preparation of 1-Iodo-2,4-dinitrobenzene<sup>1</sup>

J. F. BUNNETT AND R. M. CONNER

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Bennett and Vernon<sup>2</sup> prepared 2,4-dinitroiodobenzene in 30% yield by heating 2,4-dinitrochlorobenzene with five mole proportions of sodium iodide at reflux in ethylene glycol for 30 minutes. We have found that the yield can be raised to 70% by conducting the reaction in dimethylformamide solution. The procedure is simple, and this is now to be regarded as the method of choice for preparing this compound. Experiments which led to the development of optimum conditions are summarized in Table I, and our best procedure is described in the Experimental section.

TABLE I  
PREPARATION OF 2,4-DINITROIODOBENZENE FROM  
2,4-DINITROCHLOROENZENE

Solvent <sup>a</sup>	Mole Ratio, NaI:C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> Cl	Reflux Time, min.	Yield, %
Ethylene Glycol	5:1	60	37
DMF <sup>b</sup>	5:1	ca. 90	0 <sup>c</sup>
DMF	5:1	30	49 <sup>d</sup>
DMF	5:1	15	70
DMF	3:1	15	66
DMF	5:1 <sup>e</sup>	15	71

<sup>a</sup> DMF stands for dimethylformamide. <sup>b</sup> In this experiment, technical DMF was used without being redistilled. <sup>c</sup> A dark tar was obtained when the reaction mixture was poured into water and no effort was made to isolate a pure product from it. <sup>d</sup> The crude product was recrystallized from ethanol and then from petroleum ether (b.p. 90–100°). <sup>e</sup> One mole of 2,4-dinitrochlorobenzene (5 times the usual amount) was used in this run.

The reaction was tried once in dimethyl sulfoxide solution. From the dark sludge obtained by pouring the reaction mixture into water, only 2,4-dinitrophenyl methyl sulfide, in 5% yield, was isolated. Presumably this compound arose from the following sequence of reactions: reduction of dimethyl sulfoxide to dimethyl sulfide by iodide ion, condensation of dimethyl sulfide with 2,4-dinitrochlorobenzene to form a sulfonium salt, and demethylation of the sulfonium salt by S<sub>N</sub>2 attack of iodide ion on one of its methyl groups. It is interesting to note that Finger and Kruse<sup>3</sup> obtained small amounts of nitrophenyl methyl sulfides as by-products in the preparation of *o*- and *p*-fluoronitrobenzenes by reactions of the corresponding chloro

(1) Work supported in part by the Office of Ordnance Research, U. S. Army.

(2) G. M. Bennett and I. H. Vernon, *J. Chem. Soc.*, 1783 (1938).

(3) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956).

compounds with potassium fluoride in dimethyl sulfoxide solution.

#### EXPERIMENTAL

*2,4-Dinitroiodobenzene, optimum conditions.* To 200 cc. of redistilled dimethylformamide, 150 g. (1.0 mole) of sodium iodide and 40.5 g. (0.2 mole) of 2,4-dinitrochlorobenzene (Eastman Kodak white label) were added. The mixture was heated at reflux by means of a free flame for 15 min.; during the period of heating to reflux temperature, the flame was played against the side of the flask so as to dissolve the sodium iodide from the top downward. The hot reaction mixture was poured into ice and water and the precipitated tan solid was collected on a suction filter. The damp product was recrystallized from a mixture of 375 cc. of petroleum ether (b.p. 90–100°) and 125 cc. of benzene with use of charcoal and with final chilling to –20° in a freezing cabinet. The resulting orange-yellow crystalline product, m.p. 87–89°, weighed 41.4 g. (70%). Recrystallization of this product from petroleum ether (b.p. 90–100°) furnished lemon-yellow crystals, m.p. 88.5–90°. Körner<sup>4</sup> reported m.p. 88.5°.

A run at five times the above scale gave comparable results.

*Formation of 2,4-dinitrophenyl methyl sulfide in dimethyl sulfoxide solvent.* The reaction was conducted as described above except that 200 cc. of commercial dimethyl sulfoxide (Stepan Chemical Co.) was used as solvent and the period of reflux was 1 hr. The reaction mixture was poured into water and allowed to stand 5 days. By suction filtration, a brick-red solid was collected. This solid was extracted with hot petroleum ether (b.p. 90–100°); orange crystals were obtained by cooling the extract. Recrystallization from ethanol with use of charcoal furnished 2.7 g. (5%) of yellow-orange flakes, m.p. 126–127°. A mixed melting point with an authentic sample of 2,4-dinitrophenyl methyl sulfide of m.p. 127–128.5° was not depressed.

VENABLE CHEMICAL LABORATORY  
UNIVERSITY OF NORTH CAROLINA  
CHAPEL HILL, N. C.

(4) W. Körner, *Gazz. chim. ital.*, **4**, 323 (1874).

## 2-Diphenylmethylene-3-dimethylamino-oxazolidine-4,5-dione

GLENN S. SKINNER AND W. J. STOUT

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A series of 2-dialkylmethylene-3-alkyloxazolidine-4,5-diones<sup>1</sup> has been prepared by the action of oxalyl chloride on *N*-alkyldialkylacetamides. We have extended this reaction by using *N*-diphenylacetyl-*N,N'*-dimethylhydrazine (I) in place of the amide. The resulting compound possesses typical oxazolidinedione properties and is formulated as 2-diphenylmethylene-3-dimethylamino-oxazolidine-4,5-dione (II).

The infrared spectrum for this compound shows bands which can be attributed to a lactone and two

carbonyl functions. The spectrum agrees with those of previously reported oxazolidinediones. Likewise, the behavior toward bromine in carbon tetrachloride and potassium permanganate in acetone is the same.

The behavior of the previously studied oxazolidine-4,5-diones in ethanol depends on the type and degree of substitution. 3-Alkyl-2-monoalkylmethyleneoxazolidine-4,5-diones rearrange to the corresponding hydroxymaleimides. Similar treatment of the 2-monoalkyl- or 2-dialkylmethyleneoxazolidine-4,5-diones results in cleavage to the corresponding amides. 3-Alkyl-2-dialkylmethyleneoxazolidine-4,5-diones rearrange to trialkylpyrrolidine-2,3,5-triones. It is, therefore, of interest to report from this study that II undergoes neither of the above reactions with alcohol. In this case, the ring opens at position 2 to give ethyl diphenylacetate.

In the course of this work previously unreported *N*-dialkylacetyl-*N,N'*-dimethylhydrazines were prepared.

#### EXPERIMENTAL

*Preparation of I.* To a stirred solution of 19.5 g. (0.325 mole) of *N,N*-dimethylhydrazine in 100 ml. of ether was added dropwise an ether solution of 75.0 g. (0.325 mole) of diphenylacetyl chloride. Simultaneously at a somewhat slower rate, a solution of 13.0 g. (0.325 mole) of sodium hydroxide in 65 ml. of water was added. The white precipitate was filtered and crystallized from 95 percent ethanol, yield 72 g. (87%), m.p. 168°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>ON<sub>2</sub>: C, 75.56; H, 7.13; N, 11.02. Found: C, 75.39; H, 7.16; N, 11.01.

*N-Diethylacetyl-N,N'-dimethylhydrazine.* Similarly, from 30.0 g. (0.50 mole) of *N,N*-dimethylhydrazine in 150 ml. of ether, 67.3 g. (0.50 mole) of diethylacetyl chloride, and 20.0 g. (0.50 mole) of sodium hydroxide in 100 ml. of water, there was obtained from the ether layer 75.5 g. of a yellow oil which did not crystallize after standing 48 hr. in an ice bath. Distillation yielded 10.5 g. of a yellow oil, b.p. 85–108° (1.6 mm.) which did not solidify and 56 g., b.p. 109–114° (1.6 mm.) which was obtained as a sticky white solid, m.p. 93–97°. Redistillation gave 52 g. (66%), b.p. 109–112° (1.6 mm.), m.p. 95–96°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>ON<sub>2</sub>: C, 60.72; H, 11.46; N, 17.71. Found: C, 61.04; H, 11.43; N, 17.89.

*Preparation of II.* To a stirred solution of 60 g. (0.26 mole) of I in 500 ml. of dry benzene at 55° was added during one hour 23 ml. (0.27 mole) of oxalyl chloride. One half of the theoretical amount of hydrogen chloride had been evolved at the end of this time. The mixture was then stirred for two hours at 55°. After cooling, the yellow precipitate was filtered with suction. Upon washing with benzene and then with petroleum ether a white residue of starting material remained. Distillation of the yellow filtrate to dryness under diminished pressure left 45 g. of a yellow solid, m.p. 169–175°. Recrystallization from 1:1 toluene-ligroin gave 42.5 g. (53%) of a yellow crystalline substance, m.p. 175–176°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub>: C, 70.11; H, 5.23; N, 9.09. Found: C, 69.88; H, 5.27; N, 9.26.

*Reaction of II with ethanol.* A solution of 1.0 g. of II in 30 ml. of 95% ethanol was refluxed for 24 hr. No crystalline product separated on cooling. After the solution was concentrated under diminished pressure to one-third of its volume 0.2 g. of a white compound, m.p. 59–60°, was obtained. Addition of water to the filtrate caused the precipitation of 0.4 g. more of the same substance. Saponification gave diphenylacetic acid, m.p. 148°. The substance when mixed

(1) Glenn S. Skinner and Richard E. Ludwig, *J. Am. Chem. Soc.*, **78**, 4656 (1956).