complished only the ketonic analysis will be described below. The yield of ketone was 30 and 35% in two runs. It is probable that the yield would have been higher had the rearrangement reaction been carried out in benzene since low yields were obtained in other rearrangements in ether. However, since the ratio of anilines formed were the same regardless of the yield in other cases the experiments were not repeated in benzene for the methoxy analog. In preparation for analysis, the crude ketone mixture was slowly distilled under about 1 mm. pressure from the melted state to a cold surface. Several other methods of purification were less satisfactory.

_p_-Nitrophenyldiphenylmethylhydroxylamine (III).—A solution of 0.50 g. of III and 1.0 g. of phosphorus pentachloride in 25 cc. of benzene was refluxed for 90 minutes. Two liquid layers were present. Methanol and water were added and the mixture was refluxed for 30 minutes. The isolation of basic and neutral fractions was performed as above. The basic fraction yielded 0.35 g. (93%) of amine hydrochlorides and the neutral fraction afforded 0.33 g. (99%) of mixed ketones after purification by slow evaporative distillation. A second run on III yielded similar fractions.

Analytical Procedures. Amines.—The mixtures of amine hydrochlorides from the rearrangements of II and III were analyzed by treatment with bromine in acetic acid.[9] The excess bromine was determined iodometrically. The method was checked by analysis of known mixtures of amine hydrochlorides. The average percentage of aniline found for six closely agreeing analyses was 73.5%. The average of three checks on a known mixture containing 75% aniline was 70%. If one adds this correction of 5% to the value 73.5% one obtains 78.5% of aniline which leads to a migration aptitude of 0.55 for the _p_-chlorophenyl group.

The amine analysis in the case of aniline-nitroaniline mixtures averaged 84.0% aniline and the checks on synthetic mixtures indicated that no correction was needed. The migration aptitude for _p_-nitrophenyl calculated from this value is 0.38.

Ketones.—For the analysis of the ketone mixtures isolated and purified as described above an infrared spectrographic method was used. Known mixtures of each pair of ketones (benzophenone–_p_-nitrobenzophenone and benzophenone–_p_-methoxybenzophenone) were prepared. The optical transmission of these mixtures in chloroform and carbon tetrachloride solution, respectively, were determined at significant wave lengths. Curves relating composition to transmission were drawn and used to estimate the composition of unknown mixtures. For the benzophenone–_p_-nitrobenzophenone mixture, the wave lengths of 6.5, 7.4 and 11.7 μ were chosen as at these wave lengths the nitro ketone absorbed strongly while benzophenone absorbed weakly. The average composition of the mixture of ketones formed from rearrangement of III was 90% _p_-nitrobenzophenone and 10% of benzophenone. The value obtained by analysis of a known mixture in this concentration range checked the theoretical to 2%. The results obtained at the three wave lengths were averaged. The value for ketone composition leads to a calculated migration aptitude of 0.18.

For the benzophenone–_p_-methoxybenzophenone mixture, the wave lengths of 6.6, 8.7, 9.7 and 11.8 μ were chosen as these were the wave lengths at which _p_-methoxybenzophenone absorbed strongly while benzophenone absorbed weakly. The average composition of the mixture of ketones formed from I was 82% benzophenone and 18% _p_-methoxybenzophenone. On averaging the results obtained at the four wave lengths the theoretical value was checked to 2%. The value for ketone composition leads to a calculated migration aptitude of 9.1.

Columbus 10, Ohio

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[9] G. O. Curme, Jr., This Journal, **35**, 1162 (1913).

[Contribution from the Department of Chemistry, Purdue University]

The Synthesis of Fluorine-containing Olefins

By E. T. McBee, O. R. Pierce and M. C. Chen

Received November 22, 1952

Several new fluorine-containing alkenes and alkadienes were prepared from esters of hexafluoroglutaric, octafluoroadipic and heptafluorobutyric acids by reaction with a Grignard reagent followed by dehydration of the secondary or tertiary alcohol obtained. Reaction of the olefins with both bromine and chlorine gave normal addition products.

Discussion

As part of a broad program comprising the synthesis of fluorine-containing hydrocarbons, several new fluorinated alkenes and alkadienes were prepared. These materials were intermediates in the preparation of bromofluoro- and chlorofluoroalkenes and alkanes.

Esters of hexafluoroglutaric, octafluoroadipic and heptafluorobutyric acids reacted normally with methylmagnesium halide to give the corresponding tertiary alcohols in good yield. However, ethylmagnesium halide gave not only the expected tertiary alcohols, but also the corresponding secondary alcohols, while _n_-propyl and isopropylmagnesium halide gave principally the secondary alcohols. A more detailed discussion of the reducing action of Grignard reagents may be found elsewhere.[1-3]

Dehydration of the tertiary alcohols was accomplished using a mixture of sulfuric acid and ether. The secondary alcohols, being more difficult to dehydrate, required the use of phosphorus pentoxide and elevated temperatures. This resistance to dehydration is characteristic of alcohols in which the carbinol group is adjacent to a fluorine-containing group.[2]

Additive chlorination and bromination of the olefins was conducted in solutions of chloroform or carbon tetrachloride at temperatures ranging from 25° to that of the refluxing reaction mixture. In all cases, strong illumination of the reaction mixture was required, indicating a relative inertness of these olefins.

Table I lists the compounds prepared, their physical constants, analyses and the reaction yields.

Experimental

Starting Materials.—The two esters, diethyl hexafluoroglutarate and diethyl octafluoroadipate, were prepared by esterification of the corresponding acids obtained by the oxidation of dichlorohexafluorocyclopentene and dichlorooctafluorocyclohexene.[4] Heptafluorobutyric acid was ob-

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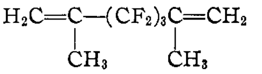
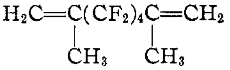
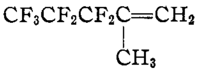
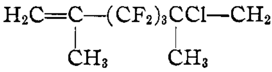
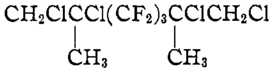
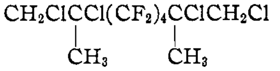
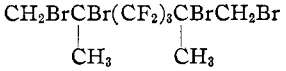
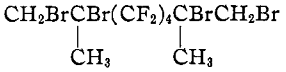
[1] E. T. McBee, O. R. Pierce and J. F. Higgins, This Journal, **74**, 1736 (1952).

[2] _Ibid._, **74**, 1387 (1952).

[3] K. N. Campbell, J. O. Knobloch and B. K. Campbell, _ibid._, **72**, 4380 (1950).

[4] E. T. McBee, P. A. Wiseman and G. B. Bachman, _Ind. Eng. Chem._, **39**, 415 (1947).

TABLE I

Formula	B.p., °C.	M.p., °C.	n^{20}_D	D^{20}_4	Carbon, %		Hydrogen, %		Yield, %
					Calcd.	Found	Calcd.	Found	
$CF_3CF_2CF_2CHOHCH_2CH_2CH_3$	131		1.3374	1.322	34.7	34.6	3.72	3.79	88
$CF_3CF_2CF_2CHOHCH(CH_3)CH_3$	123		1.3375	1.375	34.7	34.6	3.72	3.74	87
$CF_3CF_2CF_2COH(CH_3)CH_3$	108		1.3252	1.439	31.6	31.7	3.06	3.13	76
$CH_3CH_2CH_2CHOH(CF_2)_3CHOHCH_2CH_2CH_3$		80–81			44.6	44.6	6.08	6.09	77
$C_2H_5CHOH(CF_2)_3CHOHC_2H_5$		94–95			40.3	40.2	5.22	5.24	23
$(C_2H_5)_2COH(CF_2)_3COH(C_2H_5)_2$		68–69			48.2	48.25	6.80	6.91	5
$(CH_3)_2COH(CF_2)_3COH(CH_3)_2$		78–79			40.3	40.5	5.20	5.33	82
$(CH_3)_2COH(CF_2)_4COH(CH_3)_2$		81–82			37.7	37.5	4.43	4.37	98
 $H_2C{=}\underset{CH_3}{C}{-}(CF_2)_3\underset{CH_3}{C}{=}CH_2$	140		1.3682	1.110	46.5	46.4	4.31	4.31	74
 $H_2C{=}\underset{CH_3}{C}(CF_2)_4\underset{CH_3}{C}{=}CH_2$	31 at 4 mm.		1.3620	1.228	42.5	42.5	3.54	3.52	85
$CF_3CF_2CF_2CH{=}CHCH_2CH_3$	86		1.3178	1.253	37.5	37.4	3.12	3.12	85
 $CF_3CF_2CF_2\underset{CH_3}{C}{=}CH_2$	55		1.2983	1.303	34.2	34.4	2.38	2.41	71
$CF_3CF_2CF_2CH{=}C(CH_3)_2$	82		1.3254	1.288	37.5	37.7	3.12	3.16	68
$CH_3CH_2CH{=}CH(CF_2)_3CH{=}CHCH_2CH_3$	86 at 19 mm.		1.3884	1.214	50.7	50.6	5.38	5.32	12
$CH_3CH_2CH{=}CH(CF_2)_4CH{=}CHCH_2CH_3$	92 at 14 mm.		1.3800	1.250	46.4	46.4	4.52	4.47	10
$CH_3CH_2CH_2CHOH(CF_2)_4CH{=}CHCH_2CH_3$	106 at 18 mm.		1.3954	1.247	47.5	47.6	5.76	5.70	11
 $H_2C{=}\underset{CH_3}{C}{-}(CF_2)_3\underset{CH_3}{C}Cl{-}CH_2Cl$	62 at 2 mm.		1.4109	1.508	35.6	35.5	3.30	3.34	42
 $CH_2Cl\underset{CH_3}{C}Cl(CF_2)_3\underset{CH_3}{C}ClCH_2Cl$	104 at 1 mm.		1.4403	1.575	28.9	29.0	2.67	2.82	56
 $CH_2Cl\underset{CH_3}{C}Cl(CF_2)_4\underset{CH_3}{C}ClCH_2Cl$	125 at 1 mm.	30			28.3	28.3	2.35	2.37	63
 $CH_2Br\underset{CH_3}{C}Br(CF_2)_3\underset{CH_3}{C}BrCH_2Br$	133 at 1 mm.	32			19.6	20.0	1.81	1.73	56
 $CH_2Br\underset{CH_3}{C}Br(CF_2)_4\underset{CH_3}{C}BrCH_2Br$		70			19.9	19.9	1.71	1.70	23
$CF_3CF_2CF_2CHBrCHBrCH_2CH_3$	85 at 30 mm.		1.4052	1.875	21.9	21.8	1.82	1.74	59
$CF_3CF_2CF_2CHBrCBr(CH_3)_2$	84 at 27 mm.		1.4109	1.874	21.9	21.8	1.82	1.94	33

tained from the Minnesota Mining and Manufacturing Company and esterified in the usual manner using methanol.

Preparation of Alcohols.—The reactions of the esters with Grignard reagents were all conducted in a similar manner. A typical experiment is described as follows: Diethyl octafluoroadipate (125 g.) was dissolved in 500 ml. of anhydrous diethyl ether and the solution added dropwise to a solution of methylmagnesium iodide prepared from 248 g. of methyl iodide and 48.6 g. of magnesium in 1000 ml. of ether. The reaction temperature was maintained at 5° by means of an ice-bath. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 12 hours. A solution of 150 g. of ammonium chloride in 500 ml. of water was then added dropwise to the flask, the ether layer separated, the aqueous layer extracted thoroughly with ether, and the combined ether solutions dried with Drierite. After drying, the ether was removed by distillation and the remaining oil crystallized twice from benzene to give the expected tertiary dihydric alcohol. In the case of liquid products, the procedure was modified to include rectification rather than crystallization to obtain a pure material.

Preparation of Olefins.—The tertiary alcohols were dehydrated in a similar manner. A typical experiment is described as follows: 2,7-Dimethyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanediol (100 g.) was dissolved in 200 ml. of diethyl ether and 350 g. of concentrated sulfuric acid was added dropwise to the reaction mixture. After the addition was complete, the mixture was distilled until the distillation temperature reached 160°. The distillate was then washed with sodium bicarbonate solution followed by water, dried with Drierite and rectified. In the case of a liquid starting material, it was not necessary to dissolve the alcohol in ether before reaction with sulfuric acid.

The secondary alcohols were dehydrated similarly with phosphorus pentoxide. A typical experiment is described as follows: 5,5,6,6,7,7,7-Heptafluoro-3-heptanol (180 g.) was thoroughly mixed with 100 g. of phosphorus pentoxide in a distilling flask and the mixture heated slowly until distillation of the olefin occurred (pot temperature of 150–200°). The product was then washed with sodium bicarbonate solution followed by water, dried with Drierite and rectified. In the case of a solid starting material, a slurry of the alcohol and phosphorus pentoxide in benzene was used. In one instance (see Table I), both a mono- and diene were isolated from the dehydration of a dihydric alcohol.

Chlorination of 2,6-Dimethyl-3,3,4,4,5,5-hexafluoro-1,6-heptadiene.—The olefin (140 g.) was dissolved in carbon tetrachloride and the solution placed in a Pyrex test-tube (3 cm. × 120 cm.) fitted with a gas dispersion disc, thermometer well and reflux condenser. Illumination was furnished by means of a 40-watt BL fluorescent light placed alongside the tube. Chlorine was introduced, and after a short induction period, the temperature rose to 50°. The chlorination was continued for 50 hours, the mixture aerated for one hour, and then rectified to give the dichloro and tetrachloro addition compounds.

Chlorination of 2,7-Dimethyl-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene.—Chlorination of this olefin in carbon tetrachloride solution at 25° gave only the tetrachloro addition product. No reactions were conducted at higher temperatures.

Bromination of 2,6-Dimethyl-3,3,4,4,5,5-hexafluoro-1,6-heptadiene.—A solution of 50 g. of bromine in 100 ml. of carbon tetrachloride was added slowly to a solution of 180 g. of the olefin in 200 ml. of carbon tetrachloride contained in a one-liter, three-necked flask equipped with a stirrer, dropping funnel and reflux condenser. A 150-watt bulb was placed next to the flask as a source of illumination. The reaction proceeded rapidly at room temperature. After the addition was complete, the reaction mixture was washed with sodium bisulfite followed by water, dried and rectified to give principally the tetrabromo addition product along with some of the dibromo compound.

Bromination of 2,7-Dimethyl-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene.—This olefin was brominated in a similar manner with the exception that the reaction temperature was maintained at the reflux temperature of the mixture. Only the tetrabromo addition product was isolated.

Bromination of 5,5,6,6,7,7,7-Heptafluoro-3-heptene.—A solution of 150 g. of the olefin in 100 ml. of carbon tetrachloride was cooled to 12° and a solution of 120 g. of bromine in 100 ml. of carbon tetrachloride was added dropwise. The reaction was illuminated by a 150-watt light bulb placed next to the flask. After one-half the bromine was added, the temperature rose to 22° and hydrogen bromide was liberated. The temperature was lowered to 10° and the remaining bromine added. After standing for 12 hours at room temperature, the reaction mixture was refluxed for two hours causing further liberation of hydrogen bromide. The solution was then washed with sodium bicarbonate followed by water, dried and rectified. Both the dibromo addition product and an olefin resulting from its dehydrobromination were obtained. The latter material was not identified.

Bromination of 2-Methyl-4,4,5,5,6,6,6-heptafluoro-2-hexene.—A solution of 160 g. of the olefin in 150 ml. of chloroform was placed in the flask and a mixture of 125 g. of bromine in 100 ml. of chloroform was added dropwise. No cooling was employed and the reaction temperature rose rapidly to reflux with the liberation of hydrogen bromide. After the addition was complete, the mixture was refluxed for 48 hours. The solution was then washed with sodium bicarbonate followed by water, dried and rectified. The dibromo addition product was obtained as well as two bromine substituted derivatives of the starting material.

Acknowledgment.—The authors wish to express their appreciation to the Petroleum Branch, Materials Laboratory, Wright Air Development Center, Dayton, Ohio, for supporting this work.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

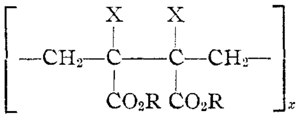
The Structure of the Polymers of α-Haloacrylates

BY C. S. MARVEL, E. D. WEIL, L. B. WAKEFIELD AND C. W. FAIRBANKS

RECEIVED NOVEMBER 5, 1952

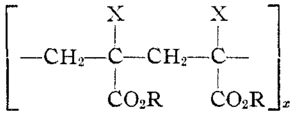
The present investigation shows that the earlier assignment of a "head-to-head" arrangement of the monomer units in polyalkyl α-haloacrylates was based on a misinterpretation of the reactions of these polymers. These polymers have been proved to have predominantly the "head-to-tail" structure.

Experimental results obtained in this Laboratory have previously been presented[1] as evidence that the polymers of α-haloacrylic esters have a "head-to-head" arrangement of monomer units I rather than the usual "head-to-tail" structure II.



$$\left[-CH_2-\overset{X}{\underset{CO_2R}{C}}-\overset{X}{\underset{CO_2R}{C}}-CH_2-\right]_x$$

I



$$\left[-CH_2-\overset{X}{\underset{CO_2R}{C}}-CH_2-\overset{X}{\underset{CO_2R}{C}}-\right]_x$$

II

X = Cl or Br, R = alkyl

Since all other vinyl homopolymers investigated to date have been shown to have predominantly a "head-to-tail" structure, further study of this apparent anomaly has been undertaken.

The evidence originally presented as indicative of the head-to-head structure of polymethyl α-bromoacrylate may be summarized as follows: 1. Treatment of the polymer with an alkali iodide in acetone or aqueous dioxane results in the liberation of approximately as much iodine as is produced in the reaction of an alkali iodide with diethyl α,β-dibromosuccinate under similar conditions. 2. The polymer loses hydrogen bromide at a lower temperature than is required to dehydrobrominate diethyl α,γ-dibromo-α,γ-diethylglutarate. 3. The product made by treating the polymer with aqueous alkali slowly reduces periodic acid. 4. Treatment of the polymer with zinc in refluxing dioxane removed 97% of the bromine, 11% more than the statistical calculations of Flory[2] indicate could be removed from structure II by formation of cyclopropane rings.

The present investigation shows that this evidence does not justify the assignment of structure I to the α-haloacrylate polymers, and evidence for structure II has been obtained.

Further study of the action of alkali iodides on polymethyl α-bromoacrylate indicates that the reaction is more complex than was originally believed. The product obtained by treating the polymer with potassium iodide in wet dioxane at 100° is a dark red tar, largely water-soluble, resembling the product obtained from the dehydrobromination of the polymer by heating with quinoline. Treatment of polymethyl α-bromoacrylate with sodium iodide in refluxing acetone yields a tan powder which has infrared bands at 1786 cm.$^{-1}$ (lactone carbonyl), 1736 cm.$^{-1}$ (unconjugated ester carbonyl) and only a trace of absorption indicative of carbon-to-carbon double bonds.[3] Polymethyl α-bromoacrylate when allowed to stand at room temperature for three weeks in a solution of sodium iodide in methyl cellosolve–dioxane mixture liberated iodine equivalent to 90% completion of the hypothetical 1,2-elimination of halogen. The product however showed strong infrared bands at 1777 cm.$^{-1}$ (γ-lactone carbonyl), 1730 cm.$^{-1}$ (conjugated ester carbonyl), and a weak band at 1625 cm.$^{-1}$ indicative of olefinic linkages. The interpretation of the reaction of alkali iodides with polymethyl α-bromoacrylate as a 1,2-elimination of halogen from structure I is placed in considerable doubt by this evidence.

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(1) C. S. Marvel and J. C. Cowan, THIS JOURNAL, **61**, 3156 (1939).

(2) P. J. Flory, *ibid.*, **61**, 1518 (1939); *cf.* F. T. Wall, *ibid.*, **62**, 803 (1940).

(3) The infrared spectra discussed in this article were obtained on samples in Nujol mull, unless otherwise specified. The authors are indebted to Mrs. Elizabeth Petersen Leighly and Miss Helen Miklas, who obtained the spectra and assisted in their interpretation.