Bis(1,1 - dihydropentadecafluoroöctyl) -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-dihydropentadecafluoroöctyl)carbamoyl 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 ($\lambda^{\text{film}}_{\text{max.}} = 5.92\ \mu$). The oil was crystallized thrice from cold absolute ethanol, m.p. 89–90°. *Anal:* Calcd. for $C_{30}H_{19}N_2OF_{15}$ (720): C, 51.7; H, 2.66; N, 3.89. Found: C, 52.3; H, 3.43; N, 4.30.

N-(1,1-dihydropentadecafluoroöctyl) -N- (1 - naphthyl)-diphenylurea V. A mixture of 0.46 grams (2.0 mmoles) of diphenylcarbamoyl chloride and 1.3 grams (2.5 mmoles) of 1,1 - dihydropentadecafluoroöctyl -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°, $\lambda^{\text{film}}_{\text{max.}}$ 5.98 μ. *Anal:* Calcd. for $C_{31}H_{19}N_2OF_{15}$ (720.5): C, 51.7; H, 2.66; N, 3.89. Found: C, 52.3; H, 3.42; H, 4.30.

Bis(1,1 - dihydropentadecafluoroöctyl) - bis(2 - naphthyl)-urea (VI). A mixture of 1.25 grams of bis(1,1-dihydropentadecafluoroöctyl)carbamoyl 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 concentrated to 1.1 grams of viscous oil. Trituration of the oil with cold benzene gave 0.45 grams insolubles ($\lambda^{\text{film}}_{\text{max.}} = 6.0\ \mu$, wk.) and 0.55 grams solubles ($\lambda^{\text{film}}_{\text{max.}}$ 5.92 μ).

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 $C_{37}H_{18}N_2OF_{30}$ (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-dihydropentadecafluoroöctyl)urea (I) and on tris(1,1-dihydropentadecafluoroöctyl)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 (±5°). 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-dihydropentadecafluoroöctyl)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 alkyl 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*):

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

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

Table I. Boiling Point Numbers of Atoms and Groups[a]

Configurations of Arsenic

	R_3As	$R_2As—$	$RAs=$	$As\equiv$
As	6.18 ± 0.11[b]	7.69 ± 0.29	7.50 ± 0.15	6.55

All Configurations of Phenyl[d]

C_6H_5	19.81 ± 0.51

Configurations of Halogen or Halogenoid

Halogen (oid)	R_2AsX	$RAsX_2$	AsX_3
F	4.07[c]	3.83 ± 0.27	3.90
Cl	7.08 ± 0.18	6.65 ± 0.26	6.16
Br	9.60 ± 0.05	9.88 ± 0.07	10.01
I	12.04 ± 0.62	. . .	. . .
CN	13.39[c]	. . .	. . .
NCO	. . .	. . .	10.16

[a] C, 0.80; H, 1.00; side chain methyl, 3.05; double bond in $CH_2=CHCH_2As(CH_3)_2$, 1.50. [b] Root mean square errors. [c] The normal boiling point of only one compound of this type is available.

[d] In methyl group(s) attached to phenyl use 0.80 for each carbon and 1.00 for each hydrogen. For chlorine on phenyl use 6.04 as in $CH_2=CHCl$.

Table II. Calculations of Boiling Points of Organoarsenic Compounds

	B.P.N.		B.P., °C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
$(CH_3)_3As$	17.58	17.38	55.4	53.1	2.3	(*25*)
$(C_2H_5)(CH_3)_2As$	20.38	20.41	85.6	86	−0.4	(*13*)
$(C_2H_5)_2(CH_3)As$	23.18	23.16	113.2	113	0.2	(*5*)
$(CH_2=CHCH_2)(CH_3)_2As$	22.68	22.74	108.4	109	−0.6	(*5*)
$(C_2H_5)_3As$	25.98	26.11	138.6	139.8	−1.2	(*11*)
$(CH_3)_2(C_6H_5)As$	33.59	33.65	199.6	200	−0.4	(*22*)
$4\text{-}CH_3C_6H_4As(CH_3)_2$[a]	36.39	36.44	219.7	220	−0.3	(*21*)
$(C_2H_5)_2(C_6H_5)As$	39.19	39.38	238.7	240	−1.3	(*21*)
$4\text{-}CH_3C_6H_4As(C_2H_5)_2$[a]	41.99	40.91	256.9	250	6.9	(*21*)
$(CH_3)(C_6H_5)_2As$	49.60	50.20	302.6	306	−3.4	(*22*)
$(C_2H_5)(C_6H_5)_2As$	52.40	52.73	318.2	320	−1.8	(*22*)
$(CH_3)_2AsH$	16.29	15.95	40.4	36.3	4.1	(*8*)
$(C_2H_5)(CH_3)AsH$	19.09	18.95	72.1	70.6	1.5	(*29*)
$(CH_3)(n\text{-}C_3H_7)AsH$	21.89	21.94	100.8	101.3	−0.5	(*29*)
$(C_2H_5)_2AsH$	21.89	22.32	100.8	105	−4.2	(*29*)
$(CH_3)_2AsCl$	22.37	22.50	105.5	106.7	−1.2	(*26*)
$(C_2H_5)_2AsCl$	27.97	28.16	155.6	157.2	−1.6	(*3*)
$(C_2H_5)(n\text{-}C_3H_7)AsCl$	30.77	30.68	178.1	177.5	0.6	(*3*)
$(CH_3)(C_6H_5)AsCl$	38.38	37.97	233.3	230.5	2.8	(*26*)
$(C_2H_5)(C_6H_5)AsCl$	41.18	40.76	251.7	249	2.7	(*30*)
$(iso\text{-}C_5H_{11})_2AsCl$	43.27	43.02	265.0	263.4	1.6	(*8*)
$(C_6H_5)_2AsCl$	54.39	55.14	329.0	333	−4.0	(*21*)
$(4\text{-}CH_3C_6H_4)(C_6H_5)AsCl$[a]	57.39	57.83	343.7	347[b]	−3.3	(*21*)
$(CH_3)_2AsBr$	24.89	24.84	129.0	128.5	0.5	(*27*)
$(CH_3)(C_2H_5)AsBr$	27.69	27.75	153.3	153.5	−0.2	(*12*)
$(CH_3(C_6H_5)AsBr$	40.90	40.91	249.9	250	−0.1	(*30*)
$(CH_3)_2F$[c]	. . .	19.36	. . .	75	. . .	(*6*)
$(CH_3)_2AsI$	27.33	27.96	150.3	154.5	−4.2	(*27*)
$(C_2H_5)_2AsI$	32.93	32.31	194.6	190	4.6	(*16*)
$(CH_3)_2AsCN$[c]	. . .	28.68	. . .	161.5	. . .	(*6*)
CH_3AsH_2	13.30	13.29	2.3	2.2	0.1	(*23*)
$C_2H_5AsH_2$	16.10	15.92	38.1	36	2.1	(*7*)
$n\text{-}C_5H_{11}AsH_2$	24.50	24.69	125.4	127.2	−1.8	(*3*)
$2\text{-}ClC_6H_4AsH_2$[a]	34.35	34.47	205.1	206	−0.9	(*24*)
CH_3AsCl_2	24.60	25.29	126.3	132.5	−6.2	(*10*)
$C_2H_5AsCl_2$	27.40	27.94	150.8	155.3	−4.5	(*10*)
$n\text{-}C_3H_7AsCl_2$	30.20	30.40	173.7	175.3	−1.6	(*10*)
$iso\text{-}C_3H_7AsCl_2$	29.45	29.56	167.7	168.6	−0.9	(*10*)
$n\text{-}C_4H_9AsCl_2$	33.00	32.85	195.2	194.1	1.1	(*10*)
$sec\text{-}C_4H_9AsCl_2$	32.25	31.24	189.5	181.8	7.7	(*10*)
$n\text{-}C_5H_{11}AsCl_2$	35.80	35.43	215.5	212.9	2.6	(*10*)
$C_6H_5AsCl_2$	40.61	41.44	248.1	253.5	−5.4	(*15*)
$4\text{-}CH_3C_6H_4AsCl_2$[a]	43.41	43.60	265.8	267	−1.2	(*21*)
$3\text{-}CH_3C_6H_4AsCl_2$[a]	43.41	44.08	265.8	270	−4.2	(*21*)
$2\text{-}CH_3C_6H_4AsCl_2$[a]	43.41	43.11	265.8	264	1.8	(*21*)
$2,4\text{-}(CH_3)_2C_6H_3AsCl_2$[a]	46.21	45.40	282.9	278	4.9	(*21*)
$2,5\text{-}(CH_3)_2C_6H_3AsCl_2$[a]	46.21	46.57	282.9	285	−2.1	(*21*)
CH_3AsBr_2	31.06	31.22	180.4	181.7	−1.3	(*21*)
$C_2H_5AsBr_2$	33.86	33.72	201.5	200.5	1.0	(*20*)
$C_6H_5AsBr_2$	47.07	46.57	288.0	285	3.0	(*15*)
CH_3AsF_2	18.96	19.50	70.7	76.5	−5.8	(*19*)
$C_2H_5AsF_2$	21.76	21.23	99.5	94.3	5.2	(*19*)

[a] The connection of arsenic is to carbon atom number one.
[b] Approximate boiling point.
[c] The only example of this configuration.

and H_2S_2 is unsuccessful (*2*); attempted derivation of the b.p.n.s for phosphorus and hydrogen from the b.p.n.s of PH_3 and P_2H_4 also is unsuccessful (*2*). However, with bivalent sulfur, selenium, and tellurium and with trivalent phosphorus, the use of typical Kinney values such as C, 0.80, H, 1.00, and side chain methyl, 3.05, allows derivation of 11 values of the b.p.n. of sulfur, 6 values of b.p.n. for selenium, 2 values of b.p.n. for tellurium (*2*) and 3 values of b.p.n. for phosphorus (*2*).

Satisfactory results occur through the following method of calculations on trivalent organoarsenic compounds. First, a separation is made according to the number of alkyl groups present, to obtain the configurations $RAs=$, $R_2As—$ and R_3As; later separation according to the number of different halogen (or hydrogen) atoms attached to arsenic furnishes the configurations R_2AsX and $RAsX_2$. Second, there is manual derivation of the b.p.n. for arsenic in $RAsH_2$, R_2AsH, and R_3As, using the Kinney b.p.n.s C, 0.80, H, 1.00, side chain methyl, 3.05, and double bond in $CH_2=CHCH_2As(CH_3)_2$, 1.50 (*14*). This derivation excludes cyclic compounds. For example, an observed b.p. of 101.3° (actually 101°/754 mm. of Hg) (*29*) for $CH_3(n\text{-}C_3H_7)AsH$ yields the total b.p.n. 21.94; subtraction of 11.00 for hydrogen and 3.20 for carbon furnishes the b.p.n. 7.74 for arsenic present as $R_2As—$.

Data for acyclic compounds and the already derived b.p.n.s for arsenic present at $RAs=$ and $R_2As—$ allow calculations of the b.p.n.s for fluorine, chlorine and bromine, and—in R_2AsX only—for iodine and cyanide. After assumption of the Kinney values C, 0.80, and H, 1.00, for methyl(s) attached to phenyl, then the phenyl equals 19.81 ± 0.51 in seventeen compounds—excluding $2\text{-}ClC_6H_4AsH_2$ because of uncertainty about chlorine and $4\text{-}CH_3C_6H_4(C_6H_5)AsCl$ because of an approximate b.p. Phenyl thus has practically the same value attached to arsenic as in $RP=$ (*2*).

In Table I there are b.p.n.s for arsenic present as R_3As, $R_2As—$, $RAs=$ and $As\equiv$; the b.p.n. for $As\equiv$ involves subtraction of 3.00 for 3 hydrogen atoms from the total b.p.n. of 9.55 for AsH_3, of b.p. −54.8°. In Table I there also are 7 new b.p.n.s for halogen, one for cyanide and a new b.p.n. for the phenyl group attached to arsenic. Respective b.p.s of 63°, 130.2°, 221° and 224° (*1*) furnish the b.p.n.s of fluorine, chlorine, bromine, and isocyanate in AsX_3.

All calculations are manual rather than by the computer, which requires the preliminary subtraction, still impossible, of the portion of the total b.p.n. due to arsenic before the computer can begin the calculations.

LIMITATION

Some selection of data is necessary. A normal b.p. of 148° (*23*) for $C_6H_5AsH_2$ does not appear in Table II, since data in Table I allow calculation of a total b.p.n. of 29.31 of a b.p. of 166.6°, and since related $C_6H_5PH_2$ has a normal b.p. of 160° (*21*). Measurement of the b.p. of $(C_6H_5)_2AsBr$ on a small amount of material (*15*) seems adequate reason for rejection. Consideration of related observed b.p.s in Table II leads to rejection of the low b.p. of 245° (*30*) for $C_6H_5(C_2H_5)(n\text{-}C_3H_7)As$.

There is no satisfaction in attempts to fit b.p.n.s to 24 compounds containing $—HC=CHAs=$, $—CH_2OAs=$, $CF_3As=$ or $(CF_3)_2As—$. Typical examples are $(CH_2=CH)_3As$, b.p. 129.8° (*20*), $ClCH=CHAsCl_2$ (*18*), $CH_3OAs(CH_3)_2$ (*4*), $(CH_3O)_3As$ (*11*) and $(CF_3)_2AsCl$ (*9*). A previous publication on $(C_2H_5O)_4Si$ and related compounds (*31*) uses the b.p.n.s Si, 4.20, O, 1.1, C, 0.8 and H, 0.7 successfully.

DISCUSSION OF RESULTS

In Table II the calculated normal boiling points of 50 selected trivalent organoarsenic compounds have an average error of 2.5° and a maximum error of 7.7°; errors exceed 5.0° for only six compounds.

Use of the Kinney equation (*14*) with typical Kinney values and the new b.p.n.s in Table I allows calculation of boiling points still unknown: a random example is $n\text{-}C_4H_9AsH_2$, b.p. 98.9°, from total b.p.n. 21.70.

A comparison is now possible for corresponding halides of boron, silicon, germanium, phosphorus, and arsenic. The b.p.n. of a given halogen in an organoarsenic halide always exceeds that in the halide of boron (*2*), silicon (*17*), germanium (*2*) or phosphorus (*2*).

Phenyl attached to either phosphorus (*2*) or arsenic has a higher b.p.n. than phenyl in phenylhalosilanes (*17*) or in benzene.

To date, the system of b.p.n.s covers planar $(CH_3)_3B$ (*28*), tetrahedral (*28*) CH_4, $SiCl_4$ and $GeCl_4$, and pyramidal (*28*) PCl_3 and AsH_3, with related organometallic compounds. It still appears unlikely that one system of calculations can give better coverage in simpler fashion than b.p.n.s do. There is too much variation in the structures of the molecules and in electronegativities to permit use of a single unified system of b.p.n.s.

LITERATURE CITED

(1) Anderson, H.H., *J. Am. Chem. Soc.* **64**, 1757 (1942).

(2) Anderson, H.H., J. Chem. Eng. Data **7**, 565 (1962); **8**, 576 (1963); **9**, 272, 448 (1964).

(3) Banks, C.K., and coworkers, *J. Am. Chem. Soc.* **69**, 927 (1947).

(4) Braddock, J.F.M., Coates, G.E., *J. Chem. Soc.* **1961**, p. 3208.

(5) Challenger, F., Ellis, L., *Ibid.*, **1935**, p. 398.

(6) Cullen, R., Walker, L.G., *Can. J. Chem.* **38**, 472 (1960).

(7) Dehn, W.M., *Am. Chem. J.* **33**, 143 (1905).

(8) Dehn, W.M., Wilcox, B.B., *Ibid.*, **35**, 1 (1906).

(9) Emeléus, H.J., Haszeldine, R.N., Walaschewski, E.G., *J. Chem. Soc.* **1953**, p. 1552.

(10) Gibson, C.S., Johnson, J.D.A., *Ibid.*, **1931**, 2518.

(11) Gryszkewicz-Trochimowski, E., Sikorski, S.F., *Bull. soc. chim. (Paris)* [4] **41**, 1570 (1927).

(12) Gudzinowicz, B.J., Martin, H.F., *Anal. Chem.* **34**, 648 (1962).

(13) Jones, W.J., Dyke, W.J.C., Davies, G., Griffiths, D.C., Webb, J.H.E., *J. Chem. Soc.* **1932**, p. 2284.

(14) Kinney, C.R., *J. Am. Chem. Soc.* **60**, 3032 (1938); *Ind. Eng. Chem.* **32**, 559 (1940); *J. Org. Chem.* **6**, 220 (1941); **7**, 111 (1942); **14**, 71 (1949).

(15) La Coste, W., Michaelis, A., *Ann. Chem.* **201**, 212 (1880).

(16) Landolt, H., *Ibid.*, **89**, 321 (1854).

(17) Lewis, R.N., Newkirk, A.E., *J. Am. Chem. Soc.* **69**, 701 (1947).

(18) Lewis, W.L., Perkins, G.A., *Ind. Eng. Chem.* **15**, 292 (1923).

(19) Long, L.H., Emeléus, H.J., Briscoe, H.V.A., *J. Chem. Soc.* **1946**, p. 1123.

(20) Maier, L., Seyferth, D., Stone, F.G.A., Rochow, E.G., *J. Am. Chem. Soc.* **79**, 5884 (1957).

(21) Michaelis, A., *Ber.* **7**, 6 (1874); **10**, 622 (1877); *Ann. Chem.* **320**, 271 (1902); **321**, 142 (1902).

(22) Michaelis, A., Link, A., *Ibid.*, **207**, 205 (1881).

(23) Palmer, A.W., Dehn, W.M., *Ber.* **34**, 3594 (1901).

(24) Palmer, C.S., Adams, R., *J. Am. Chem. Soc.* **44**, 1362 (1922).

(25) Renshaw, R.R., Holm, G.E., *Ibid.*, **42**, 1470 (1920).

(26) Steinkopf, W., Mieg, W., *Ber.* **53**, 1016 (1920).

(27) Steinkopf, W., Schwen, G., *Ibid.*, **54**, 1437 (1921).

(28) Wells, A.F., "Structural Inorganic Chemistry," 3rd. Ed., pp. 642, 663, 768, 827, Clarendon Press, Oxford, England, 1962.

(29) Wigren, N., *Ann. Chem.* **437**, 285 (1924); *J. prakt. Chem.* **126**, 223 (1930).

(30) Winmill, T.F., *J. Chem. Soc.* **101**, 718 (1912).

(31) Wright, J.R., J. Chem. Eng. Data **5**, 206 (1960).

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