TABLE I

No.	Starting Material: Diamines M.p.	Starting Material: Diamines Wt., g.	Starting Material: Cyanogen Bromide, Wt., g.	Dicyanamides Produced: Yield, Wt., g.	Yield, %	M.P.	Nitrogen, % Calcd.	Nitrogen, % Found
1. Hepta-	27–28	12.3	10.6	6.7	78	60–62	31.08	30.89
2. Octa-	50–52	13.7	10.6	8.0	87	73–74	28.84	28.35
3. Nona-	35–37	15.0	10.6	8.1	82	40–42	26.89	26.93
4. Deca-	60–61	16.4	10.6	9.2	87	75–76	25.20	24.97

in all common solvents. The crystals of alkylenedicyanamide were placed, for example, on a surface of a glass or metal plate and kept in molten state below a temperature of about 70°. A transparent glassy film resulted having excellent adhesing properties. The same film could be obtained by coating the plate with a solution of alkylenedicyanamide in ethanol or acetone followed by drying at a suitable temperature.

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Condensation Products of Glycine *t*-Alkyl Esters[1]

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Amino acid *t*-alkyl esters have recently been shown[2] to be considerably more resistant to self-condensation than the ordinarily employed amino acid esters of primary alcohols. These results were confirmed by Anderson and Callahan[3] who were unable to observe any change of the refractive index of glycine *t*-butyl ester after storage at −20°.

Storing glycine *t*-alkyl esters at room temperature over extended periods of time, however, leads to formation of glycine peptide esters which may be separated by paper chromatography and electrophoresis. For comparison various esters were prepared *via* the trityl derivatives according to Zervas.[4] The trityl moiety could selectively be removed with acetic acid without hydrolyzing the *t*-alkyl ester group.

The chromatographic procedures essentially verified the expected condensation pattern of glycine esters as described by Poroshin, Kozarenko, and Khurgin,[5] although monomer and dimer of the *t*-alkyl glycinate were still present after twelve months, owing to the low reaction rate. The precipitated solid of the samples consisted of the tri-, tetra-, penta-, hexa-, and heptaester (with the penta- as the main component). Piperazinedione could be found in small quantities only. In comparison the condensate of isobutyl glycinate had completely solidified after ten months at room temperature. Monomer, dimer, and trimer had disappeared and the main constituents were isobutyl tetraglycinate (44.5%), the pentaester (15.5%), diketopiperazine (16.2%), and the hexaester, besides small amounts of the free peptides.

t-Butyl and *t*-amyl DL-alaninate were quite unreactive. After fifteen months there was no evidence of peptides being formed.

The present findings indicate that the condensation patterns of isobutyl and *t*-butyl glycinate differ mainly as far as their rates are concerned, though the cyclization appears to be more suppressed with the bulky *t*-alkyl esters. The slow production and precipitation of higher peptide esters in the latter case (while a large excess of the monomer is still available) favor the formation of penta-to heptaesters.

EXPERIMENTAL[1]

Materials. Tritylglycine was prepared by saponification of its ethyl ester with potassium hydroxide.[4] Tritylglycylglycine was analogously obtained from its ethyl ester, which was accessible from tritylglycine cyanmethyl ester.[6] It could also be prepared by direct tritylation of diglycine.[4] The trityl peptide esters of the *t*-alcohols were obtained *via* the mixed anhydride method.[4] The following procedure for removal of the trityl group is representative for the *t*-alkyl peptide esters listed in Table I.

Trityltriglycine *t*-butyl ester (2.44 g.) was heated in 15 ml. of 80% aqueous acetic acid for 1.5 min. on the water bath. The mixture was diluted with 40 ml. of water and allowed to cool. Precipitated triphenylcarbinol was removed by filtration, and the filtrate was evaporated *in vacuo*. The oily residue was dissolved in ethanol, and the solvent was removed as before. The solution was acidified with methanolic hydrochloric acid, ether was immediately added, and the crystalline precipitate was collected and crystallized twice from ethanol-ether, methanol-ether, or water-acetone. The yield was 0.995 g. (70%). The purity of each peptide ester was

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TABLE I

PHYSICAL CONSTANTS AND ELEMENTARY ANALYSIS OF GLYCINE PEPTIDE ESTERS

	M.P.[a]	Formula	R_f[b]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Trityldiglycine *t*-butyl ester	167–168	$C_{27}H_{30}N_2O_3$		75.31	75.56	7.02	6.99		
Trityldiglycine *t*-amyl ester	148–149	$C_{28}H_{32}N_2O_3$		75.64	75.78	7.25	7.12		
Diglycine *t*-butyl ester hydrochloride	172–173	$C_8H_{17}ClN_2O_3$	0.63	42.76	42.85	7.62	7.57	12.46	12.59
Diglycine *t*-amyl ester hydrochloride	160–161	$C_9H_{19}ClN_2O_3$	0.69	45.28	45.15	8.02	7.79	11.72	11.91
Diglycine isobutyl ester·HCl	139–140	$C_8H_{17}ClN_2O_3$	0.63	42.76	42.71	7.62	7.64	12.46	12.40
Trityltriglycine *t*-butyl ester	149–150	$C_{29}H_{33}N_3O_4$		71.43	71.71	6.82	6.74		
Trityltriglycine *t*-amyl ester	145–147	$C_{30}H_{35}N_3O_4$		71.84	72.20	7.03	7.45		
Triglycine *t*-butyl ester·HCl	174–175	$C_{10}H_{20}ClN_3O_4$	0.51	42.62	42.76	7.15	7.02	14.91	14.65
Triglycine *t*-amyl ester·HCl	170	$C_{11}H_{22}ClN_3O_4$	0.56	44.66	44.54	7.49	7.43	14.21	14.37
Triglycine isobutyl ester·HCl	154–155	$C_{10}H_{20}ClN_3O_4$	0.51	42.62	42.55	7.15	7.18	14.91	15.10
Tetraglycine *t*-butyl ester·HCl	179–180	$C_{12}H_{23}ClN_4O_5$	0.40	42.54	42.73	6.84	6.90	16.53	16.37
Tetraglycine isobutyl ester·HCl	162–163	$C_{12}H_{23}ClN_4O_5$	0.40	42.54	42.76	6.84	6.75	16.53	16.74

[a] All melting points were determined in capillary tubes. The temperatures were not corrected. [b] Average R_f values of the pure compounds in Solvents II. In a mixture of several peptide esters the respective R_f value of each peptide becomes smaller than the value cited.

checked by chromatography in order to exclude contamination with peptide.[7]

Paper chromatography. Descending chromatography was carried out with the solvent systems (I): *n*-butyl alcohol–acetic acid–water 4:1:1 (freshly prepared), and (II): *sec*-butyl alcohol–formic acid–water 75:13:12 (aged more than 14 days[8]) on Whatman No. 1 filter paper allowing the solvent front to migrate 52–53 cm. The detecting spray reagent consisted of 0.5 g. of ninhydrin dissolved in a mixture of 100 ml. of absolute ethanol and 10 ml. of acetic acid.

A second method to detect peptides, peptide esters, and diketopiperazine was that of chlorination and subsequent treatment of the chromatogram with tolidine-potassium iodine as described by Reindel and Hoppe.[9]

For the quantitative determination 5–20 $\times 10^{-18}$ moles of the esters were spotted in 5; 10; and 15-μl. aliquots of both the known and the unknown solutions in alternating order on Whatman No. 1 filter paper. The chromatograms were prepared with solvent II. The color was produced by carefully dipping the air-dried chromatogram into a solution of 1.0 g. of ninhydrin in 100 ml. of ethanol and 10 ml. of acetic acid. After drying the chromatograms at room temperature for 10 min. they were kept in an oven (saturated with water vapor[10]) for 25 min. at 60°. After one more hour at room temperature the spots were cut out and extracted with 10 ml. of 0.1% cadmium acetate in methanol.[11,12] The extinction was measured in a Beckman spectrophotometer, model B, at 505 mμ. The resulting values were reproducible within ± 5%.

Diketopiperazine in the polycondensate of isobutyl glycinate was estimated after hydrolyzing it to diglycine with 0.2*N* barium hydroxide for 30 min. at room temperature. The hydrolysate (after precipitating the barium ion with 0.2*N* sulfuric acid) was chromatographed with solvent II, and the readings were compared with those of a standard solution containing diglycine and tetraglycine.

Paper electrophoresis on Whatman No. 1 MM, 1300 volts at 30 volts/cm. and a buffer according to Michl[13] gave a good separation of *t*-butyl glycinate up to the heptaglycinate while diketopiperazine remained close to the origin where the sample had been spotted.

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Preparation of Aromatic Nitramines. Alkaline Nitration Using Phenyllithium as Base[1]

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A variety of methods exists for the preparation of aromatic nitramines such as the oxidation of diazotates,[2] the direct nitration of amines,[3] and the alkaline nitration of amines using an alkyl nitrate and a basic condensing agent.[4] The first of these methods suffers from the facts that large quantities of solution must be manipulated to obtain small amounts of nitramine and the yield of by-products is high. The direct nitration procedure

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