low for total chloride. In one case, however, the method of purification apparently removed the pyridine impurity and a sample stored over Drierite for 199 days had the same "active chloride" content and rotation as when freshly prepared.

Chloride from 3,5-Cyclolestan-6α-ol.—Three preparations of chloride from 3,5-cyclocholestan-6α-ol and thionyl chloride were carried out, one in ether with pyridine, a second in ether without amine, and a third in pentane with N,N-diisopropyl-*o*-toluidine.[11] Only the last gave enough "pure" material for experimental purposes, and the details of only this preparation will be given.

3,5-Cyclocholestan-6α-ol[3] (3.2 g., 0.0083 mole) and the amine (1.86 cc., 1.66 g., 0.0087 mole) were dissolved in 50 cc. of redistilled pentane, and the solution was cooled to −70°. Thionyl chloride (0.63 cc., 0.0088 mole) was added, and a white precipitate formed immediately. Pentane (60 cc.) was added, the solution was allowed to warm up, and the white solid was filtered off, washed with pentane, and vacuum dried to a weight corresponding to almost theoretical for amine hydrochloride (*ca.* 2.2 g.). The solvent was removed at the aspirator, the oil was dissolved in dry acetone, and the acetone solution was cooled in a Dry Ice bath. The white solid which resulted was filtered off and vacuum dried to yield 0.74 g. (22%) of material, $[\alpha]^{22}\text{D}$ +43.5° (*c* 1.84, $CHCl_3$) (within 3 minutes), $[\alpha]^{22}\text{D}$ −25.5° (after 24 hours). The "active chloride" content was 78.6%, the total chloride 89.4%.

Anal. Calcd. for $C_{27}H_{45}Cl$: C, 80.05; H, 11.20; Cl, 8.75. Found: C, 80.35; H, 11.11; Cl, 7.82.

The acetone filtrates from the above preparation yielded additional fractions with "active chloride" contents of 50–60%, but these were sticky or rapidly turned brown, and so were discarded.

Hydrolysis of 3,5-Cyclocholestan-6β-yl Chloride.—One of the two runs, the unbuffered one, will be described in detail. A 10-ml. quantity of water was added to 1.6706 g. of chloride (83.6% "active," 97% mixed chlorides) dissolved in 90 ml. of dioxane. After 39 hours, the solution was diluted with water and extracted with chloroform. The chloroform solution was washed with water and then evaporated on the steam-bath. The residual solvent was removed at the oil pump and the semi-solid was dissolved in redistilled pentane and chromatographed through stock alumina (33 g., 2 × 11 cm.). Designating pentane by P and ether by E, the following fractions were obtained: (1) 100 ml. of P, from which the residue was 1.2921 g. of material, m.p. 93–95°, mixed m.p. with cholesteryl chloride, 94–96°; (2) 50 P, no residue; (3) 60 P, no residue; (4) 80 E, 76.2 mg. of residue leading to 133 mg. of digitonide; (5) 80 E, 185.6 mg. of residue, m.p. 145–147°, mixed m.p. with cholesterol, 146–147°; (6) 50 E, no residue. From these results the weights of products were summarized as: 1292 mg. of cholesteryl chloride; 44 mg. of 3,5-cyclocholestan-6β-ol; 32 + 186 mg. cholesterol; 94% recovery. Of the 1292 mg. of cholesteryl chloride, an estimated 210 mg. was present in the original chloride specimen.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

t-Carbinamines, $RR'R''CNH_2$. III. The Preparation of Isocyanates, Isothiocyanates and Related Compounds[1]

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Secondary and tertiary alkyl isocyanates were obtained in 50–80% yields from the base-catalyzed cleavage of N-alkylcarbamates. The principal products from primary alkyl isocyanates were trialkyl isocyanurates. *tert*-Alkyl isocyanates and isothiocyanates were obtained from the distillation of the corresponding symmetrical disubstituted ureas and thioureas. Elimination of olefins occurred when these urea derivatives were heated with strong acids. Derivatives of the isocyanates and isothiocyanates and other related compounds were prepared.

Thermal dissociation of carbamates to isocyanates and alcohols is difficult and requires temperatures above 250°. The lower N-alkylcarbamates, which distil without decomposition under atmospheric pressure, must therefore be cracked in vapor phase operation.[2] The requisite temperatures for liquid phase cleavage can be attained by the distillation of esters of high boiling alcohols.[2] Although Raney nickel effects the cleavage of urethans, it has little effect on N-substituted carbamates.[3]

The dissociation of mono-N-alkylcarbamates has now been found to proceed rapidly at 170–230° in the presence of strong bases. Although this reaction is general, its usefulness for the synthesis of isocyanates is complicated by two side reactions. These are recombination of the isocyanate with the alcohol which accompanies it in the distillate and condensation of the isocyanates to trimers or other polymeric materials.

The base-catalyzed pyrolysis of a series of N-alkylcarbamates was investigated (Table I). Tertiary alkyl isocyanates (RR'R''CNCO) were obtained in good yield. The products do not combine with alcohols in the absence of strong base catalysts, and resist thermal or base-catalyzed polymerization.

Secondary alkyl isocyanates (RR'CHNCO) were obtained in moderate yield. Recombination, which is auto-catalyzed,[4] was the principal side reaction, but could be retarded by keeping the distillate cold and by prompt separation of the alcohol from the isocyanate. Trimerization was relatively slow and only small amounts of the impure isocyanurates, contaminated by the corresponding 1,3-dialkylureas, were obtained.

Primary alkyl isocyanates (RCH_2NCO) were also obtained but their rapid trimerization led to the corresponding isocyanurates as the principal or sole product. The presence of small amounts of the isocyanates in the distillates was demonstrated by titration with amine.

A wide variety of bases effectively promoted the cleavage of N-alkyl-carbamates. In a series of experiments based on ethyl N-*t*-octylcarbamate,[5] bivalent oxides and hydroxides gave the best re-

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(1) Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 10, 1951.

(2) C. E. Schweitzer, U. S. Patents 2,409,712 and 2,416,068.

(3) M. Métayer, *Bull. soc. chim. France*, 802 (1951).

(4) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 19 (1949).

(5) In this series, *t*-octyl represents 1,1,3,3-tetramethylbutyl.

sult. Lime was therefore selected for the catalyst in the synthetic study.

The new method is a convenient, rapid and simple route for the preparation of secondary and tertiary alkyl isocyanates based on commonly available amines and the lower chloroformates. No special or corrosion-resistant equipment is required and the reaction conditions are easily attained. The principal by-product, recovered carbamate, can be recycled.

The preparation of *t*-alkyl isocyanates and isothiocyanates by pyrolysis of the corresponding urea derivatives was also studied. The cleavage of most 1,3-dialkylureas or -thioureas requires extreme conditions and the addition of strong acids, either to the vapor space[6a] or to the pot.[6b–e] The reported resistance of dialkylureas to cleavage was confirmed in the attempted distillation of di-2-octylurea and bis-(3,5,5-trimethylhexyl)-urea at 275° from which no liquid products were obtained. Similar treatment of di-*n*-butylthiourea was accompanied by extensive decomposition and no isothiocyanate was isolated. Distillation of di-*t*-octylurea or -thiourea in the presence of mineral acids or phosphorus pentoxide resulted in charring and in the formation of isobutylene polymers.[7]

By contrast, *t*-octyl isocyanate and *t*-butyl isothiocyanate were obtained in good yield from di-*t*-octylurea[8] and di-*t*-butylthiourea[8] by distillation at 220 and 150°, respectively. The vapors were led into cold, dilute aqueous acid to prevent recombination of the *t*-carbinamines with the desired products.

Similar treatment of di-*t*-butylurea and di-*t*-octylthiourea was less successful. In accordance with its reported behavior,[9] di-*t*-butylurea sublimed at its melting point (*ca.* 250°) with only slight dissociation, even in the presence of alkali.

The distillation of di-*t*-octylthiourea at 120–180° was accompanied by extensive cleavage to olefin, hydrogen sulfide and unidentified sulfur-containing liquids. *t*-Octyl isothiocyanate was obtained in 20% yield. When the compound was heated under reflux with dilute hydrochloric acid, the isothiocyanate and diisobutylene were produced in about equal amount. *t*-Octyl isothiocyanate is unaffected by aqueous mineral acids, so that the sensitive material must have been the substituted thiourea.[7] The isothiocyanate was best prepared by the customary decomposition of the dithiocarbamate obtained from *t*-octylamine.[10]

Although the method lacks generality, the cleavage of substituted ureas is attractive because it is based on cheap reagents. It is a convenient route to *t*-octyl isocyanate and *t*-butyl isothiocyanate.

Derivatives of the new isocyanate and isothiocyanate have been prepared. Substituted urea derivatives containing the *t*-butyl group are well-known.[9,11] The corresponding *t*-octyl derivatives were obtained in generally good yield from the reactions of amines with *t*-octyl isocyanate and isothiocyanate. The latter reacted rather slowly, especially with weak or hindered amines. Attempts were made to accelerate its reaction with aniline or cyclohexylamine by heating at 80–130°. Diisobutylene was eliminated and thiocarbanilide or dicyclohexylthiourea was obtained.[12] 1-*t*-Octyl-3-phenylthiourea was successfully prepared from *t*-octylamine and phenyl isothiocyanate.

The resistance of *t*-octyl isothiocyanate to acid hydrolysis has been mentioned. It was slowly attacked by 95% formic acid to give diisobutylene and di-*t*-octylthiourea. This reagent has been reported to effect the hydrolysis of *t*-butyl isothiocyanate to *t*-butylamine.[11e] Alkaline hydrolysis[13] gave di-*t*-butylthiourea in good yield.

The base-catalyzed reaction of *t*-octyl isocyanate with alcohols was used to prepare methyl and allyl N-*t*-octylcarbamates. *t*-Alkyl isothiocyanates reacted similarly with methanol. The resulting N-alkylthiocarbamates could not be purified by distillation because of their instability.

Miscellaneous related compounds bearing *t*-octyl groups were also obtained by adaptation of published procedures. These included 1,3-di-*t*-octylcarbodiimide,[11d,14] 1-*t*-octylhydantoin,[15] 1-*t*-octylparabanic acid,[16] and 1,5-di-*t*-octylbiuret.[17]

Experimental[18]

Ethyl N-2-Octylcarbamate.—Ethyl chloroformate (144 g., 1.33 moles) was added in 20 minutes to a well-stirred mixture of 2-octylamine[19] (156 g., 1.21 moles), benzene (100 ml.), potassium carbonate (100 g.) and water (300 ml.) with cooling. The benzene layer, combined with a benzene extract of the water layer, was distilled to give 224 g. of the colorless oil (91.5%), b.p. 88–90° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4371, d^{25}_{25} 0.9051.

Anal. Calcd. for $C_{11}H_{23}NO_2$: N, 7.0. Found: N, 6.9.

Ethyl N-*t*-octylcarbamate was prepared in 96% yield by the method of Curry and Mason,[20] b.p. 123–125° (24 mm.), m.p. 20–22°, $n^{25}\mathrm{D}$ 1.4429, d^{25}_{25} 0.9222.

Anal. Calcd. for $C_{11}H_{23}NO_2$: N, 7.0. Found: N, 6.9.

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(8) These compounds were prepared from the *t*-carbinamines by conventional reaction with urea[24] and carbon disulfide,[6c] respectively.

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(10) M. L. Moore and F. S. Crossley, in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 599.

(11) (a) W. Rudneff, *Ber.*, **12**, 1023 (1879); (b) M. Brander, *Rec. trav. chim.*, **37**, 88 (1917); (c) A. Bühler and H. Fierz-David, *Helv. Chim. Acta*, **26**, 2133 (1943); (d) E. Schmidt, W. Striewsky and F. Hitzler, *Ann.*, **560**, 222 (1948); (e) E. Schmidt, W. Striewsky, M. Seefelder and F. Hitzler, *ibid.*, **568**, 192 (1950); (f) W. Siefken, *ibid.*, **562**, 75 (1949).

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(14) E. Schmidt and W. Striewsky, *Ber.*, **74**, 1285 (1941).

(15) E. Abderhalden and E. Riesz, *Fermentforschung*, **12**, 180 (1930); G. Frerichs and H. Beckerts, *Arch. pharm.*, **237**, 333 (1899).

(16) L. Siemonson, *Ann.*, **333**, 115 (1904); S. Gabriel, *ibid.*, **348**, 85 (1906).

(17) A. W. Hofmann, *Ber.*, **4**, 265 (1871); F. B. Dains and E. Wertheim, This Journal, **42**, 2303 (1920); H. Bietz and A. Jeltsch, *Ber.*, **56**, 1918 (1923).

(18) We wish to thank C. P. Lo, R. Zeitschel, H. F. Wilson, L. J. Exner and A. J. McFaull, who prepared some of these compounds, T. P. Callan, who supervised the analyses, and Helen Miklas, who determined infrared absorptions.

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(20) H. M. Curry and J. P. Mason, This Journal, **73**, 5043 (1951).

TABLE I

PREPARATION OF ISOCYANATES, RNCO, BY PYROLYSIS OF N-ALKCARBAMATES

R	Temp., °C.	Conversion,[a] %	Yield,[b] %	B.p., °C.	Mm.	$n^{25}D$	d^{25}_{25}	Nitrogen, % Calcd.	Nitrogen, % Found
CH_3-	175–200	0[c]							
n-C_4H_9-	150–200	12[d]							
$(CH_3)_2CH$-	175–210	53[e]	58	74–75[f]		1.3799	...	...	...
C_6H_{11}-[g]	200–225	50[h]	65	63–65	18[i]	1.4514	0.9359	11.2	10.8
2-C_8H_{17}-	203–227	66	81	68	5	1.4230	.8260	9.0	8.9
$(CH_3)_3C$-		66	70	85–87[j]		1.3824	.8359	14.1	13.6
t-C_8H_{17}-	190–220	79	79	170–172		1.4243	.8588	9.0	8.9

[a] Yield based on starting carbamate. [b] Based on unrecovered carbamate. [c] Product was trimethyl isocyanurate. [d] By titration of distillate. Principal product was tributyl isocyanurate. [e] Alcoholic extract of pot residue gave 3% of impure triisopropyl isocyanurate, m.p. 160–165°. *Anal.* Calcd. for $C_{12}H_{21}N_3O_2$: N, 16.5. Found: N, 17.7. [f] T. Curtius, W. Sieber, F. Nadenheim, O. Hambsch and W. Ritter, *J. prakt. Chem.*, **125**, 152 (1930), reported b.p. of 72°. [g] Cyclohexyl. [h] Impure tricyclohexyl isocyanurate from pot residue, m.p. 230–232°. *Anal.* Calcd. for $C_{21}H_{33}N_3O_3$: N, 11.2. Found: N, 11.6. [i] W. Siefken and A. Doser, U. S. Patent 2,326,501, reported b.p. 54° (11 mm.). [j] Ref. 12 reported b.p. 85°.

2-Octyl Isocyanate.—A mixture of ethyl N-2-octylcarbamate (60 g., 0.3 mole) and calcium hydroxide (2 g.) was heated at 203–227° under a short Vigreux column. The vapor temperature was steady at 203°. The receiver was cooled in an ice-bath. There was essentially no residue other than catalyst. The distillate in 50 ml. of pentane was washed with four 5-ml. portions of cold water to remove the ethanol. After drying over magnesium sulfate, the solution was distilled to give 30.5 g. (66%) of a slightly lachrymatory liquid, b.p. 68° (5 mm.), and 11 g. of the carbamate. The yield on unrecovered starting material was 81%.

Anal. Calcd. for $C_9H_{17}NO$: N, 9.0. Found: N, 8.9.

Other isocyanates were prepared similarly (Table I). Since the reaction of *t*-octyl isocyanate with ethanol in the absence of strong base is very slow, the aqueous wash was omitted. In the synthesis of *t*-butyl isocyanate, however, removal of ethanol was required because of the similarity of its boiling point to that of the desired product.

Aliquots of distillates containing methyl and *n*-butyl isocyanates were analyzed by addition of excess *t*-octylamine. After 15 minutes, the excess amine was determined acidimetrically.

Ethyl N-*t*-octylcarbamate (20 g.) was distilled in the presence of 1-g. quantities of various bases. The isocyanate content of the distillate was determined as before. The percentage yields thus obtained were as follows: CaO, 79; CdO, 81; ZnO, 72; $NaOOCCH_3$, 66; $NaOCH_3$, 59; CeO_2, 55; MnO_2, 45; Cu_2O, 37; NiO, 35; Al_2O_3, Fe_2O_3 or HgO, 20–22; $CaCO_3$, 0.

The infrared absorption spectra were measured in carbon tetrachloride solution. A strong isocyanate band was found in cyclohexyl (2275 cm.$^{-1}$), 2-octyl (2275 cm.$^{-1}$) and *t*-octyl (2270 cm.$^{-1}$) isocyanates.[21]

Trimethyl Isocyanurate.—Methylamine (62 g., 2 moles) was passed into dimethyl carbonate (180 g., 2 moles) at 5°. The mixture was allowed to reflux gently under a condenser cooled with Dry Ice and acetone. Sodium methylate (5 g.) was then added to the crude methyl N-methylcarbamate which was then distilled, b.p. 270–285°. (The reported boiling point of the carbamate is 158°.[22] The distillate solidified, m.p. 173–176°,[23] yield 85 g. (75%).

1,3-Di-*t*-octylurea[24].—A mixture of *t*-octylamine (286 g., 2.2 moles) and urea (60 g., 1 mole) was stirred for 15 hours at 140–150°. Ammonia was absorbed in standard acid and the calculated amount was obtained. The cooled residue was slurried with petroleum ether (b.p. 60–80°). The solid was collected, washed with water, and recrystallized from petroleum ether or 80% ethanol to give 158 g. (55%) obtained in two crops, m.p. 151–152°; after two more recrystallizations from isoöctane, m.p. 152–153°.

Anal. Calcd. for $C_{17}H_{36}N_2O$: N, 9.9. Found: N, 9.7.

***t*-Octyl Isocyanate.**—The distillation apparatus consisted of a 100-ml. standard taper flask connected by a gooseneck adapter to a short tube (6 mm. diam.) which was sealed through the side of a 1-liter 3-necked flask. The gooseneck had a T-connection near its highest point, through which nitrogen was admitted to prevent sucking-back of the trap solution. The large flask contained sufficient solution to cover the inlet tube and was fitted with a stirrer, thermometer and reflux condenser.

Di-*t*-octylurea (71 g., 0.25 mole) was distilled at 205–220° (pot) in 40 minutes. The vapors were led below the surface of a solution of sulfuric acid (25 g.) in water (500 ml.), which was stirred and cooled in an ice-bath. The oil was separated and the acid was extracted with ether. Titration of the combined oil and extract showed an isocyanate yield of 89%. Distillation gave 30.5 g. (79%) of *t*-octyl isocyanate, b.p. 64–68° (30 mm.), and 2 g. of residual di-*t*-octylurea. Basification and steam distillation of the acid gave *t*-octylamine in 89% yield by analysis.

***t*-Butyl isothiocyanate**[11c,e] was obtained by a similar distillation of di-*t*-butylthiourea[11c,e] (m.p. 174–175° in sealed, evacuated capillary) in 78% yield, b.p. 64° (52 mm.), $n^{25}D$ 1.4780, d^{25}_{25} 0.9079.

Anal. Calcd. for C_5H_9NS: N, 12.2; S, 27.8. Found: N, 11.9; S, 27.5.

1,3-Di-*t*-octylthiourea.—*t*-Octylamine (129 g., 1 mole) was added to a mixture of carbon disulfide (48 g. 0.62 mole) and water (130 ml.). After 2 hours, a 50% aqueous sodium hydroxide solution (45 g.) was added to the almost solid mass. The whole was stirred under reflux for 3 hours. The oil which separated on cooling solidified. It was collected, washed with water and petroleum ether, and dried to give 111 g. (74%) of fine needles, m.p. (evacuated capillary) 110–112°.

Anal. Calcd. for $C_{17}H_{36}N_2S$: N, 9.3. Found: N, 9.1.

***t*-Octyl isothiocyanate** was prepared essentially according to the method of Moore and Crossley,[10] but with the temperature held below 25°. It was a liquid of pleasant odor, yield 81%, b.p. 67° (2.5), 108–112° (28 mm.), $n^{25}D$ 1.4811, d^{25}_{25} 0.9043.

Anal. Calcd. for $C_9H_{17}NS$: N, 8.2; S, 18.8. Found: N, 8.2; S, 18.8.

The isothiocyanate was also obtained in 20% yield from the distillation of di-*t*-octylthiourea at 120–160°, together with diisobutylene (71% yield).

In another experiment, the thiourea (30 g., 0.1 mole) and 1:4 aqueous hydrochloric acid (50 ml.) were stirred together at 92°. The solid melted and the flask was filled with fumes. After two hours, the oil was removed, washed with dilute aqueous sodium carbonate and water, and distilled to give 5 g. (45%) of diisobutylene and 8 g. (47%) of the isothiocyanate, b.p. 95–99° (25 mm.).

Anal. Found: N, 7.9; S, 18.6.

***t*-Octylurea** was not obtained from the fusion of *t*-octylamine with excess of urea. Only di-*t*-octylurea and urea were isolated together with a solid, m.p. 90–110°, which analyzed to be a mixture of mono- and di-*t*-octylurea.

It was prepared in 37% yield by the reaction of aqueous solutions of potassium cyanate and *t*-octylamine hydrochloride in equimolar amounts below 20°. Repeated

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[21] W. H. T. Davison, *J. Chem. Soc.*, 3712 (1953), reported this band for aryl isocyanates (2269 cm.$^{-1}$) and octadecyl isocyanate (2270 cm.$^{-1}$).

[22] A. Franchimont and E. Klobbie, *Rec. trav. chim.*, **7**, 353 (1888).

[23] A. Wurtz, *Ann. chim.*,]3] **42**, 61 (1854), reported m.p. 175–176°, b.p. 274°.

[24] A. Sonn, *Ber.*, **47**, 2437 (1914); C. A. Weisel, H. S. Mosher and F. C. Whitmore, THIS JOURNAL, **67**, 1055 (1945); R. H. Wiley, P. Beasley and L. H. Knabeschuh, *ibid.*, **76**, 311 (1954).

crystallization of the sirupy crude product from petroleum ether gave needles, m.p. 72–73°.

Anal. Calcd. for $C_9H_{20}N_2O$: N, 16.3. Found: N, 16.1.

1,1-Dimethyl-3-*t*-octylurea.—*t*-Octyl isocyanate (15.5 g., 0.1 mole) was heated in a pressure bottle with dimethylamine (8 g.) and ethanol (40 ml.) for 2 hours. After evaporation of solvent, the residual oil solidified (20 g.). Recrystallization from 50% alcohol gave 12.5 g. (62%) of needles, m.p. 84–85°.

Other urea derivatives were prepared similarly (Table II).

TABLE II

t-OCTYLUREAS, $RCONHC_8H_{17}$-*t*

R	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
$(CH_3)_2N-$	84–85	14.0	13.7
$\underline{CH_2C(CH_3)_2N}-$	88–89	12.3	12.3
$(CH_3)_3CNH-$	154–155	12.3	12.2
$HOOCCH_2NH-$	127–128	12.2	12.3[a]
C_6H_5NH-	136–138	11.3	11.2
$C_6H_{11}NH-$	148–148.5	11.0	10.9

[a] Neutral equivalent: calcd., 230; found, 230.

1-Isopropyl-3-*t*-octylthiourea was obtained from the reaction of *t*-octyl isothiocyanate (17.1 g., 0.1 mole), isopropylamine (5.9 g., 0.1 mole) and ethanol (30 ml.) at 40–45°. The oil which remained after evaporation of solvent solidified partially. The solid was collected, washed with water and petroleum ether, and dried; 11 g. (48%), m.p. 79°.

Other thiourea derivatives were prepared similarly (Table III).

TABLE III

t-OCTYLTHIOUREAS, $RCSNHC_8H_{17}$-*t*

R	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
NH_2-	83–85	14.9	14.5	17.0	17.2
CH_3NH-	106–108	13.8	13.8	15.8	15.6
$(CH_3)_2N-$	74–75	12.8	12.9	14.8	14.4
$(CH_3)_2NCH_2-CH_2NH-$	84–86	16.2	16.0	12.4	12.2
$(CH_3)_2CHNH-$	79	12.2	12.1	13.9	13.8
$(CH_3)_3CNH-$	99–100	11.5	11.4	13.1	13.0
C_6H_5NH-[a]	117–119	10.6	10.2	12.1	11.9

[a] Prepared from *t*-octylamine and phenyl isothiocyanate.

1-*t*-Octyl-3-phenylthiourea.—The reaction of *t*-octyl isothiocyanate (17.1 g., 0.1 mole) and aniline (13 g., 0.14 mole) in boiling ethanol (15 ml.) gave, after 48 hours, 3.2 g. of thiocarbanilide, m.p. 149.5–150°. From the filtrate, there was obtained 3.1 g. of the mixed thiourea contaminated with thiocarbanilide, m.p. 102–112°.

The desired compound was obtained by similar treatment of *t*-octylamine (16.8 g., 0.13 mole) with phenyl isothiocyanate (12.5 g., 0.09 mole) in alcohol in 23% yield; recrystallized from benzene, m.p. 117–119°.

1,3-Dicyclohexylthiourea was made in 81% yield from the reaction of equimolar amounts of *t*-octyl isothiocyanate and cyclohexylamine heated under reflux for 17 hours; recrystallized from petroleum ether, m.p. 174.5–176°.[25]

Anal. Calcd. for $C_{13}H_{24}N_2S$: N, 11.7; S, 13.3. Found: N, 11.3; S, 12.9.

Methyl N-*t*-Octylcarbamate.—*t*-Octyl isocyanate (10.3 g.) was added to a solution of sodium methylate (0.3 g.) in methanol (25 ml.). After the initial vigorous reaction subsided, the solution was heated under reflux for one hour. The catalyst was neutralized with sulfuric acid. Distillation gave 9.8 g. (79%) of a liquid with a fruity odor, b.p. 125–127° (30 mm.), $n^{25}D$ 1.4432, d^{25}_{25} 0.9368.

Anal. Calcd. for $C_{10}H_{21}NO_2$: N, 7.5. Found: N, 7.4.

Allyl N-*t*-octylcarbamate was obtained in 84% yield from a similar reaction of the isocyanate with a solution of sodium in allyl alcohol, b.p. 122–124° (26 mm.), $n^{25}D$ 1.4417, d^{20}_{20} 0.9049.

Anal. Calcd. for $C_{12}H_{23}NO_2$: N, 6.6. Found: N, 6.6.

1,3-Di-*t*-Octylcarbodiimide[11d,14]—Mercuric oxide (125 g.) was added to a solution of 1,3-di-*t*-butylthiourea (28 g., 0.13 mole) in dry ether (500 ml.) with vigorous stirring. Mercuric sulfide was collected after four hours and washed with ether. After removal of solvent and rapid distillation at 3 to 5 mm., redistillation gave 23 g. (68%) of an oil, b.p. 110–112° (3 mm.), $n^{20}D$ 1.4603.

Anal. Calcd. for $C_{17}H_{34}N_2$: C, 76.6; H, 12.9; N, 10.5. Found: C, 76.9; H, 12.8; N, 10.5.

1-*t*-Octylhydantoin.[15]—*t*-Octylamine (154.8 g., 1.2 moles) and chloroacetylurea[26] (27.3 g., 0.2 mole) were stirred under reflux for four hours. Ammonia was evolved. The cooled residue was acidified with concentrated hydrochloric acid and poured into water. The product was treated with decolorizing carbon in ethanol to give 31.8 g. (75%) of a white solid, m.p. 135–138°. A second recrystallization gave m.p. 140–141°.

Anal. Calcd. for $C_{11}H_{20}N_2O_2$: N, 13.3. Found: N, 13.0.

1-*t*-Octylparabanic acid[16] was obtained by the oxidation of 1-*t*-octylhydantoin in ethanol with excess of bromine water. The solid which separated was free of bromine, m.p. 150–151°.

Anal. Calcd. for $C_{11}H_{18}N_2O_3$: N, 12.4. Found: N, 12.2.

1,5-Di-*t*-octylbiuret.[17]—A mixture of methyl allophonate (35.4 g., 0.3 mole) and *t*-octylamine (77.4 g., 0.6 mole) was heated at 120–130° for 12 hours and finally at 160–165° for 2 hours. Ammonia was evolved and the mixture gradually became homogeneous. The solid obtained on cooling was recrystallized from ethylene dichloride, 35 g. (35%), m.p. 120–122°; after a second recrystallization from isooctane, m.p. 124–125°.

Anal. Calcd. for $C_{18}H_{37}N_3O_2$: N, 12.8. Found: N, 12.7.

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