mation of such complexes, Schiessler and Flitter[2] found that *n*-tridecane yields a crystalline complex while 7-methyltridecane does not. The inhibiting effect of the methyl group prompted further research.

The purpose of this investigation was to define the length of the smallest straight carbon chain which will allow complex formation of 2-methylalkanes and to determine whether hydrocarbons with a central methyl branch will form complexes if the straight carbon chain is sufficiently long. The reactions between a saturated solution of urea in methanol and the following five hydrocarbons were studied: 2-methyldecane, 2-methylpentadecane, 2-methylheptadecane, 2-methyltricosane and 10-methyleicosane.

In the 2-methylalkane series the amount of complex formed, as well as the rate of formation of the complex, increased as the length of the straight carbon chain was increased. 2-Methyldecane yielded only a trace of crystalline complex, while 2-methyltricosane was precipitated almost quantitatively. These results indicate the borderline for the formation of insoluble complexes of urea and 2-methylalkanes at 25° C. probably falls just below 2-methyldecane. The studies of Redlich and co-workers,[3] employing hydrocarbon mixtures, suggest that 2-methylalkanes below 2-methyldodecane will not form stable urea complexes at 25° C.

10-Methyleicosane produced a crystalline complex in a yield of about 22%, showing that the inhibitive effect of a centrally located methyl group can be overcome if the straight chain is sufficiently long. Analysis of the complex gave 16.3 molecules of urea per molecule of 10-methyleicosane. Redlich and co-workers[3] formulated the following equation for the composition of urea complexes of the normal alkanes:

$$m = 0.653n + 1.51$$

where m = number of urea molecules,
n = number of carbon atoms

From a study of the crystalline structure of urea complexes, Smith[4] obtained the equation: $m = 0.6925n + 1.49$. Using all 21 carbon atoms of 10-methyleicosane, the calculated values of m are 15.2 and 16.0, respectively. Since the experimental value, 16.3, is slightly higher, it would seem that all the carbon atoms, including the methyl group, are involved in the inter-action with the expanded urea lattice.

None of the five hydrocarbons formed a complex with thiourea.

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EXPERIMENTAL

Reagents. C. P. urea and thiourea, Coleman and Bell, Norwood, Ohio. Methanol, commercial synthetic. Methyl ethyl ketone, technical, Shell Chemical. Hydrocarbons, synthesized[5] by the authors and others at this laboratory.

Procedure. A 10 ml. sample of the hydrocarbon and 100 ml. of a saturated solution of urea in methanol were placed in a large ampoule. The ampoule was sealed and shaken mechanically. Shaking time was 2.5 days except in the case of 2-methyldecane where 4 days of shaking were necessary for complex formation. The ampoule was then opened and the solid complex collected on a sintered glass funnel. The complex was washed with urea-methanol solution, and then with methylcyclohexane to remove any adhering hydrocarbon. The crystalline material was air dried and decomposed with a very small amount of hot water. The formation of an oily hydrocarbon layer confirmed the presence of a complex.

The procedure for testing with thiourea was identical to that above, except that 3 drops of methylethyl ketone were added to each ampoule to aid complex formation. All the tests were run at 25° C.

The urea complex of 10-methyleicosane was analyzed by decomposing 4.411 g. with hot water. The hydrocarbon was extracted with 4 portions of hexane. Evaporation of the hexane yielded 1.026 g. of hydrocarbon. This composition corresponds to 16.3 molecules of urea per molecule of 10-methyleicosane.

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Reactions of the Perfluoronitriles. II. Syntheses of 2,4,6-*tris*(Perfluoroalkyl)-1,3,5-Triazines[1,2]

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McBee, Pierce, and Bolt[3] have reported a synthesis of 2,4,6-*tris*(trifluoromethyl)-1,3,5-triazine by trimerization under pressure of trichloroacetonitrile in the presence of a strong acid, hydrogen

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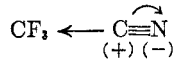
(2) Presented at the Fluorine Symposium, 126th Meeting. AMERICAN CHEMICAL SOCIETY, Minneapolis, Minn., September, 1955.
(3) E. T. McBee, O. R. Pierce, and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

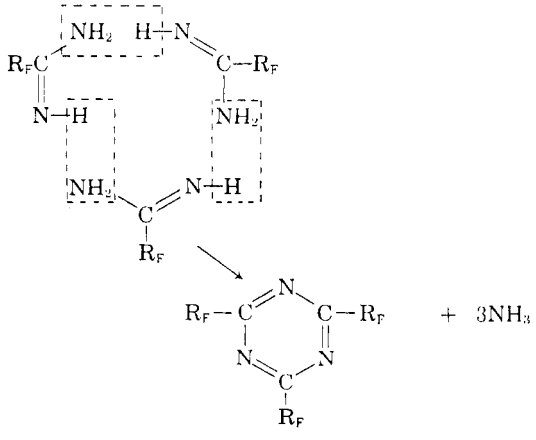
chloride, and subsequent fluorination of the cyclic product by hydrogen fluoride and antimony pentachloride. This method of preparation was improved somewhat by Norton[4] by the use of aluminum chloride with hydrogen chloride to promote the initial polymerization of trichloroacetonitrile.

This paper describes the formation of *s*-triazines from perfluoroalkyl nitriles. In this reaction no acid catalyst is necessary and therefore the perfluoronitrile molecule may be considered activated by the inductive effect of the fluorocarbon group and to exist predominantly in the state represented by:



Trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile have been trimerized under heat and pressure to produce the 2,4,6-*tris*(perfluoroalkyl)-1,3,5-triazines. The minimum pressure for this reaction is 700–900 p.s.i. and the optimum temperature between 300° and 350°. Under these conditions, the reaction time is between 30 and 120 hr., depending on the nitrile used. Trimerization of trifluoroacetonitrile is considerably more rapid than that of the nitriles with longer perfluoroalkyl chains, but the yield of triazine based on unrecovered starting material is in the range of 45 to 60% for each of the nitriles studied. The conversion range (based on starting material) is generally higher for trifluoroacetonitrile (approximately 30%) than for heptafluorobutyronitrile (from 8 to 10%).

The 2,4,6-*tris*(perfluoropropyl)-1,3,5-triazine and the 2,4,6-*tris*(perfluoroethyl)-1,3,5-triazine were prepared also by condensation reactions of heptafluorobutyramidine and of pentafluoropropionamide involving cyclization and elimination of ammonia,



where R_F represents C_3F_7 or C_2F_5. Preparation of the triazines by this method begins with preparation of the amidine from the nitrile and liquid ammonia.[5] The amidines are heated in a glass flask above their melting point and the course of the reaction followed by the evolution of ammonia.

Although the perfluoronitriles are starting points in both of the above methods of preparing the perfluoroalkyl-substituted *s*-triazines, the method proceeding through the amidine involves no high pressure apparatus and is carried out at lower temperatures and is therefore somewhat more convenient if pressure equipment is not available.

The 2,4,6-*tris*(perfluoroalkyl)-1,3,5-triazines are neutral, colorless liquids. As has been noted previously,[3] they produce a burning sensation in the respiratory tract when inhaled. They may be hydrolyzed by aqueous base to form the alkali metal salt of the fluorocarbon acid or they may undergo alcoholysis to form the ester of the fluorocarbon acid. They are not attacked by concentrated acid. A sample of 2,4,6-*tris*(pentafluoropropyl-1,3,5-triazine was sealed in a glass tube with concentrated sulfuric acid and heated at 300° for 72 hr. with no detectable change.

Infrared absorption spectra of each of the perfluoroalkyl-substituted *s*-triazines prepared shows a characteristic strong band at 1565 cm.$^{-1}$ (6.4 μ). This is probably characteristic of the —C=N— in these conjugated cyclic compounds since studies of organic compounds of similar structure have placed the —C=N— absorption in the 1580–1520 cm.$^{-1}$ range.[6]

EXPERIMENTAL

Trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile. These compounds were prepared by dehydration of the perfluoroamides as described by Swarts[7] and by Gilman and Jones.[8]

Pentafluoropropionamidine and heptafluorobutyramidine. These compounds were prepared by reaction of the perfluoronitriles with liquid ammonia.[5]

Cyclization of perfluoroalkyl nitriles. All trimerizations of the perfluoroalkyl nitriles were carried out in a stainless steel pressure vessel of 300-ml. capacity. The nitriles were condensed in the previously evacuated reaction vessel by transfer through a vacuum system line. Temperature of the reactions was controlled automatically. The products were fractionated in a column of 9 theoretical plates packed with glass helices.

(*a*) *2,4,6-tris(Trifluoromethyl)-1,3,5-triazine.* Trifluoroacetonitrile (55 g., 0.58 mole) was placed in the stainless steel reaction vessel as described above and heated to 300°. Pressure in the reaction vessel rose to 1000 p.s.i., then decreased over 16 hr. heating at 300° to 600 p.s.i. Little decrease in pressure was shown during the last 5 hr. After cooling to room temperature, the reaction vessel was opened and 22 g. (0.23 mole) of unreacted trifluoroacetonitrile collected in a Dry-Ice-cooled trap. The high boiling material, 16 g., was poured from the vessel and refractionated to give 14 g. of 2,4,6-*tris*(trifluoromethyl)-1,3,5-triazine, b.p.,

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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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