(1-Nitrocyclohexyl)methyl 3,5-dinitrobenzoate (3,5-dinitrobenzoate of I). From benzene–light petroleum (b.p. 60–68°), white platelets, m.p. 131–132.5°. $\nu_{C=O}$ (cm.$^{-1}$) 1733 in Nujol, 1742 in CS_2; ν_{NO_2} 1545, 1347 in Nujol, 1339 in CS_2.

Anal. Calcd. for $C_{14}H_{15}N_3O_8$: C, 47.59; H, 4.28; N, 11.90. Found: C, 47.49; H, 4.19; N, 12.06.

(1-Aminocyclohexyl)methanol (II). (1-Nitrocyclohexyl)-methanol was hydrogenated in methanol with Raney nickel catalyst at an initial pressure of 2 atm. at room temperature in a Parr low pressure hydrogenation apparatus, causing the mixture to become quite warm. After removal of the catalyst and solvent, the crude product was taken up in ether and extracted with dilute hydrochloric acid. The acid extract was washed with ether, strongly basified with concentrated potassium hydroxide solution, salted out with sodium chloride, and extracted repeatedly with ether. Drying and evaporation of the ether extracts, followed by vacuum distillation of the residue, gave colorless, syrupy (1-aminocyclohexyl)methanol (60% yield), having a potent sperm-like odor. Our analytical sample had the following properties: n_D^{25} 1.4959; ν_{OH} (cm.$^{-1}$) ~3260 (broad), ν_{NH} 1589; m.p. ~37–39.5° (but readily supercools); b.p. 84° (1 mm.). Reported: n_D^{20} 1.4970,[5] 1.4964[3]; b.p. 117–118° (27 mm.),[5] 114–118° (14 mm.),[3] 111–114° (13 mm.).[2]

Anal. Calcd. for $C_7H_{15}NO$: C, 65.07; H, 11.70; N, 10.84. Found: C, 64.99; H, 11.45; N, 10.85.

(1-Aminocyclohexyl)methanol hydrochloride (hydrochloride of II).[11] From chloroform-petroleum (b.p. 90–100°), white crystals, m.p. 161.5–163.5°. Reported:[5] m.p. 158–159°, but no analyses were given.

Anal. Calcd. for $C_7H_{16}ClNO$: C, 50.75; H, 9.74; N, 8.46. Found: C, 51.05; H, 9.71; N, 8.43.

(1-Aminocyclohexyl)methanol sulfate (sulfate of II). White needles, m.p. 237.5–240.5°, from ethanol.

Anal. Calcd. for $C_{14}H_{32}N_2O_6S$: C, 47.17; H, 9.05; N, 7.86. Found: C, 46.71; H, 9.01; N, 8.08. Qualitative analysis showed sulfur to be present.

(1-Benzamidocyclohexyl)methyl benzoate (dibenzoyl derivative of II). The compound was prepared by the Schotten-Baumann reaction. From methylene chloride–light petroleum (b.p. 60–68°), white featherlets, m.p. 100–102°. ν_{NH} (cm.$^{-1}$) 3330, 1537 in Nujol, 3420 in CS_2; $\nu_{C=O}$ 1720, 1643 in Nujol, 1719, 1671 in CS_2.

Anal. Calcd. for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.76; H, 6.81; N, 4.16.

(1-Acetamidocyclohexyl)methyl acetate (diacetyl derivative of II). The ester was obtained by warming (1-aminocyclohexyl)methanol with acetic anhydride on the steam bath for 4.5 hr. From methylene chloride-light petroleum (b.p. 60–68°), thick, white needles, m.p. 63–66.5°. ν_{NH} (cm.$^{-1}$) 3290, 3190, 1552 in Nujol solution, 3410, 3300 in CS_2, 3410, 3310 in $CHCl_3$; $\nu_{C=O}$ 1745, 1644 in Nujol solution, 1736, 1654 in CS_2, 1725, 1651 in $CHCl_3$.

Anal. Calcd. for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98; N, 6.57. Found: C, 62.21; H, 8.98; N, 6.58.

(1-Acetamidocyclohexyl)methanol (acetamide of II). A solution of (1-acetamidocyclohexyl)methyl acetate (1.00 g., 0.00469 mole) and concentrated sulfuric acid (0.25 cc.) in 95% ethanol (15 cc.) was refluxed for 2.5 hr. After distillation of the ethanol, the residue was made slightly basic with sodium bicarbonate solution and extracted repeatedly with ether. Evaporation of the ether extracts, solution of the residual oil in methylene chloride and light petroleum (b.p. 60–68°), concentration, and cooling in an ice bath caused precipitation of small white needles (0.23 g., 0.00134 mole, 29%). Several recrystallizations from methylene chloride-light petroleum gave small white needles of (1-acetamidocyclohexyl)methanol, m.p. 121–123°. ν_{NH} (cm.$^{-1}$) 3300, 1548 in Nujol, 3430, 3310 in $CHCl_3$; $\nu_{C=O}$ 1646 in Nujol, 1653 in $CHCl_3$.

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 63.16; H, 9.97; N, 8.15.

(1-Formamidocyclohexyl)methanol (formamide of II). (1-Aminocyclohexyl)methanol (3.9 g., 0.030 mole) and anhydrous formic acid (10 cc., 0.26 mole) were refluxed for 4 hr. When the reactants were mixed, considerable heat was evolved and a white precipitate formed, probably the formic acid salt, but this dissolved as the reactants were warmed to reflux. The cooled solution was poured into water (30 cc.), neutralized, and saturated with solid sodium carbonate and allowed to evaporate to dryness at room temperature. The crystalline residue was extracted repeatedly with methylene chloride. Evaporation of the methylene chloride and recrystallization from methylene chloride-light petroleum (b.p. 60–68°) gave white crystals (1.01 g., 0.0064 mole, 21%). Three more recrystallizations yielded dense, granular white crystals of (1-formamidocyclohexyl)methanol (0.73 g., 0.0046 mole, 15%), m.p. 124–125.5°. ν_{NH} (cm.$^{-1}$) 1548 in Nujol, 3400 in $CHCl_3$; ν_{OH} ~3180 (broad) in Nujol; $\nu_{C=O}$ 1659 in Nujol, 1674 in $CHCl_3$.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.13; H, 9.73; N, 8.94.

3-Oxa-1-azaspiro[4,5]decan-2-one (III) *(2-oxazolidone of II).* The compound was obtained in 34% yield by heating (1-aminocyclohexyl)methanol with a 100% molar excess of urea at 185° for 1 hr. without catalyst. From methylene chloride-light petroleum, white, chunky crystals, m.p. 82–84.5°. ν_{NH} (cm.$^{-1}$) 3210, 1544 in Nujol, 3240 in CCl_4; $\nu_{C=O}$ 1748 in Nujol and in CCl_4. Reported:[2] m.p. 81–82°.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.22; H, 8.26; N, 9.01.

N,N′-Bis(1-hydroxymethylcyclohexyl)oxamide (oxamide of II). (1-Aminocyclohexyl)methanol (4.4 g., 0.034 mole), diethyl oxalate (9.9 g., 0.068 mole), and 1,4-dioxane (125 cc.) were refluxed for 15 hr. The mixture was poured into water, causing the precipitate to dissolve, giving an acidic solution. The solution was made slightly basic with sodium bicarbonate and extracted several times with ether. The ether extracts were dried, distilled, and the residual dioxane solution was evaporated on the steam bath in a current of air, leaving a brown oil, which crystallized on standing. Four recrystallizations, one with charcoal, from methylene chloride-light petroleum (b.p. 60–68°) yielded white platelets of *N,N′*-bis(1-hydroxymethylcyclohexyl)oxamide (0.75 g., 0.0024 mole, 14%), m.p. 174.5–176.5°. ν_{NH} (cm.$^{-1}$) 3420, 3350, 1518 in Nujol, 3370, 1516 in $CHCl_3$; $\gamma_{C=O}$ 1664 in Nujol, 1672 in $CHCl_3$.

Anal. Calcd. for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97. Found: C, 61.46; H, 8.82; N, 8.92.

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[11] Prepared by James H. Cooley.

Urea Complexes of Some Higher Methylalkanes

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The principal requirement for the formation of crystalline channel inclusion complexes by urea and a hydrocarbon is the presence of a sufficiently long normal carbon chain in the hydrocarbon molecule. While studying the requirement for the for-

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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 coworkers,[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.

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.

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