of the urethan in 50 ml. of ether was added dropwise to 0.195 mole of lithium aluminum hydride dissolved in 140 ml. of ether. After the addition was complete, the mixture was refluxed for an hour and the excess hydride decomposed with water. A solution of 57 g. of potassium sodium tartrate in 100 ml. of water was added and, after stirring for an hour, the organic layer was separated and the aqueous layer extracted with three 100-ml. portions of ether. The combined ether solutions were dried over Drierite and distilled through a Todd spiral-wire column to give 9.6 g. (60% yield) of methyl-1,1-dihydroperfluoropropylamine (b.p. 61–62°), 1.5 g. of ethyl N-1,1-dihydroperfluoropropylcarbamate (b.p. 63–66° at 2 mm.), and 1.7 g. of nonvolatile residue.

The methyl-1,1-dihydroperfluoropropylamine was identified by conversion to the *p*-nitrobenzamide, m.p. 56–57.5° (lit.[3] m.p. 56–57°). Admixture with an authentic sample of the *p*-nitrobenzamide gave no depression of the melting point.

The intermediate fraction (b.p. 63–66° at 2 mm.) solidified on standing and after recrystallization from methanol-water had a m.p. of 57–57.5°. Mixture with an authentic sample of ethyl N-1,1-dihydroperfluoropropylcarbamate (see the following experiment) gave no depression of the melting point.

Reaction of lithium aluminum hydride with an excess of ethyl N-n-perfluoropropylcarbamate. This reaction was carried out in the same manner as the reduction just described, except that the ether solution of the hydride was added dropwise to the urethan to insure an excess of the carbamate at all times. From 25 g. (0.097 mole) of the urethan and 0.048 mole of lithium aluminum hydride were obtained 13.5 g. (63% yield) of ethyl N-1,1-dihydroperfluoropropylcarbamate (b.p. 81–83° at 16 mm.) and 6.5 g. of ethyl N-perfluoropropionylcarbamate (b.p. 102–104° at 16 mm.).

The ethyl N-1,1-dihydroperfluoropropylcarbamate melted at 57–58° after recrystallization from ethanol-water and the melting point was not depressed by admixture with an authentic sample. The authentic sample was prepared for comparison purposes by adding 0.016 mole of sodium hydroxide in 2 ml. of water to a well stirred mixture of 1.5 g. (0.008 mole) of 1,1-dihydroperfluoropropylamine hydrochloride,[5] 10 ml. of water, 5 ml. of ether, and 0.88 g. (.008 mole) of freshly distilled ethyl chlorocarbonate. The mixture, kept at 5° during the addition of the sodium hydroxide, was allowed to warm to room temperature, the organic layer was separated, and the aqueous layer was extracted with two 4-ml. portions of ether. The combined ether layers were dried over Drierite and the ether evaporated to give 1.5 g. (87.5% yield) of crude ethyl N-1,1-dihydroperfluoropropylcarbamate. One recrystallization from chloroform gave white crystals, m.p. 57.5–58°.

Anal. Calc'd for $C_6H_8F_5NO_2$: C, 32.60; H, 3.63. Found: C, 32.61; H, 3.83.

The identity of the ethyl N-perfluoropropionylcarbamate fraction (m.p. 59–60° after recrystallization from toluene) was established by admixture with an authentic sample (see the following experiment) to give no depression of the melting point.

Hydrolysis of ethyl N-n-perfluoropropylcarbamate. Addition of 5 g. (0.0194 mole) of ethyl N-*n*-perfluoropropylcarbamate to 6 ml. of 10% sodium hydroxide resulted in an exothermic reaction. When the reaction subsided, a crystalline precipitate formed which was separated by filtration and dried. This material, 4.9 g. (100% yield), melted at 60–61° (lit.[4] m.p. 60–61°) after recrystallization from toluene. The structure was confirmed by conversion to urethan and perfluoropropionamide by the method previously reported.[4]

Ethyl N-n-perfluoroheptylcarbamate reduction with excess lithium aluminum hydride. By a procedure identical with that described in the N-*n*-perfluoropropylurethan experiment, 17 g. (0.037 mole) of ethyl N-*n*-perfluoroheptylcarbamate in 35 ml. of ether were reduced with 0.09 mole of lithium aluminum hydride in 70 ml. of ether to give 6.81 g. (51% yield) of methyl-1,1-dihydroperfluoroheptylamine (b.p. 57–59° at 26 mm.; n_D^{20} 1.3120), 3.92 g. of ethyl N-1,1-dihydroperfluoroheptylcarbamate (b.p. 108–110° at 10 mm.), and 0.73 g. of nonvolatile residue.

The methyl-1,1-dihydroperfluoroheptylamine was identified by the similarity of its physical properties to those reported[3] for the amine (n_D^{20} 1.3119; b.p. 55° at 26 mm.) and by conversion to the benzamide, m.p. 63.5–64° (lit.[3] m.p. 63°).

The ethyl N-1,1-dihydroperfluoroheptylcarbamate was recrystallized from carbon tetrachloride to yield a white solid, m.p. 43–44°.

Anal. Calc'd for $C_{10}H_8F_{13}NO_2$: C, 28.5; H, 1.92. Found: C, 28.47; H, 2.00.

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Preparation of 3-Substituted-2,5-Oxazolidinediones

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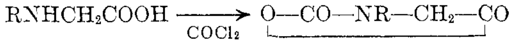
Of the many 2,5-oxazolidinediones that have been prepared as intermediates for the formation of polyamino acids,[2] only a few contain substituents on the nitrogen. They include N-phenyl,[3] N-*p*-tolyl,[4] N-benzyl[5] and several N-alkyl groups.[6–8] None of these is a strongly electrophilic substituent. Therefore, it was of interest to study the effect of further variations in the nature of the nitrogen-bearing substituent on the ease of formation of the oxazolidinediones.

The N-substituted glycine derivatives were converted to the N-carboxy anhydrides by the phosgenation method of Farthing[9]:



$$\mathrm{RNHCH_2COOH} \xrightarrow[\mathrm{COCl_2}]{} \mathrm{O{-}CO{-}NR{-}CH_2{-}CO}$$

The initial experiments in which R was *p*-methoxyphenyl were unsuccessful, since an N-chlorocarbonyl derivative was formed, which could not be cyclized. This result was unexpected, in view of the

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[5] Haszeldine and Leedham, *J. Chem. Soc.*, 1548 (1953).

[1] From the M.S. theses, University of Delaware, of F. L. McCarthy, 1956, R. L. Johnson, 1952, and E. V. Nagle, 1951.

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[9] A. C. Farthing, *J. Chem. Soc.*, 3213 (1950).

TABLE I

PREPARATION OF 3-SUBSTITUTED-2,5-OXAZOLIDINEDIONES

				Calculated				Found			
3-Substituent	Yield, %[a]	Solvent[b]	M.P., °C.[c]	C	H	N	Mol. Wt.	C	H	N	Mol. Wt.[d]
p-HOOCC$_6$H$_4$—	20	T	ca. 236[e]	54.33	3.20	6.33	221	54.52	3.70	6.27	255
p-NO$_2$C$_6$H$_4$—	45	T or D	193–195	48.65	2.72	12.61	222	47.93	2.41	12.42	223
p-CH$_3$COC$_6$H$_4$—	40	T or D	170			6.40	219			6.35	218
CH$_3$CO—	32	E	138	41.27	3.52	9.78	143	41.64	3.76	9.55	142
p-CNC$_6$H$_4$—	12[f]	E	167			13.86				13.87	

[a] Yield of pure material. [b] Solvent for recrystallization, used with petroleum ether; T = tetrahydrofuran, D = dioxane, E = ethyl acetate. [c] All substances melted with decomposition. [d] From neutral equivalent. [e] Decomposition not sharp, beginning at this temperature. [f] Yield could be improved by continuous extraction with ethyl acetate.

fact that 3-p-tolyl-oxazolidinedione was satisfactorily prepared by Fuchs.[4] Subsequent work showed that, when strongly electron-attracting substituents were present on the nitrogen, the oxazolidine ring was formed with moderate ease. Five examples of compounds of this type are given in Table I.

These oxazolidinediones showed no tendency to form polymers in the presence of water as initiator. This is parallel to the reluctance to polymerize of the higher N-alkyl derivatives studied by Wessely, Riedl, and Tuppy.[7]

EXPERIMENTAL

Known N-substituted glycine derivatives. N-Acetylglycine was obtained by Dakin's method.[10] N-p-Carboxyphenylglycine, prepared by the method of Mauthner and Suida,[11] had a melting point (258°) in agreement with that of Takeda and Kuroda[12] (255°), not that of the former authors (219–221°). N-p-Nitrophenylglycine[13] was most conveniently prepared from bromoacetic acid, previously used only for the ortho isomer.[14]

N-p-cyanophenylglycine. A solution of 6.0 g. (0.05 mole) of recrystallized p-aminobenzonitrile and 10 g. (0.11 mole) of chloroacetic acid in 150 cc. of hot water was refluxed until the product began to separate out. On cooling, 4.3 g. of product (49% yield) was obtained, m.p. 234° after washing with ether and recrystallizing twice from water.

Anal. Calc'd for $C_9H_8N_2O_2$: N, 15.91. Found: N, 15.69, 15.83. Alcoholysis gave the known p-carbethoxyphenylglycine ethyl ester.[15]

N-p-acetylphenylglycine. A mixture of 2 g. (0.0148 mole) of p-aminoacetophenone and 2 g. (0.0144 mole) of bromoacetic acid was heated at 100–115° for 20 min., then cooled and treated with 100 ml. of 3*M* ammonium hydroxide. After standing for 12 hr., the ammonia solution was filtered, the insoluble part reextracted with ammonia, and the product precipitated from the extracts with concentrated hydrochloric acid; m.p. 225° with decomposition, yield 22%.

Anal. Calc'd for $C_{10}H_{11}NO_3$: N, 7.25; neut. equiv., 193. Found: N, 7.24; neut. equiv. 195.

N-p-anisyl-N-chlorocarbonylglycine. Phosgenation of N-p-anisylglycine[16] (0.05 mole) in dioxane gave a 36% yield of this substance, m.p. 131–132° after separation from unreacted N-p-anisylglycine with ether and recrystallization from ethyl acetate by adding petroleum ether.

Anal. Calc'd for $C_{10}H_{10}ClNO_4$: N, 5.75. Found: N, 5.86, 5.79. The substance did not undergo ring closure by heating at 40°.

Oxazolidinediones. The N-substituted amino acid (0.01 to 0.03 mole), suspended in about 250 ml. dioxane, was treated with phosgene for 2 to 4 hr. at room temperature, except for the last two substances in Table I, which required a temperature of 40–45°. After the amino acid had dissolved, the solvent was removed at 35–40° and 2 mm., and the residue crystallized from a suitable solvent by the addition of low-boiling petroleum ether. Under these conditions N-o-nitrophenylglycine did not react with phosgene.

All the oxazolidinediones gave an immediate reaction with aniline with the evolution of carbon dioxide. However, when the compounds were exposed to moisture at room temperature or at 100–135°, polymers were not formed. On standing in air-filled, closed specimen bottles for a year, the p-nitrophenyl-, p-cyanophenyl- and p-acetophenyloxazolidinediones reverted to the original free acids, and the p-carboxyphenyl derivative was partly converted. The N-acetyloxazolidinedione was stable under these conditions.

Determination of oxazolidinediones by acidimetry. The possibility of analysis by the neutral equivalent was tested[17] on four of the oxazolidinediones. Three of these reacted rapidly with aqueous base, giving results having an accuracy of ±0.5% (shown as molecular weights in Table I). Samples varying from 10 to 100 mg. were dissolved in an excess of 0.1*N* sodium hydroxide, which was back-titrated with standard hydrochloric acid to the phenolphthalein endpoint. A blank titration was also run. When applicable, this method requires fewer special solutions than the sodium methylate titration of Berger, Sela, and Katchalski.[18]

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Cyclodehydrations in Liquid Sulfur Dioxide

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Phosphorus pentoxide has long been used as a cyclizing agent, commonly in suspension in boiling benzene or toluene. It is usual that the phosphorus pentoxide in such a medium forms a sticky coagu-