TABLE I

PHYSICAL PROPERTIES OF THE CHLORINATED FLUOROETHERS

Compound	B.p., °C.	B.p., Mm.	d^{20}_4	$n^{20}D$	MR^a	MR^b	AR_F	Chlorine, % Calcd.	Chlorine, % Found
$ClCH_2OCF_2CFHCl^c$	104.5	624	1.5269	1.3768	27.46	27.52	1.12	37.76	38.75
$CHCl_2OCF_2CFHCl$	112.5	626	1.5620	1.3883	31.99	32.40	1.13	48.92	49.09
CCl_3OCF_2CFHCl	131	629	1.6631	1.4090	36.85	37.39	1.17	56.31	56.18
$CCl_3OCF_2CFCl_2$	142	626	1.7141	1.4187	41.73	42.11	1.13	61.91	61.36
$ClCH_2CH_2OCF_2CFHCl^c$	84	100	1.4620	1.3935	32.08	32.44	1.23	36.04	37.15
$CH_3CHClOCF_2CFHCl^c$	63	100	1.4020	1.3755	31.74	32.17	1.14	36.04	35.95
$CH_2ClCHClOCF_2CFHCl$	97	100	1.5426	1.4080	36.61	37.02	1.13	45.95	46.02
$CHCl_2CHClOCF_2CFHCl^c$	85	23	1.6438	1.4291	41.47	41.66	1.06	53.34	53.17
$CCl_3CCl_2OCF_2CFCl_2$	94	10	1.7819	1.4575	56.07	56.00	0.973	67.25	67.02
$CCl_2{=}CClOCF_2CFCl_2$	89	40	1.7054	1.4440	45.97	46.30	1.14	59.42	59.35

[a] Calculated by adding the atomic increments. [b] Observed values, calculated by means of Lorentz-Lorenz equation. [c] Also reported by Rapp, Barr, *et al.*, THIS JOURNAL, **74**, 751 (1952).

rinated ethers and subsequent treatment of the reaction mixture with cold concentrated ammonia produced dichlorofluoroacetamide melting at 125°.

Preparation of $CCl_2{=}CCl{-}O{-}CF_2CFCl_2$.—To a mixture of 27 g. of powdered zinc in ethanol was added slowly 128 g. (0.37 mole) of $CCl_3CCl_2{-}O{-}CF_2CFCl_2$ with efficient stirring. A vigorous reaction occurred with evolution of heat which was removed by cooling in an ice-bath. After the addition of ether was completed, the mixture was refluxed gently for one hour. The reaction mixture was then filtered to remove zinc chloride and the filtrate washed with water and dried.

Fractionation gave 98 g. of $CCl_2{=}CCl{-}O{-}CF_2CFCl_2$ distilling at 89° at 40 mm. pressure. This structure was assigned on the basis of analysis and molar refraction.

Table I summarizes the physical properties of the various chlorination products.

In summary, it may be stated that the initial chlorination of $CH_3{-}O{-}CF_2CFClH$ and $C_2H_5{-}O{-}CF_2CFClH$ takes place exclusively in the alkyl portion of the ether with the hydrogen of the CFClH group being the last to be replaced by chlorine.

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Properties of Some Perfluorinated N-Bromo Amides[1]

BY J. D. PARK, W. R. LYCAN[2] AND J. R. LACHER

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The preparation and brominating properties of some halogenated N-bromoacetamides have been previously described[3] and the brominating activity of the N-Br bond related to the infrared intensity of the N-H fundamental band at 2.93 μ.[4]

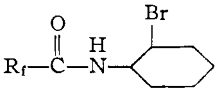
In this work, the N-bromoperfluoramides $CF_3CF_2CONHBr$, $CF_3CF_2CF_2CONHBr$ and $CF_3CF_2CF_2CF_2CONHBr$ were prepared following the method previously described.[3] These three compounds were separately treated with toluene; the percentage side chain bromination was compared to the percentage ring bromination and the absorption coefficient, α, calculated for the N-H fundamental band at 2.93 μ. Table I shows that the correlation found between these two factors falls in line with those previously described.[4]

The three N-bromo amides also were treated with cyclohexene which, like toluene, provides an opportunity for bromination to occur by free radical and ionic bromine. Table II shows the results of this study. Along with allylic bromination and addition of bromine across the double bond, some adducts of the type

TABLE I

CORRELATION OF INFRARED ABSORPTION COEFFICIENT, α, WITH BROMINATION STUDIES ON TOLUENE

Compound	α	Ring bromination, %	Side chain bromination, %
$CF_3CF_2CONHBr$	178	69.9	30.1
$CF_3CF_2CF_2CONHBr$	200	73.9	26.1
$CF_3CF_2CF_2CF_2CONHBr$	246	86.7	13.3
$CF_3CONHBr$ (for comparison)	250	88	12



where R_f = CF_3CF_2-, $CF_3CF_2CF_2-$ and $CF_3CF_2CF_2CF_2-$, were isolated in each case.

TABLE II

BROMINATION STUDIES ON CYCLOHEXENE

Compound	3-Bromocyclohexene, %	1,2-Dibromocyclohexane, %	Adduct, %
$CF_3CF_2CONHBr$	17.2	9.5	14.9
$CF_3CF_2CF_2CONHBr$	11.5	9.5	16.9
$CF_3CF_2CF_2CF_2CONHBr$	0	14	14.6

It will be noted from Table II that the percentage of bromination resulting from homolytic cleavage of the N-Br bond decreases and that the total of the two products resulting from heterolytic cleavage of the N-Br bond increases in the same order as the absorption coefficients (Table I) increase. The 3-bromocyclohexene had a b.p. of 77–83° (35 mm.) and $n^{20}D$ 1.5279 (lit. 80° (35 mm.), $n^{20}D$ 1.5280). The 1,2-dibromocyclohexane had a b.p. of 100–105° (15 mm.) and $n^{20}D$ 1.5534 (lit. 99–103° (16 mm.), $n^{20}D$ 1.5532).

The properties of the various new compounds are given in Table III.

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(2) This paper represents in part work done at the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree.

(3) J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **74**, 2189 (1952).

(4) J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **74**, 5578 (1952).

TABLE III

SUMMARY OF PROPERTIES

Compound	M.p., °C.	Analyses, %		
			Calcd.	Found
$CF_3(CF_2)_3COOEt$	...[a]	F,	58.5	58.2
$CF_3CF_2CONH_2$	95–96	F,	58.3	58.3
$CF_3CF_2CONHBr$	69	Br,	30.03	29.84
$CF_3(CF_2)_2CONHBr$	80	Br,	27.37	27.43
$CF_3(CF_2)_3CONHBr$	87	Br,	23.35	23.36
o-$BrC_6H_5NHCOCF_2CF_3$	126	Br,	24.65	24.43
		N,	4.35	4.32
o-$BrC_6H_5NHCOCF_2CF_2CF_3$	139	Br,	21.36	21.09
		N,	3.74	3.82
o-$BrC_6H_5NHCOCF_2CF_2CF_2CF_3$	133	Br,	18.84	19.02
		N,	3.30	3.29

[a] B.p. 110° (627 mm.), n^{20}_{D} 1.3060.

DEPARTMENT OF CHEMISTRY
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Unsymmetrical Tetraalkylmethanes. I. Coupling of Alkylmagnesium Bromides with Tertiary Bromides[1]

BY NORMAN RABJOHN AND M. J. LATINA[2]

RECEIVED NOVEMBER 20, 1953

The coupling reaction of Grignard reagents with tertiary alkyl bromides was investigated as a means of obtaining unsymmetrical tetraalkylmethanes which contain a minimum of sixteen carbon atoms. A number of other investigators[3,4] have employed this procedure, but have worked with compounds of lower carbon content and apparently have made only quaternary hydrocarbons in which at least two of the alkyl groups are similar.

We have found, in agreement with others, that the coupling process is not clean-cut and the yields of the desired hydrocarbons are low. Two C_{16}-hydrocarbons were prepared in the present study in yields of 10 and 15% and a C_{20}-hydrocarbon, 5-ethyl-5-octyldecane, was obtained in 16% yield. However, attempts to prepare a C_{24}- and a C_{30}-hydrocarbon by coupling *n*-dodecylmagnesium bromide with 5-ethyl-5-bromodecane and 7-butyl-7-bromotetradecane, respectively, failed. Treatment of 5-ethyl-5-bromodecane with *n*-propyllithium also led to negative results.

The solidification points of the three unsymmetrical tetraalkylmethanes which were prepared were found to be in the range of -70 to $-75°$.

Experimental[5]

Tertiary Alcohols.—These compounds were synthesized in 40–60% yields in the typical fashion from the appropriate Grignard reagents and ketones. Ethyl-*n*-propyl-*n*-butylcarbinol was obtained from the reaction of *n*-propylmagnesium bromide with ethyl *n*-butyl ketone; b.p., 101–103° (20 mm.), n^{19}_{D} 1.4385; lit.[6] b.p., 88.8–89.6° (15 mm.), n^{20}_{D} 1.4378. Methylethyl-*n*-amylcarbinol was prepared from ethylmagnesium bromide and methyl *n*-amyl ketone; b.p. 100-102° (30 mm.), n^{20}_{D} 1.4321; lit.[7] b.p. 80–81° (15 mm.), n^{20}_{D} 1.4315. Ethyl-*n*-butyl-*n*-amylcarbinol resulted from the condensation of *n*-amylmagnesium bromide with ethyl *n*-butyl ketone; b.p. 119–120° (20 mm.), n^{18}_{D} 1.4430; lit.[8] n^{20}_{D} 1.4424. *n*-Butyl-*n*-hexyl-*n*-heptylcarbinol was prepared by treating *n*-butyl *n*-hexyl ketone with *n*-heptylmagnesium bromide in the usual manner. The product was isolated in 66% yield, b.p. 157–159° (1 mm.), n^{19}_{D} 1.4520.

Anal. Calcd. for $C_{18}H_{38}O$: C, 79.92; H, 14.16. Found: C, 79.90; H, 14.05.

Tertiary Bromides.—The bromides were prepared essentially by the procedure of Halse[9] as modified by Whitmore and Williams[7] for tertiary chlorides. The tertiary alcohols were saturated with hydrogen bromide at ice-bath temperature and the resulting bromides were separated from the water which had formed. Excess hydrogen bromide was removed on a water aspirator and the products were washed with an equal volume of concentrated sulfuric acid. They were allowed to stand over anhydrous sodium carbonate and sodium sulfate in a refrigerator for 12–15 hours. After removing the drying agents, the tertiary bromides resulted in yields of 70–80%. Since the bromides could not be distilled without decomposition, they were used without further purification. The following bromides were obtained in the above manner: (a) 5-ethyl-5-bromodecane, n^{20}_{D} 1.4650. *Anal.* Calcd. for $C_{12}H_{25}Br$: C, 57.82; H, 10.11. Found: C, 57.81; H, 10.20.

(b) 3-Methyl-3-bromoöctane, n^{20}_{D} 1.4545. *Anal.* Calcd. for $C_9H_{19}Br$: C, 52.20; H, 9.25. Found: C, 52.28; H, 9.46.

(c) 4-Ethyl-4-bromoöctane, n^{20}_{D} 1.4635. *Anal.* Calcd. for $C_{10}H_{21}Br$: C, 54.30; H, 9.57. Found: C, 54.30; H, 9.65.

7-Butyl-7-bromotetradecane could not be prepared by this process since the corresponding carbinol solidified at ice-bath temperature. Accordingly, hydrogen bromide was introduced into the carbinol at room temperature, and the resulting product failed to give satisfactory analytical data.

Coupling of Grignard Reagents with the Tertiary Bromides.—The method of preparation of 6-ethyl-6-butyltetradecane is illustrative and similar to that of Campbell and Eby.[4] *n*-Octylmagnesium bromide was prepared from 24 g. (1 gram atom) of magnesium, 193 g. (1.0 mole) of *n*-octyl bromide and 500 ml. of anhydrous ether. The bromide was added over a period of 2 hours and the reaction mixture was stirred for an additional hour. The ether was removed by distillation and the temperature of the reaction mixture was raised to 140°; then 200 g. (0.8 mole) of 5-ethyl-5-bromodecane was added within 2 hours. A white slurry formed and stirring became difficult. The mixture was heated for 4 more hours and allowed to stand overnight. Water was added slowly with cooling and stirring, followed by 10% hydrochloric acid solution until all solids had dissolved. The mixture was extracted several times with ether and the combined extract was washed with water, 10% sodium bicarbonate solution, again with water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residual oil was distilled from a Clark flask. The higher boiling fraction was purified through a medium bore Todd column to give 38 g. (16%) of a colorless liquid; b.p. 179–183° (18 mm.), n^{20}_{D} 1.4480, d^{20}_{4} 0.799; *MR* calcd. 94.6, found 94.7.

Anal. Calcd. for $C_{20}H_{42}$: C, 85.02; H, 14.98. Found: C, 85.16; H, 14.86.

The sixteen-carbon hydrocarbon, 5-ethyl-5-propyldecane, was obtained by coupling *n*-hexylmagnesium bromide with 5-ethyl-5-bromoöctane in the above manner. There was isolated 39 g. (15%) of a colorless liquid, b.p. 136–138° (20 mm.), n^{20}_{D} 1.4420, d^{20}_{4} 0.788; *MR* calcd. 76.1, found 76.0.

Anal. Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 85.08; H, 15.27.

In an analogous fashion, 18 g. (10%) of 6-methyl-6-ethyltridecane was obtained from the reaction of 3-methyl-3-bromoöctane with *n*-heptylmagnesium bromide. The colorless liquid boiled at 139–142° (15 mm.), n^{20}_{D} 1.4418, d^{20}_{4} 0.780; *MR* calcd. 76.1, found 76.8.

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(1) This work was supported in part by a grant from the Lubrizol Corporation.

(2) From the Ph.D. thesis of M. J. Latina, 1953.

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