methane proceeded only very slowly. To carry out the reaction it was necessary to adopt a large excess of nitric acid.[14] Reactions with 0.5 to 0.8 *M* aromatic and 2 to 4 *M* nitric acid were carried out over a 12-hr. interval. The analytical samples were obtained after treatment of the mixture with aqueous base and extraction into methylene chloride. The vapor phase chromatograms demonstrated the presence of residual aromatic and the absence of dinitrotoluenes. The relative rate was calculated on the basis of the relative amounts of nitrotoluenes to nitro-*t*-butylbenzenes rather than the more valid logarithmic expression. The error introduced by this approximation is minor for compounds differing only by a factor of two. In point of fact, the procedure adopted underestimates the relative rate by a maximum of 10%.

Analytical procedures. The vapor-phase chromatography method will not be detailed in view of the previous presentation of the procedure.[6] The methods utilized in the two laboratories were extraordinarily similar.

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(14) Experiments relating to this problem are reported by Ingold and Bird, ref. 7.

Cyanamide Derivatives. LIX.[1] Preparation and Polymerization of Alkylenedicyanamide[2]

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During the course of our studies on alkyl derivatives of cyanamide, an attempt was made to prepare alkylenedicyanamides. In regard to this problem, one patent,[3] which turned out to be erroneous, has been reported. In that patent, only hexamethylenedicyanamide was recorded as a viscous liquid having a boiling point of 150–155° at 50 mm.

It seemed to us that the synthesis of alkylenedicyanamides might be performed by the reaction of alkylenediamine with cyanogen halide[4] or by the reaction of alkylenedihalide with cyanamide. We chose the former route and succeeded in obtaining alkylenedicyanamides almost quantitatively.

In the method, an alcoholic solution of alkylenediamine was treated with a solution of cyanogen bromide in a mixture of ether and alcohol and the crystals of alkylenediamine dihydrobromide formed were filtered off. Concentration of the resulting solution followed by the addition of water gave alkylenedicyanamide crystals in a good yield. The crystals of hexa-, hepta-, octa-, nona-, and decamethylenedicyanamide were successfully prepared by this method.

These compounds have relatively low melting points and are soluble in alcohol and acetone, but sparingly soluble in water, ether or benzene. To keep them unchanged for a long time, it may be better to preserve them in a cooled place, preferably in the refrigerator.

It is very interesting to note that the alkylenedicyanamides produced transparent insoluble-infusible homopolymers when they were polymerized with each other. It is thought that these polymers may have the structure of polydicyandiamide or polymelamine, probably the former. They were found to be very useful in the manufacture of adhesives, films, fibers, and other plastics. We also found that alkylenedicyanamides could be copolymerized with alkylenediamines to obtain ion exchange resins which may have the structure of polyguanidine.

EXPERIMENTAL[5]

Hexamethylenedicyanamide. A solution of 11.0 g hexamethylenediamine (0.095 mole) in 33 cc. of isopropyl alcohol was added dropwise with stirring to a solution of 10.6 g. of cyanogen bromide (0.10 mole) in a mixture of 35 cc. of ether and 32 cc. of isopropyl alcohol, keeping the temperature at 5–10°. The reaction was almost completed[6] after the last portion of hexamethylenediamine solution had been added. The crystals of hexamethylenediamine dihydrobromide formed were filtered off and washed with isopropyl alcohol. The filtrate combined with the wash was concentrated at diminished pressure below a temperature of 50°. The resulting concentrate was added gradually with stirring in 30 cc. of water and then cooled with ice, resulting in the separation of the crystals of hexamethylenedicyanamide almost completely.[7] The crystals were filtered, washed with cold water and dried in a vacuum desiccator. Yield 7.0 g., 89%, m.p. 61–63°. After recrystallization from alcohol, the melting point rose to 64–65°.

Anal. Calcd. for $C_8H_{14}N_4$: C, 57.80; H, 8.49; N, 33.71. Found: C, 57.82; H, 8.71; N, 33.71. Mol. wt., Calcd.: 166. Found: 163, 170 (cryoscopic in *tert-butyl alcohol*).

An infrared spectrum indicated a very distinct adsorption at 2200 cm.$^{-1}$, pointing to the presence of nitrile group. It also indicated the presence of imino group bands at 3220–3240 cm.$^{-1}$ and of methylene group bands at 2920, 2860, 1470, and 740 cm.$^{-1}$

Identity was further confirmed by converting it to hexamethylenediurea by hydrolysis with acid, m.p. 197–198°.

Hepta-, octa-, nona-, and decamethylenedicyanamide were prepared by the same procedure. The yields, melting points and nitrogen analyses for these compounds are listed in Table I.

Polymerization. The crystals of alkylenedicyanamides (hexa-, hepta-, octa-, nona-, or deca-) were once melted and then kept in molten state at a suitable temperature.[8] A transparent glassy mass resulted which was infusible and insoluble

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(1) Part LVIII, K. Shirai and K. Sugino, *J. Org. Chem.*, **25**, 1046 (1960).

(2) This paper was prepared for delivery before the annual meeting of the Chemical Society of Japan held on Apr. 1960.

(3) H. Dreyfus, British Pat. **549,368**, Nov. 18, 1942. [*Chem. Abstr.*, **38**, 878 (1944)]; U. S. Pat. **2,349,851**, May 30, 1944 [*Chem. Abstr.*, **39**, 1174 (1945).]

(4) For monofunctional cyanamides, see R. Kitawaki, M. Yamashita, and K. Sugino, *J. Chem. Soc. Japan* (Pure Chem. Sec.), **78**, 567 (1957).

(5) All melting points are uncorrected.

(6) At the end of the reaction, the resulting mixture should be kept slightly acidic.

(7) In the cases of hepta- and nonamethylenedicyanamide, the rates of crystallization were very slow.

(8) Attention is required to keep the reaction temperature at a desired range (for example: 50–55° for hexa-) by preventing spontaneous heat evolution.

TABLE I

	Starting Material			Dicyanamides Produced				
	Diamines		Cyanogen Bromide,	Yield,			Nitrogen, %	
No.	M.p.	Wt., g.	Wt., g.	Wt., g.	%	M.P.	Calcd.	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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(1) Paper 134. This work was aided by grants from the United States Public Health Service and the University of California.

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(3) G. W. Anderson and F. M. Callahan, *J. Am. Chem. Soc.*, **82**, 3359 (1960).

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