95.0–96.0°; n_D^{25}, 1.3161; d^{25}, 1.593; mol. wt., calcd. 285, found 288 (Victor Meyer vapor density). Reported[3] b.p., 98.3–98.5°; n_D^{25}, 1.3231; d^{26}, 1.5857.

(*b*) *2,4,6-tris(Pentafluoroethyl)-1,3,5-triazine.* Pentafluoropropionitrile (65 g., 0.45 mole) was condensed in the stainless steel reaction vessel and heated at 300° for 120 hr. The reaction vessel was then cooled, 27 g. of unreacted pentafluoropropionitrile recovered and 38 g. of higher boiling material poured from the vessel. Fractionation of this higher boiling portion gave 2,4,6-*tris*(pentafluoropropyl)-1,3,5-triazine, b.p., 121–122°, n_D^{26}, 1.3131, d^{25}, 1.651.

Anal. Calcd. for $C_9H_{15}N_3$: mol. wt., 435; N, 9.65; sapon. equiv., 435. Found: mol. wt., 431; N, 8.99; sapon. equiv., 431.

(*c*) *2,4,6-tris(Heptafluoropropyl)-1,3,5-triazine.* Heptafluorobutyronitrile (195 g., 1.0 mole) was condensed in a 300-ml. capacity stainless steel reaction vessel and heated to 350°. Initial pressure at 350° was 1879 p.s.i.; pressure decreased to 1670 p.s.i. after 114 hr. At this time the temperature was raised to 400° and the consequent pressure to 1980 p.s.i. No further decrease in pressure was found during the 16-hr. period at 400°. The reaction vessel was cooled to room temperature and 168 g. of unreacted heptafluorobutyronitrile recovered. The remaining higher boiling material (20 g.) was poured from the reaction vessel and fractionated to give 15 g. of 2,4,6-*tris*(heptafluoropropyl)-1,3,5-triazine, b.p., 164.5–165.0°; n_D^{25}, 1.3095, d^{25}, 1.716.

Anal. Calcd. for $C_{12}F_{21}N_3$: sapon. equiv., 585; N, 7.18. Found: sapon. equiv., 576; N, 6.96.

Deammoniation and cyclization of perfluoroalkyl amidines

(*a*) *2,4,6-tris(pentafluoroethyl)-1,3,5-triazine.* Pentafluoropropionamidine (55 g., 0.34 mole) was placed in a round-bottom flask equipped with a reflux condenser and heated in an oil bath at 125° for 3 hr. After this time, the evolution of ammonia was essentially complete. The remaining liquid was fractionated to give 17 g. of 2,4,6-*tris*(pentafluoroethyl)-1,3,5-triazine, colorless liquid, b.p., 122°; n_D^{25}, 1.3135; d^{25}, 1.6504; yield, 35%.

(*b*) *2,4,6-tris(Heptafluoropropyl)-1,3,5-triazine.* Heptafluorobutyramidine (36 g., 0.185 mole) was heated in a round-bottom flask equipped with a reflux condenser by an oil bath at 150° for 4 hr. Fractionation of the resulting liquid gave 23 g. of 2,4,6-*tris*(heptafluoropropyl)-1,3,5-triazine, b.p. 165°, n_D^{25}, 1.3095; yield 64%.

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Preparation of Some *p*-Phenylazobenzoyl Peptides

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In the course of other studies in this laboratory we have had occasion to prepare the *p*-phenylazobenzoyl derivatives of four dipeptides, type formula $C_6H_5—N=N—C_6H_4CONHCHRCONHCHR'COOH$. As they have not been previously reported, we wish to report the preparation. The dipeptides (glycylglycine, glycyl-DL-alanine, DL-alanylglycine, and DL-alanyl-DL-alanine) were prepared by the method of Sheehan and Frank.[1] The condensation with *p*-phenylazobenzoyl chloride was essentially an extension of the procedure which Karrer, Keller, and Szönyi[2] used in preparing *p*-phenylazobenzoyl amino acids by the Schotten-Baumann reaction.

EXPERIMENTAL

General procedure. A solution of 0.489 g. (0.002 mole) *p*-phenylazobenzoyl chloride in 40 ml. ether was added slowly to a stirred aqueous solution made from 0.002 mole dipeptide and 0.002 mole sodium hydroxide, at 0–5°, and the mixture stirred 1.5 hr. at 0–5°. A further 0.002 mole of alkali in aqueous solution was added in small amounts over 3 hr. and stirring at 0–5° continued a further 3 hr. after completing the addition.

Acidification with dilute hydrochloric acid precipitated the product as an orange solid which was filtered and dried. The solid was heated under reflux with petroleum ether (30–60°) to extract any unconverted acid chloride, then with benzene to extract any *p*-phenylazobenzoic acid. The residue was then recrystallized from ethanol to constant melting point.

Mixed melting point determinations of product with *p*-phenylazobenzoic acid and with the appropriate amino acid derivatives in turn showed that it was none of these.

Further very small amounts of peptide derivative could be obtained by separating the ether layer from the acid filtrate, evaporating to dryness from a water bath, heating the small quantity of residual solid successively with petroleum ether and benzene, and recrystallizing from ethanol. Identity with main product was confirmed by mixed melting point determination.

This general procedure was used to prepare all four derivatives. An alternative procedure, differing only in detail, was used for preparing *p*-phenylazobenzoyl glycylglycine, but was not used for the other derivatives.

Alternative procedure. The acid chloride (4.89 gm. or 0.02 mole, in 40 ml. ether) was added at 0–5° over 0.5 hr. to an aqueous solution made from 2.64 g. glycylglycine (0.02 mole) and 0.04 mole sodium hydroxide, and agitation continued 3 hr. at 0–5°. The ether layer was separated from the aqueous layer, washed three times with 0.02*N* NaOH, and the washings added to the main aqueous layer. Acidification of the aqueous solution with dilute hydrochloric acid precipitated the product, which was isolated and purified as described in the general procedure.

p-Phenylazobenzoyl glycylglycine. A yield of 0.56 g. (82.3%), m.p. 236–237° (corr.) was obtained by the general procedure.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: N, 16.46. Found: N, 16.22.

Using the alternative procedure, 5.5 g. product (80.9%), m.p. 236° (corr.) was obtained, identical with that from the general procedure.

p-Phenylazobenzoyl glycyl-DL-alanine. The yield was 0.4 g. (60%), m.p. 236.5–237.5°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.70.

p-Phenylazobenzoyl DL-alanylglycine. The yield was 0.5 g. (71%), m.p. 224.5–225.5°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.67.

p-Phenylazobenzoyl DL-alanyl-DL-alanine. The yield was 0.56 g. (76%), m.p. 233–234°.

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: N, 15.21. Found: N, 15.05.

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CANADA

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