

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Berthelot, P.E.M., *Ann. Chim. Phys.* [6] 6, 358 (1885); *Bull. Soc. Chim France*, N.S. 43, 260 (1885); *Compt. Rend.* 100, 81 (1885).

- (2) Kelley, K.K., *U. S. Bur. Mines, Bull.* 476, U. S. Dept. of Interior, Washington, D. C., 1949.
(3) Mykytiuk, D.P., M.S. thesis, University of Massachusetts, Amherst, Mass., 1959.
(4) Rossini, F.D., and coworkers, *Natl. Bur. Std. (U. S.) Circ.* 500, U. S. Dept. of Commerce, Washington, D. C., 1952.

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Tetrasubstituted Ureas as Thermally Stable Fluids

Blocking of β -Elimination by Fluorine Substitution

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Six tetrasubstituted ureas were synthesized and evaluated for thermal and oxidative stability. This work was based on the premise that unsymmetrical tetrasubstituted ureas containing only aromatic and fluorinated alkyl substituents could not decompose by the β -elimination mechanism and would have low enough melting points to be useful as high-temperature fluids. These compounds were found to have good oxidative and thermal stability, but relatively high volatility and limited liquid range.

AWARENESS of the high bond energies of such bonds as B—O, Al—O, and Sn—O has led in recent years to numerous attempts to prepare high temperature inorganic-organic polymers which would be stable to 1000° F.

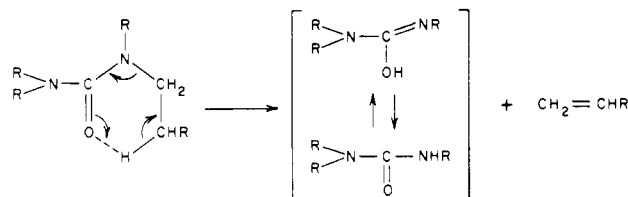
One fundamental difficulty in the study of these inorganic-organic systems is that part of the bond dissociation energy of many of these bonds is a function of electronegativity difference—in other words there is a large ionic contribution. The consequences are hydrolytic and oxidative susceptibility, and the ability to change partners.

For the immediate future, it is suggested that practical results will be obtained by utilizing current concepts to improve more familiar systems. The carbon-carbon bond requires 80–90 kcal. to effect homolytic cleavage. This represents a decomposition rate of about 1% per hour at 700° C. Most organic compounds decompose at temperatures far below those expected from consideration of bond dissociation energies since, whenever possible, a molecule will decompose by processes requiring less energy than that of simple homolytic cleavage. A well-documented example is the cleavage of esters, a process which takes place so smoothly at moderate temperatures that the reaction is used as a convenient route to olefins. It is generally assumed that a quasi six-membered ring is involved (3).



This mechanism amounts to concerted cleavage of a beta C—H bond and the ester C—O bond assisted by simultaneous attack of a carbonyl group. Blocking this mechanism by use of phenyl esters or by substitution of alkyl groups or fluorine on the β -carbon atom increases thermal stability.

Aliphatic ureas probably decompose thermally through a similar mechanism, the initial stage of which is shown.

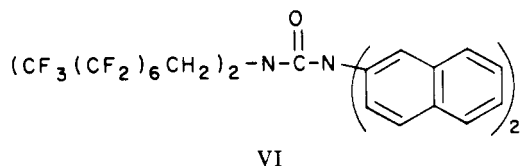
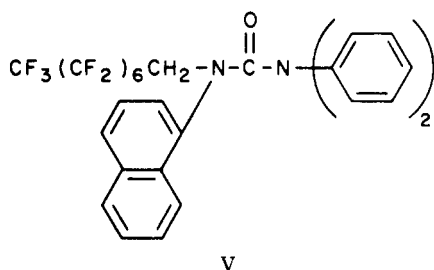
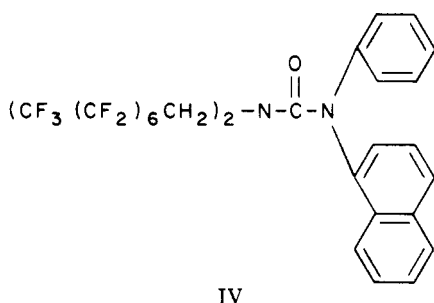
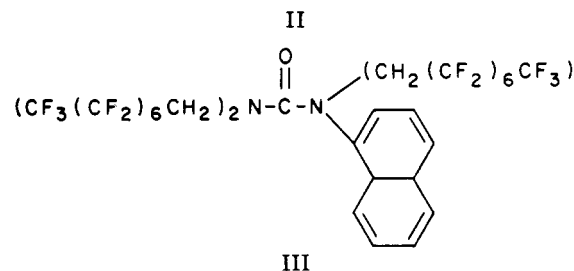
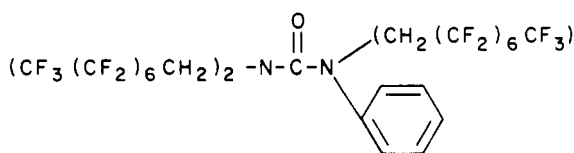
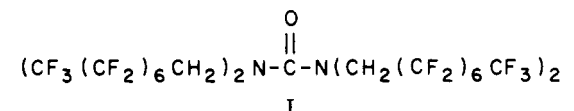


This mechanism is not permitted to tetra-aryl ureas which, in consequence, show enhanced stability (1). Their utility as thermally stable fluids, however, is limited by their high melting points. The work reported here was

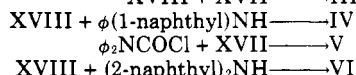
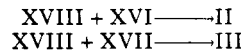
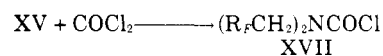
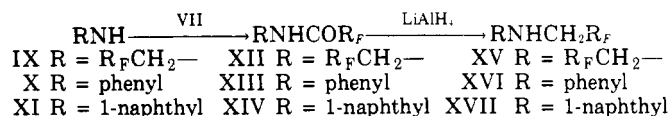
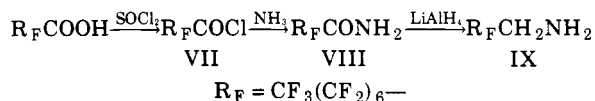
based on the premise that one or more fluorinated alkyl substituents would provide low melting tetrasubstituted ureas without seriously impairing thermal stability.

These tetrasubstituted ureas were prepared:

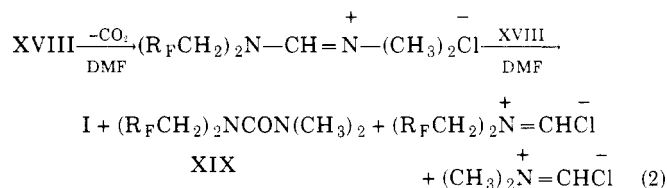
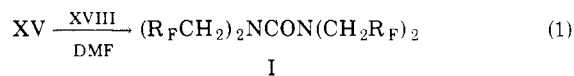
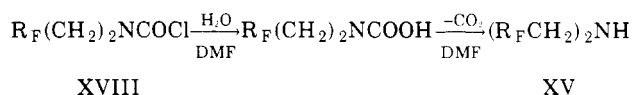
Tetrakis(1,1-dihydropentadecafluorooctyl)urea(I)
 Tris-(1,1-dihydropentadecafluorooctyl)phenylurea(II)
 Tris-(1,1-dihydropentadecafluorooctyl)-1-naphthylurea(III)
 Bis-(1,1-dihydropentadecafluorooctyl)-1-naphthylphenylurea(IV)
 N-(1,1-dihydropentadecafluorooctyl)-N-(1-naphthyl)-diphenyl-urea(V)
 Bis-(1,1-dihydropentadecafluorooctyl)-bis-(2-naphthyl)urea(VI)



Compounds II-VI were synthesized according to the following generalized scheme; the final step in each case was the reaction of the appropriate secondary carbamoyl chloride and secondary amine at 200-350° C.



When bis (1,1-dihydropentadecafluorooctyl)amine (IX) was heated with bis (1,1-dihydropentadecafluorooctyl)carbonyl chloride (XIII) at 300-350° C., no reaction took place. A number of experiments using pyridine, dimethylsulfoxide, and sodium hydride in toluene failed to give any urea. When the reaction was carried out in refluxing dimethylformamide, tetrakis(1,1-dihydropentadecafluorooctyl)urea (I) was obtained in yields of 20-40%. Surprisingly, on heating the carbamoyl chloride alone in dimethylformamide at 100°, a 50% yield of the urea was obtained. At least two different mechanisms may be formulated to account for the reaction course.



Mechanism 1 requires a solvent-catalyzed hydrolysis and decarboxylation followed by a catalyzed addition of the amine to carbamoyl chloride. Catalysis at each step seems a necessary postulate since hydrolysis of the carbamoyl chloride in water-tetrahydrofuran is quite slow, and the addition of the amine to the carbamoyl chloride does not occur in the absence of dimethylformamide. This mechanism suggests that addition or removal of traces of water or addition of amine to the system should have some effect on the yield of urea. However, no such effects were found. Evolution of carbon dioxide was noted.

Mechanism 2 is quite different in that solvent directly participates in the reaction via the known (2) intermediate

type, $(\text{R}_\text{F}\text{CH}_2)_2\text{NC}=\text{O}-\text{OCH}=\text{N}(\text{CH}_3)_2\text{Cl}$, which on losing carbon dioxide may form the amine-immonium ion which can then react with more carbamoyl chloride, giving (I) and the dimethylurea (XIX). No evidence was found for the presence of the dimethylurea or either of the chloro-immoniumchlorides; however, they could well have been overlooked in the workup. Mechanism 2 or some variation of it is favored despite the fact that most evidence bearing on the matter is equivocal.

For present purposes, a quick screening indicated that thermal stabilities were in the range of interest. For example, more than 96% of tris(1,1-dihydropentadecafluorooctyl)phenylurea (II) was recovered unchanged after 15 hours in a sealed tube at 365–375° C.

Oxidative stability tests indicated that the best compound, tris(1,1 - dihydropentadecafluorooctyl)phenylurea (II), was comparable to the commercial Cellutherm lubricant (Cellutherm 2505-B, a trimethylolpropane ester supplied by Celanese Corp.). However, (II) was appreciably more volatile than Cellutherm. Replacement of the phenyl or the 1,1-dihydropentadecafluorooctyl moiety by naphthyl decreased volatility but also decreased oxidative stability. None of the ureas prepared had sufficiently low melting points to be of immediate practical importance.

SYNTHESIS

Tetrahydrofuran was distilled from lithium aluminum hydride and stored under nitrogen. Dimethylformamide was stored over calcium hydride.

Infrared spectra were taken on a Beckman IR-4 with sodium chloride optics.

Gas-liquid chromatography was carried out on an Aerograph Chromatograph (Wilkens Instrument) using a 6 foot $\times$ $\frac{1}{4}$ inch column packed with silicone, 30W, 3% on firebrick. Merck acid-washed alumina was used in the liquid-solid chromatography.

1,1-Dihydropentadecafluorooctylamine (IX). A solution of 35 grams (0.085 mole) of pentadecafluorooctanoic acid (Peninsular Chemical Research, and Matheson, Coleman, and Bell), 7.3 ml. (12 grams, 0.10 mole) of thionyl chloride, 0.5 ml. of dimethylformamide, and 100 ml. of benzene was refluxed for three hours. Ether (350 ml.) was added and dry ammonia was passed through the solution for one hour, while cooling with an ice bath. The reaction mixture was extracted with three 250-ml. portions of water (slow separations). Benzene (1 liter) was added to the organic phase; the solution was brought to boiling, decanted from the excess water, boiled down to a volume of 700 ml., and cooled to 5° C.; the pentadecafluorooctanamide (VIII) was separated by filtration and washed with cold benzene; wt. = 26 grams (75% yield); m.p. 138–140° C.; $\lambda_{\text{max}}^{\text{nujol}}$ 2.99, 3.15, 5.85, 6.25 μ .

Lithium aluminum hydride (4) (16.7 grams, 0.44 mole) was added to dry tetrahydrofuran (250 ml.) in a two-liter flask equipped with mechanical stirrer, gas inlet tube, addition funnel, and condenser, all of which had been previously flamed out in a stream of dry nitrogen. A solution of 81 grams (0.20 mole) of perfluorooctanamide in dry tetrahydrofuran (500 ml.) was added within a half-hour period to the stirred suspension under dry nitrogen at 0° C. The suspension was brought to boiling (two hours), refluxed for 16 hours under nitrogen, cooled with a dry ice-methanol bath, and decomposed by adding successively a solution of 17 ml. of water in 250 ml. of tetrahydrofuran (cautiously), 51 ml. of 15% solution of sodium hydroxide, and 17 ml. of water. The suspension was filtered and the insolubles were washed well with ether. The filtrate was concentrated by boiling on a steam bath, collecting the distillate after the vapor temperature rose to 55° C. In order to recover codistilled product, the distillate was saturated with dry hydrogen chloride and the resulting suspension was evaporated to dryness at 20 mm. of Hg pressure. The residue was dissolved in water, excess sodium hydroxide solution was added, and the solution was extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and evaporated on a steam bath to a volume of 15 ml. This was combined with the main reaction product and distilled at atmospheric pressure through a 15-inch spinning band column.

Thirty-nine grams (50% yield) of 1,1-dihydropentadecafluorooctyl amine (IX) was collected; b.p. 150–152°; n_D^{25} 1.3075.

N - (1,1 - Dihydropentadecafluorooctyl)pentadecafluorooctanamide (XII). Pentadecafluorooctanoyl chloride (VII) was prepared by refluxing for 2½ hours a solution of 100 grams of pentadecafluorooctanoic acid, 50 ml. of thionyl chloride, and 0.5 ml. of dimethylformamide. It was purified by distillation through an 18-inch Vigreux column. (A large excess of thionyl chloride should be avoided because the product forms an azeotrope with it.) A 70% yield was obtained; b.p. 133–134°; n_D^{25} = 1.3039; $\lambda_{\text{max}}^{\text{film}}$ 5.55 μ .

The 1,1-dihydropentadecafluorooctylamine (IX) (16.0 grams, 0.040 mole) was added dropwise within a 5-min. interval to a mechanically stirred emulsion of 18.0 grams (0.042 mole) of pentadecafluorooctanoyl chloride (VII) in 16 ml. of dry pyridine with cooling. The thick suspension was stirred at 35° C. for 30 min. Water (65 ml.) was added dropwise. The reaction mixture was cooled in ice, and filtered. The crude product was washed well with water and recrystallized from an ethanol-water mixture (9:1); wt. = 27 grams (85% yield); m.p. 95–105°. A sample of the amide was recrystallized twice by dissolving in boiling acetone, adding five volumes of benzene, and boiling off most of the acetone to give an analytical sample, m.p. 106–110°; $\lambda_{\text{max}}^{\text{nujol}}$ 5.82 μ . *Anal.*: Calcd. for $C_{16}H_{33}NOF_{30}$ (795.2); C, 24.2; H, 0.38; N, 1.76. Found: C, 24.1; H, 0.46; N (Dumas), 1.73.

Bis(1,1-dihydropentadecafluorooctyl)amine (XV). The reduction of N-(1,1-dihydropentadecafluorooctyl)pentadecafluorooctanamide (XII) (52 grams) by lithium aluminum hydride (7.6 grams) in the manner previously described required a 40-hour reflux period (4). The solvents were removed at 20 mm. of Hg pressure. Ether was added to the residue and a small amount of insoluble material was filtered off. The filtrate was saturated with dry hydrogen chloride and the amine hydrochloride was collected by filtration; wt. = 44 grams (80% yield).

The hydrochloride salt was distributed between ether and sodium bicarbonate solution. The ether solution was separated, dried over sodium sulfate, and concentrated to a white solid residue which was recrystallized from cold benzene to give a good recovery of product; m.p. 42143°; $\lambda_{\text{max}}^{\text{film}}$ 2.94 μ . *Anal.*: Calcd. for $C_{16}H_{33}NF_{30}$ (781.2); C, 24.6; H, 0.64; F, 73.0. Found: C, 25.1; H, 0.60; F, 73.65.

1,1 - Dihydropentadecafluorooctylphenylamine (XVI). N-Phenylpentadecafluorooctanamide (XIII) (8.5 grams, 0.017 mole) was prepared from perfluorooctanoyl chloride (VII) and aniline in 66% yield, m.p. 105–107°, and was reduced with lithium aluminum hydride (1.2 grams, 0.031 mole) in the manner previously described (4). The reaction solution after removal of the inorganic salts was concentrated to a residue of 8 grams, which was crystallized from methanol-water (20 ml.:6 ml.) at 25° to give 4.5 grams (55% yield) of the phenylamine (XVI); m.p. 42–43°; $\lambda_{\text{max}}^{\text{CCl}_4}$ 2.90 μ . A sample was evaporatively transferred at 60–70°/0.1 mm. of Hg for analysis; m.p. 43°. *Anal.*: Calcd. for $C_{14}H_{25}NF_{15}$ (475.2); C, 35.3; H, 1.68; N, 2.95. Found: C, 35.5; H, 1.76; N, 2.94.

Bis(1,1 - dihydropentadecafluorooctyl)carbamoyl chloride (XVIII). Bis-(1,1-dihydropentadecafluorooctyl)amine (XV) (15.0 grams) was placed in a stainless steel bomb of 120-ml. capacity, which was then evacuated and flushed with dry nitrogen. Phosgene (50 grams) was introduced and the bomb was shaken at 140° for 16 hours; cooled to 25°, and vented. The contents were dissolved in ether and the solution was washed with 0.1N hydrochloric acid and with water, dried over sodium sulfate, and concentrated to a fluid oil; wt. = 16 grams (100% yield). The bis-(1,1-dihydropentadecafluorooctyl)-carbamoyl chloride was crystallized in good yield from cold petroleum ether; m.p. 22°, n_D^{25} 1.3287; $\lambda_{\text{max}}^{\text{heat}}$ 5.7 μ . A sample was evaporatively transferred at 70°/0.1 mm. of Hg for analysis. *Anal.*: Calcd. for

$C_{17}H_4NOClF_{30}$ (843.7): C, 24.2; H, 0.48; Cl, 4.21. Found: C, 23.9; H, 0.56; Cl, 4.33.

Tetrakis(1,1-dihydropentadecafluorooctyl)urea (I). A suspension of 3.16 grams (0.0037 mole) of bis(dihydropentadecafluorooctyl)carbamoyl chloride (XVIII) and 2 ml. of dimethylformamide (stored over calcium hydride) was stirred at 95° for 16 hours. The suspension was cooled to 0° and the dimethylformamide was decanted. The product was washed with benzene and dissolved in 250 ml. of ether. The ether solution was washed with 6*N* hydrochloric acid, then with water, dried over sodium sulfate, concentrated to a volume of 10 ml., cooled to 0°, and filtered. The white crystalline urea (I) was washed with chloroform and dried. Wt. = 1.5 grams (50% yield); m.p. 87–90°. A sample was recrystallized twice from ether; m.p. 91–92°; $\lambda_{\text{max}}^{\text{nujol}}$ 5.92 μ . *Anal.*: Calcd. for $C_{33}H_8N_2OF_{60}$ (1588): C, 24.9; H, 0.50; F, 71.8. Found: C, 25.2; H, 0.62; F, 71.1.

Tris(1,1 - dihydropentadecafluorooctyl)phenylurea (II). *N* - (1,1 - dihydropentadecafluorooctyl)phenylamine (XVI) (2.3 grams, 0.0048 mole) and 4.1 grams (0.0048 mole) of bis(1,1 - dihydropentadecafluorooctyl)carbamoyl chloride (XVIII) were introduced into a thick-walled glass tube. The tube was evacuated, sealed, heated in a furnace at 240° for 16 hours, cooled to 25°, and opened. The contents were triturated with ether, and a small amount of black material was filtered off. The filtrate was concentrated to a viscous oil, the infrared spectrum of which showed trace amounts of both starting materials. Distillation, using a Hickman molecular still, afforded both starting materials in the first fractions, followed by a pure sample of the urea (II) at 150°/0.1 mm. of Hg. This sample showed no evidence of contamination in infrared and gas chromatographic analysis, but appeared turbid. A clear, viscous oil was obtained after trituration with heptane; $\lambda_{\text{max}}^{\text{neat}}$ 5.92 μ . *Anal.*: Calcd. for $C_{31}H_{11}N_2OF_{45}$ (1282.4): C, 29.05; H, 0.86; N, 2.18. Found: C, 28.6; H, 0.65; N, 2.14.

***N* - (1 - naphthyl) - pentadecafluorooctanamide (XIV).** 1-Naphthylamine (XI) (7.2 grams, 0.050 mole) was added to a stirred mixture of pentadecafluorooctanoyl chloride (VII) (21.7 grams, 0.050 mole) and 19 ml. of dry pyridine. The mixture was cooled to 25° C. and stirred for 30 min.; then 70 ml. of water was added and the mixture cooled in ice. The solid was filtered and washed with water, wt. 25 grams. Recrystallization from 250 ml. benzene gave 19 grams white crystals, m.p. 141–143°; another crystallization afforded material, m.p. 143–144.5°. *Anal.*: Calcd. for $C_{10}H_8NOF_{15}$ (539.2): C, 40.2; H, 1.49; N, 2.60. Found: C, 40.0; H, 1.26; N, 2.55.

1,1 - Dihydropentadecafluorooctyl - 1 - naphthylamine (XVII). A solution of 17.7 grams (33 mmole) of the amide (XIV) in 100 ml. tetrahydrofuran was added dropwise to a suspension of 2.5 grams (64 mmole) of lithium aluminum hydride in 75 ml. of tetrahydrofuran at 0° (4). The mixture was refluxed for 16 hours, cooled with a dry ice-methanol bath, and decomposed by cautious addition of a solution of 2.5 ml. water in 25 ml. of tetrahydrofuran. Eight ml. of 15% NaOH solution and 2.5 ml. additional water were added dropwise to the mixture at 25°. The mixture was stirred for an hour and filtered. The precipitate was washed with ether and the solvents were evaporated from the filtrate. The crude amine (20 grams) was dissolved in 250 ml. of pentane, treated with charcoal, and evaporated; the residue weighed 16 grams. Two recrystallizations from ethanol gave 8.7 grams of product, m.p. 81–82°. *Anal.*: Calcd. for $C_{18}H_{10}NF_{15}$ (525.3): C, 41.2; H, 1.92; N, 2.67. Found: C, 41.7; H, 1.85; N, 2.68.

Tris(1,1 - dihydropentadecafluorooctyl) - 1 - naphthylurea (III). A mixture of 1.18 grams (2.2 mmole) of 1,1-dihydropentadecafluorooctyl-1-naphthylamine (XVII) and 1.90 grams (2.2 mmole) bis(1,1-dihydropentadecafluorooctyl)-carbamoyl chloride (XVIII) in an evacuated sealed glass tube was heated at 265° for 20 hours. Ether trituration

gave 2.57 grams of a viscous dark oil. The oil was evaporatively distilled at 0.1 mm. of Hg, giving three fractions—25–140°, trace oil and crystals; 160°, 0.6 grams; 180°, 1 gram clear oil which was crystallized from heptane, m.p. 47–55°, wt. 0.75 grams, $\lambda_{\text{max}}^{\text{film}}$ 5.9 μ . A small sample, which had begun to melt at 47°, was taken up to 53° and cooled slowly to 25°. It subsequently melted at 57–60°. *Anal.*: Calcd. for $C_{35}H_{13}N_2OF_{45}$ (1332): C, 31.5; H, 0.98; N, 2.10. Found: C, 31.5; H, 1.34; N, 2.09.

Table I. Thermal Stability^a of Tetrakis(1,1-dihydropentadecafluorooctyl)urea (I)

Temp., ° C.	Time (Hrs.)	Per cent Recovered	M.P. (° C.)
270	63	99	88–90
296	30	95	84–90
320 ^b	63	80	81–90
360	15	40	74–85

^a Infrared spectra were identical for all samples. ^b Sample heated at 320°/63 hours was recycled with same results.

Table II. Thermal Stability of Tris(1,1-dihydropentadecafluorooctyl)phenylurea (II)

Temp., ° C.	Time (Hrs.)	Per cent Recovered	IR Spectrum
300	30	100	Unchanged
325	63	> 96	Unchanged
370	15	> 96	Unchanged
395	30	15	Weak 2.9–3.4 μ absorption
415	15	30	Weak 2.9–3.4 μ absorption

Table III. Oxidative Stability Tests

Compound	Temp., ° C.	Time (Hr.)	Results
Cellutherm	371	6	Some carbon; darkened; still fluid.
(I)	316	3	Partial decomp.; etching of walls.
(II)	371	6	Partial decomp.; etching
(III)	316	6	Partial decomp.; deposits.
(IV)	316	6	Partial decomp.; deposits.
(V)	260	44	Considerable deposits on walls.

Table IV. Volatility Test—175° C

Compound	Time (Hr.)	Weight Remaining (Mg.)
Cellutherm	0	25
	5	19
	19	0
(I) ^a	0	13
	0.25	2
(II)	0	22
	1	17
	5	0
(III)	0	28
	5	10
	19	0
(IV)	0	28
	5	8
	19	0
(V)	0	37
	5	24
	19	12
	67	1 ^b
(VI)	0	16
	5	10
	19	3
	67	0

^a Tested at 150° C. ^b (Decomposition).

Bis(1,1 - dihydropentadecafluorooctyl) -1- naphthylphenylurea (IV). A mixture of 0.163 grams (3.0 mmole) phenyl-1-naphthylamine and 2.77 grams (3.2 mmole) bis(1,1-dihydropentadecafluorooctyl)carbonyl chloride (XVIII) was heated in an evacuated sealed glass tube at 320° for two hours. The contents of the tube were dissolved in ether (15 ml.) and filtered. Dry hydrogen chloride was passed into the ether. The ether solution was filtered to remove hydrochloride salt and washed twice with water, then dried over sodium sulfate. The ether was evaporated, giving 2.2 grams of viscous oil.

The oil was dissolved in hexane and placed on a chromatographic column (diameter = 30 mm.) containing 90 grams of alumina. The column was eluted with 175 ml. of cyclohexane:benzene (1:1). This effluent contained starting materials. Another 200 ml. of mixed solvent eluted 1.40 grams viscous oil ($\lambda_{\text{max}}^{\text{film}} = 5.92 \mu$). The oil was crystallized thrice from cold absolute ethanol, m.p. 89–90°. *Anal.*: Calcd. for $\text{C}_{30}\text{H}_{19}\text{N}_2\text{OF}_{15}$ (720): C, 51.7; H, 2.66; N, 3.89. Found: C, 52.3; H, 3.43; N, 4.30.

N-(1,1 - dihydropentadecafluorooctyl) -N-(1 - naphthyl)-diphenylurea V. A mixture of 0.46 grams (2.0 mmoles) of diphenylcarbonyl chloride and 1.3 grams (2.5 mmoles) of 1,1 - dihydropentadecafluorooctyl -1- naphthylamine XVII was heated at 230° for 17 hours in a sealed tube. The tube was cooled, and the contents were dissolved in ether; the solution was filtered and concentrated to 1.6 grams of a dark oil.

A solution of this oil in five ml. of cyclohexane was placed on a column of seven grams of alumina. Elution with 100 ml. of cyclohexane gave 1.06 grams of a yellow oil which was discarded. Subsequent elution with 50 ml. of benzene gave 0.61 grams of a yellow oil which showed about 5% impurity on gas chromatography. This material was evaporatively distilled, and a fraction collected at 200°/0.1 mm. of Hg was crystallized from pentane at -10° to yield 0.54 gram of a chromatographically pure sample m.p. 71–74°, $\lambda_{\text{max}}^{\text{film}} = 5.98 \mu$. *Anal.*: Calcd. for $\text{C}_{31}\text{H}_{19}\text{N}_2\text{OF}_{15}$ (720.5): C, 51.7; H, 2.66; N, 3.89. Found: C, 52.3; H, 3.42; N, 4.30.

Bis(1,1 - dihydropentadecafluorooctyl) - bis(2 - naphthyl)-urea (VI). A mixture of 1.25 grams of bis(1,1-dihydropentadecafluorooctyl)carbonyl chloride (XVIII) (1.5 mmole) and 0.40 grams of di-2-naphthylamine (1.5 mmole) was treated at 355° for one hour in an evacuated sealed tube. Trituration of the tube contents with ether gave 0.43 grams of black insoluble material. The ether solution was con-

centrated to 1.1 grams of viscous oil. Trituration of the oil with cold benzene gave 0.45 grams insolubles ($\lambda_{\text{max}}^{\text{film}} = 6.0 \mu$, wk.) and 0.55 grams solubles ($\lambda_{\text{max}}^{\text{film}} = 5.92 \mu$).

The benzene soluble fraction was dissolved in 10 ml. warm cyclohexane and chromatographed on 15 grams alumina (column diameter = 13 mm.) using cyclohexane:benzene (1:1). The first 30 ml. of effluent was discarded, and the product appeared in the next 60 ml. (wt. 0.16 grams). This was crystallized from cold ethanol; the crystals melted upon warming to room temperature. *Anal.*: Calcd. for $\text{C}_{37}\text{H}_{18}\text{N}_2\text{OF}_{30}$ (1077): C, 41.2; H, 1.69; N, 2.61. Found: C, 41.3; H, 1.63; N, 2.29.

EVALUATION

Thermal stability tests were carried out on tetrakis(1,1-dihydropentadecafluorooctyl)urea (I) and on tris(1,1-dihydropentadecafluorooctyl)phenylurea (II) by placing small samples (50–100mg.) of purified materials in evacuated, sealed tubes. The tubes were placed in an aluminum block furnace for specified periods of time at constant temperature ($\pm 5^\circ$). After the heating period, each sample was evaporatively distilled to the other end of the tube; the recovered urea was weighed and its infrared spectrum taken. In the case of tetrakis(1,1-dihydropentadecafluorooctyl)urea (I), melting points of the recovered samples were also noted. Tables I and II summarize the results.

Oxidative stability tests were carried out to obtain preliminary information by heating the urea samples in sealed glass tubes in excess oxygen at temperatures which led to significant changes in the materials. Celanese high temperature lubricant Cellutherm 2505-B (a trimethylolpropane ester) was used as a standard for comparison. Results are summarized in Table III.

Comparative volatility data were obtained by measuring weight loss with time at a fixed temperature in a static oven test. Again, Cellutherm 2505-B was used as a standard. Results are summarized in Table IV.

LITERATURE CITED

- (1) Chapelow, C.C., Jr., WADC Technical Report 57-657.
- (2) Gold, H., *Angew. Chem.* **72**, 956 (1960).
- (3) Hurd, C.D., Blunck, F.H., *J. Am. Chem. Soc.* **60**, 2419 (1938).
- (4) Husted, D.R., Ahlbrecht, A.H., *Ibid.* **75**, 1608 (1953); Micovic, V.M., Mihailovic, M., *J. Org. Chem.* **18**, 1190 (1953).

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Boiling Points and Boiling Point Numbers of Trivalent Organoarsenic Compounds

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Application of the Kinney equation, b.p. in °C. = 230.14 (total boiling point number)^{1/3} - 543, furnishes satisfactory results in calculations of normal boiling points of 50 trivalent organoarsenic compounds; the average error is 2.5°. This involves use of typical Kinney values such as carbon, 0.80, hydrogen, 1.00, and side chain methyl, 3.05. Of the 50 trivalent organoarsenic compounds 11 have only alkyl or aryl and aryl groups attached to arsenic, 8 have hydrogen attached to arsenic, and 31 have halogen attached to arsenic. Ten new boiling point numbers for arsenic, halogen and the phenyl group serve in these calculations.

ACCEPTABLE RESULTS occur in application of the Kinney equation (14):

$$\text{b.p. in } ^\circ\text{C.} = 230.14 (\text{total boiling point number})^{1/3} - 543 \quad (1)$$

in calculations of the normal boiling points of hydrocarbons (14), silanes and organosilicon compounds (17), germanes

and alkylgermanium compounds (2), boranes and alkylboron compounds (2), alkyl derivatives of bivalent sulfur, selenium and tellurium (2), and also alkyl derivatives of trivalent organophosphorus compounds (2).

Attempted derivation of the boiling point numbers (b.p.n.s) for sulfur and hydrogen from the b.p.n.s. of H_2S