TABLE IV

BROMINATION PRODUCTS FROM THE ADDUCTS

From compound	Yield, %	B.p. °C.	Mm.	$n^{20}_{\rm D}$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found
I[a]	52	121–123	3	1.15524	33.56	33.61	3.84	3.86	55.94	55.97
II	85	119	10	1.5013	29.75	29.58	2.79	2.87	49.68	49.70
III	85	121–122	10	1.4711	29.04	29.18	2.42	2.44	43.01	42.92
IV	89	92–93	10	1.4580	25.53	25.60	1.60	1.64	42.55	42.36
V	53	126–128	10	1.5037	32.14	31.87	3.27	3.32	47.62	47.69
VI	97	91	10	1.4871	27.17	27.17	2.90	2.99	51.61	51.50
VII	84	95	10	1.4606	26.67	26.78	2.50	2.91	44.44	44.59
VIII	91	89	10	1.4343	23.08	23.08	1.65	1.60	43.96	43.81
IX	73	110	10	1.4896	29.63	29.82	3.40	3.49	49.38	49.29

[a] There also was obtained from this reaction mixture a compound resulting from the loss of HBr from the dibromide, b.p. 93–94° (10 mm.), $n^{20}_{\rm D}$ 1.5100. *Anal.* Calcd. for C_8H_9FBr: C, 46.83; H, 4.88; F, 39.02. Found: C, 46.50; H, 5.35; F, 39.32.

With Anthracene.—3,3,3-Trifluoropropene (8 g., 0.083 mole), anthracene (7 g., 0.039 mole) and benzene (25 g.) were heated in a sealed tube at 200° for 20 hours. Two and four-tenth grams of 3,3,3-trifluoropropene was recovered by distillation at room temperature and 3.5 g. of anthracene was recovered by filtration. Evaporation under vacuum of the remaining benzene solution and recrystallization of the crude product from aqueous ethanol gave 4.5 g. (83.5%) of the adduct, m.p. 122–123°.

Bromination of the Adducts.—The general method of preparation of the dibromides of the bicyclo[2.2.1]-2-heptenes and cyclohexenes is illustrated by the following example: A solution of 5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]-2-heptene (21.6 g., 0.1 mole) in carbon tetrachloride (15 ml.) was placed in a 100-ml., 3-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel. The flask was cooled in a Dry Ice–trichloroethylene-bath maintained at −20 to −10°. A solution of 16 g. (0.1 mole) of bromine in 15 ml. of carbon tetrachloride was added slowly. After the addition was complete, the reaction mixture was brought to room temperature and stirred for one hour. The excess bromine was then removed by shaking with sodium bisulfite solution. The organic layer was separated, washed with water, dried over calcium chloride and distilled under reduced pressure. The 1,2-dibromo-5,6,6-trifluoro-5-trifluoromethylbicyclo[2.2.1]heptane (33.5 g., 89%) boiled at 92–93° (10 mm.), $n^{20}_{\rm D}$ 1.4580.

The yields and physical properties of the dibromides are listed in Table IV. A monobromo compound was obtained in the bromination of 5-fluoromethylbicyclo[2.2.1]-2-heptene.

Debromination Procedure.—A mixture of 1,2-dibromo-4-pentafluoroethylcyclohexane (12.3 g., 0.03 mole), zinc dust (6.5 g., 0.1 g. atom) and 50 ml. of absolute ethanol was refluxed for 24 hours. The solution was decanted from the metal, diluted with water and acidified with 10% sulfuric acid. The organic layer was separated. The aqueous portion was extracted twice with ether. The ether extracts were combined with the organic layer, washed with brine and dried over anhydrous magnesium sulfate. Distillation gave 3.7 g. (54%) of 4-pentafluoroethylcyclohexene, b.p. 119°, $n^{20}_{\rm D}$ 1.3725.

Absorption Spectra.—Ultraviolet absorption spectra were determined with a Cary recording spectrophotometer in 95% ethanol at a concentration of 3.3×10^{-4} mole per liter. The infrared spectra were obtained for the pure liquids with a Perkin-Elmer model 21 recording spectrometer in capillary cells of 0.0125 to 0.0325 mm. thickness.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reactions of Perfluoronitriles with Grignard Reagents[1]

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Straight chain alkyl and phenyl Grignard reagents react with perfluoroaceto-, propio-, and butyronitriles to give the expected ketones. The reaction of isopropylmagnesium bromide with heptafluorobutyronitrile yields heptafluorobutyraldehyde unless a reverse addition technique is used. *t*-Butylmagnesium chloride and heptafluorobutyronitrile react to give the exchange products, trimethylacetonitrile and heptafluoropropylmagnesium chloride.

Discussion

Jones[2] has described the reaction of trifluoroacetonitrile with benzylmagnesium chloride; subsequent work by Nes and Burger[3] elucidated the structure of the original product to be *o*-methyltrifluoroacetophenone. In an attempt to extend the reaction to other Grignard reagents with fluorine-containing nitriles a general method has been developed for the preparation of perfluoroalkyl alkyl ketones and perfluoroalkyl aryl ketones. No evidence was obtained that migration of the perfluoroaryl group took place as indicated by Nes and Burger.[3]

The results of the reaction of several Grignard reagents with trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile are in Tables I and II. The main competing reaction was the aldol condensation of the resulting ketones, presumably catalyzed by the Grignard reagent.[4] With methylmagnesium iodide this condensation was the main reaction, and no simple ketone was obtained.

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[1] This paper represents part of a thesis submitted by D. D. Meyer to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. G. Jones, THIS JOURNAL, **70**, 143 (1948).

[3] W. R. Nes and A. Burger, *ibid.*, **72**, 5409 (1950).

[4] K. Sisido, H. Nozaki and O. Kurihara, *ibid.*, **74**, 6254 (1952).

Table I

Reactions of Grignard Reagents with Perfluoronitriles in Ether at 0°

Grignard reagent	Nitrile	Product	Yield, %
CH_3MgI	C_3F_7CN	$CH_3C(C_3F_7){=}CHCOC_3F_7$	46
C_2H_5MgI	C_3F_7CN	$C_2H_5COC_3F_7$	79
C_2H_5MgI	C_2F_5CN	$C_2H_5COC_2F_5$	25
C_3H_7MgBr	C_3F_7CN	$C_3H_7COC_3F_7$	52
C_3H_7MgBr	CF_3CN	$C_3H_7COCF_3$	53
$(CH_3)_2CHMgBr$	C_3F_7CN	C_3F_7CHO	35
		$(CH_3)_2CHCOC_3F_7$[a]	44
$(CH_3)_3CMgCl$	C_3F_7CN	$(CH_3)_3CCN$	33
		$(CH_3)_3CCOC_3F_7$	8
C_6H_5MgBr	C_3F_7CN	$C_6H_5COC_3F_7$[b]	89
C_6H_5MgBr	C_2F_5CN	$C_6H_5COC_2F_5$[b]	92
C_6H_5MgBr	CF_3CN	$C_6H_5COCF_3$[b]	89
$C_6H_5CH_2MgCl$	C_3F_7CN	$C_6H_5CH_2COC_3F_7$	75

[a] Reverse addition. [b] Reference 9.

Table II

Physical Properties of New Compounds

Compound	B.p., °C.	$n^{20}D$	d^{20}_{20}	Carbon, %		Hydrogen, %		Semicarbazone m.p., °C.	Nitrogen, %	
				Calcd.	Found	Calcd.	Found		Calcd.	Found
$CH_3C(C_3F_7){=}CHCOC_3F_7$	53 (4 mm.)	1.3440	1.650	29.56	29.51	0.99	1.30	....	...	...
$C_2H_5COC_3F_7$	83	1.3028	1.370	31.86	32.12	2.21	2.70	105–105.5	14.84	14.73
$C_2H_5COC_2F_5$	62	1.3015	1.259	34.09	34.80	2.84	3.03	108–109[a]	15.73	15.68
$C_3H_7COC_3F_7$[b]	101.5	1.3181	1.334	35.00	34.81	2.92	3.00	97–97.5	14.14	14.40
$C_3H_7COCF_3$[b]	67	1.3279	1.097	42.86	43.15	5.00	5.20	76–76.5[a]	17.50	17.84
$(CH_3)_2CHCOC_3F_7$	92.5	1.3100	1.308	35.00	35.34	2.92	2.99	104.5–105	14.14	14.43
$(CH_3)_3CCHOHC_3F_7$	135	1.3485	1.310	37.50	37.58	4.30	4.56	....	...	...
$(CH_3)_3CCOC_3F_7$	102	1.3268	1.254	37.80	38.01	3.54	3.54	....	...	...
$C_6H_5CH_2COC_3F_7$	51 (3 mm.)	1.4108	1.395	45.83	46.05	2.43	2.29	132–132.5	12.17	12.38

[a] 2,4-Dinitrophenylhydrazone. [b] Reported without analysis by L. B. Barkley and R. Levine, This Journal, **75**, 2059 (1953).

The reaction of Grignard reagents containing a β-hydrogen atom with fluorine-containing carbonyl compounds gives large amounts of reduction products.[5] The only example of the reduction of a nitrile by a Grignard reagent is that reported by Mosher[6] who observed the formation of trimethylacetaldehyde from the reaction of trimethylacetonitrile with isopropyl- or *t*-butylmagnesium chloride.

When heptafluorobutyronitrile was treated with isopropylmagnesium bromide reduction occurred and heptafluorobutyraldehyde was obtained. If reagent addition was reversed, however, the normal addition reaction obtained and heptafluoropropyl isopropyl ketone resulted.

The addition of *t*-butylmagnesium chloride to heptafluorobutyronitrile resulted in an exchange reaction, and the products obtained were trimethylacetonitrile and heptafluoropropane, the latter presumably resulted from the hydrolysis of heptafluoropropylmagnesium chloride. This type of exchange reaction has been reported previously with nitriles that can form resonance stabilized carbanions upon removal of the cyano group.[7,8] Small amounts of the ketone arising from the normal addition reaction between heptafluorobutyronitrile and *t*-butylmagnesium chloride were also obtained but could not be separated from the accompanying trimethylacetonitrile by distillation. The yields of the products were determined by infrared analysis of the mixtures. Pure 2,2-dimethyl-4,4,5,5,6,6,6,-heptafluoro-3-hexanone for the calibration curve was synthesized by the reaction of methyl heptafluorobutyrate with excess *t*-butylmagnesium chloride, and subsequent oxidation of the resulting secondary alcohol with sodium dichromate and sulfuric acid.

The reaction of phenylmagnesium bromide with perfluoronitriles gave excellent yields of aryl perfluoroalkyl ketones. These compounds have previously been synthesized by the Friedel–Crafts reaction,[9] and were identified by their physical constants and derivatives. The reaction of benzylmagnesium chloride with heptafluorobutyronitrile proceeds normally and does not give the rearranged product obtained by Jones[2,3] in the reaction of this Grignard reagent with trifluoroacetonitrile. The structure of the ketone was established by degradation with alkali.

Experimentally, it is found that perfluoronitriles react with organomagnesium compounds much more rapidly than do non-fluorinated nitriles. Since fluorine-containing nitriles do not form stable complexes with magnesium bromide,[10] it is possible that a mechanism for the reaction of a perfluoronitrile with a Grignard reagent involves a direct attack of the organomagnesium compound on the carbon of the cyano group, which would have en-

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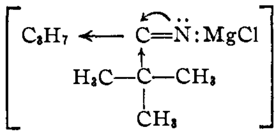
[5] E. T. McBee, O. R. Pierce and J. F. Higgins, This Journal, **74**, 1336 (1952).

[6] H. Mosher and W. Mooney, *ibid.*, **73**, 3948 (1951).

[7] J. Erickson and M. Barnett, *ibid.*, **57**, 560 (1935).

[8] F. F. Blicke and E. Tsao, *ibid.*, **75**, 5587 (1953). Its occurrence with a fluorine-containing nitrile can be best understood by considering the inductive effects in the intermediate formed by the addition of *t*-butylmagnesium chloride to the cyano group.



$$\left[\begin{array}{c} C_3H_7 \longleftarrow \overset{\frown}{C}{=}\ddot{N}{:}MgCl \\ \uparrow \\ H_3C—C—CH_3 \\ | \\ CH_3 \end{array}\right]$$

Regeneration of the carbon–nitrogen triple bond would result in the elimination of either the heptafluoropropyl or the *t*-butyl group with a pair of electrons. The fluorine-containing residue can most easily be eliminated as a carbanion since it is drawing electrons from the carbon of the cyano group while the *t*-butyl residue is pushing electrons toward this atom.

[9] J. H. Simons, W. T. Black and R. F. Clark, *ibid.*, **75**, 5621 (1953).

[10] E. T. McBee, O. R. Pierce and D. D. Meyer, *ibid.*, **77**, 83 (1955).

hanced positive character because of the large inductive effect of the fluorine atoms. This mechanism differs from the one proposed by Swain[11] for reactions of Grignard reagents with nitriles, which involves an initial complex between the Grignard reagent and the nitrile, followed by an intramolecular shift of the organic portion of the organomagnesium compound.

Experimental[12]

Trifluoroacetonitrile, Pentafluoropropionitrile and Heptafluorobutyronitrile.—These compounds were prepared in a manner similar to the method described by Gilman and Jones.[13] However, the fluorine-containing esters were added directly to liquid ammonia, and no solvent was used.

The Reaction of Perfluoronitriles with Grignard Reagents.—The organomagnesium compounds were prepared in the usual manner in approximately half mole quantities and were filtered through glass wool with nitrogen pressure into a one-liter, three-necked flask or an addition funnel, depending upon whether normal or reverse addition was used. For normal addition, the flask was equipped with an efficient stirrer, a Dry Ice reflux condenser, and a gas inlet tube reaching above the surface of the Grignard solution. The nitrile (0.25 to 0.33 mole) was distilled from a weighed ampule during a one- to two-hour period into the chilled Grignard solution. The hydrolysis was carried out in the same flask by the dropwise addition of 300 ml. of 20% aqueous sulfuric acid. The ether layer was separated, dried and distilled to remove the ether; the residual liquid was vaporized quickly into a Dry Ice trap under reduced pressure and then rectified from an efficient column.

The same procedure was followed for reverse addition except the nitrile was distilled into 200 ml. of dry ether in the flask, and the inlet tube was replaced by an addition funnel containing the Grignard solution, which was added over a one- to two-hour period, Table II.

2,2-Dimethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanone.—A Grignard reagent was prepared from 48.6 g. (2.0 g. atoms) of magnesium turnings in 500 ml. of anhydrous ether and 184 g. (2.0 moles) of freshly distilled *t*-butyl chloride. Methyl heptafluorobutyrate (152 g., 0.67 mole) was added dropwise to this solution while the flask was cooled in an ice-bath, and the reaction mixture was stirred for ten hours at room temperature. The reaction mixture was poured onto ice and ammonium chloride, and the product was taken up in ether. Rectification gave 78.5 g. of 2,2-dimethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanol, b.p. 135°, n^{20}_{D} 1.3485, and 18.3 g. of heptafluorobutanol, b.p. 95°, $n^{20}_{\mathrm{D}} < 1.3000$ (lit. values b.p. 95°, n^{20}_{D} 1.2944).[14]

The secondary alcohol, 86 g. (0.33 mole), and 100 ml. of glacial acetic acid were poured in a 500-ml., three-necked flask, and a mixture of 75 g. of sodium dichromate, 100 ml. of water and 75 g. of sulfuric acid was added dropwise with stirring over a 2.5-hour period. The reaction mixture was extracted with benzene, dried over Drierite, and rectified to give 15.6 g. of 2,2-dimethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanone, b.p. 102°, n^{20}_{D} 1.3268 (Table II).

Preparation of Derivatives.—The semicarbazones and 2,4-dinitrophenylhydrazones were prepared according to the procedures described by Simons.[9] The semicarbazone of heptafluorobutyrophenone melted at 147–147.5° instead of 133–135° as reported by these authors.

Anal. Calcd. for $C_{11}H_8F_7N_3O$: N, 12.69. Found: N, 12.66.

Carbonyl derivatives of 2,2-dimethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanone and 6-methyl-1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-5-nonene-4-one could not be obtained under the usual conditions.

1-Phenyl-3,3,4,4,5,5,5-heptafluoro-2-pentanone was shown to be a benzyl rather than a phenyl ketone by warming a sample of the compound with 10% aqueous potassium hydroxide, cooling and acidifying with hydrochloric acid. The precipitate thus obtained was crystallized from ether–petroleum ether and melted at 76°. A mixed melting point with an authentic sample of phenylacetic acid showed no depression. The infrared spectrum of this ketone showed a carbonyl absorption peak at 5.75 μ. The alkyl perfluoroalkyl ketones reported here have carbonyl absorption peaks at 5.75–5.80 μ, and the aryl perfluoroalkyl ketones absorb at 5.85–5.92 μ.

Infrared Absorption Spectra.—The infrared absorption spectra were determined for pure liquids in sealed cells of 0.0125–0.0325 mm. thickness or in capillaries, depending upon the boiling point of the compounds.[15] The instrument was a double beam Perkin–Elmer spectrophotometer, Model 21.

The calibration curve for the analysis of mixtures of trimethylacetonitrile and 2,2-dimethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanone was obtained from mixtures of known composition (100, 80, 60 and 50% nitrile) in a sealed cell of 0.0325 mm. thickness. The method outlined by Garhart[16] was used to evaluate the spectra thus obtained.

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[11] C. G. Swain, THIS JOURNAL, **69**, 2306 (1947).

[12] Unless otherwise noted, all rectifications were performed with a Todd Precise Fractionation Assembly employing a 12-mm. barrel packed with $^{1}/_{8}$-inch Pyrex glass helices, and melting points were determined with a Fisher–Johns melting point stage. All temperatures are uncorrected.

[13] H. Gilman and R. G. Jones, THIS JOURNAL, **65**, 1458 (1943).

[14] Technical Bulletin, "Preparation of 1,1-Dihydroheptafluorobutyl Alcohol by Catalytic Reduction," Minnesota Mining and Mfg. Co., St. Paul, Minn.

[15] Infrared spectra by Mrs. L. H. Walsh.

[16] M. D. Garhart, F. J. Witmer and Y. A. Tajima, *Anal. Chem.*, **24**, No. 5 ,851 (1952).