TABLE I

ETHYL 2-ALKYLACETOACETATES

Alkyl group	Halide	Reflux, hr.	Distn. range °C.	Distn. range Mm.	Yield, %	B.p., °C. (25 mm.)	$n^{25}D$	Analytical data[a,b] Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Cyclopentyl	Br	17	135–140	25	63.5	139	1.4533	66.64	66.47	9.15	9.15
Cyclohexylmethyl	I	21	160–170	27–30	55.4	166	1.4588	68.99	68.74	9.80	9.89
2-Cyclohexylethyl	Br	48	168–178	20	54.5	175	1.4587	69.96	69.74[c]	10.07	10.12[c]

[a] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [b] Boiling points uncorrected. [c] Microanalysis by Goji Kodama, University of Michigan.

TABLE II

2-ALKYLFUMARIC ACIDS

Alkyl group	Yield, %	M.p.,[a] °C.	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]	Neut. equiv. Calcd.	Neut. equiv. Found
Cyclopentyl	36.9	230.5–231.5	58.69	58.71	6.57	6.53	92	93
Cyclohexylmethyl	28.7	204.5–206.0	62.24	62.34	7.55	7.66	106	106
2-Cyclohexylethyl	27.7	224.0–224.5	63.70	63.88	8.02	7.96	113	114
2-Phenylethyl[c]	13.7	198.5–200.0	64.44	65.22[d]	5.49	5.37[d]	110	110

[a] Melting points are uncorrected. [b] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [c] Acetoacetic ester reported by K. von Auwers and K. Möller, *J. prakt. Chem.*, **109**, 124 (1925). [d] Microanalysis by Goji Kodama, University of Michigan.

TABLE III

2-ALKYLMALEIC ANHYDRIDES

Alkyl group	Yield, %	B.p.,[a] °C.	B.p., Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]
n-Butyl[c]	77.9	135	30	1.4654	62.32	62.15[e]	6.54	6.49[e]
i-Butyl[d]	45.5	134	30	1.4642	62.32	62.12[e]	6.54	6.50[e]
Cyclopentyl	84.3	95	0.7	1.5002	65.07	65.38	6.02	6.21
Cyclohexylmethyl	41.2	127	1.7	1.4980	68.02	67.96	7.26	7.22
2-Cyclohexylethyl	29.0	139	1.6	1.4647	69.20	69.28	7.75	7.58

[a] Boiling points are uncorrected. [b] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [c] Fumaric acid reported by R. Fittig and F. Fichter, *Ann.*, **304**, 241 (1899). [d] Fumaric acid reported by Demarcay, ref. 6. [e] Microanalysis by Goji Kodama, University of Michigan.

and Table II lists the alkylfumaric acids resulting from the Demarcay–Walden reaction. All but one of the compounds listed in Table II were converted to the corresponding maleic anhydrides by distillation from phosphorus pentoxide[9]; and in addition, two previously known alkylfumaric acids were converted to the corresponding alkylmaleic anhydrides, which are reported in Table III.

Experimental

Ethyl 2-Akylacetoacetates.—These compounds were prepared according to a standard procedure[10] using freshly distilled ethyl acetoacetate (b.p. 72–79° (23 mm.)) and magnesium-dried ethanol. In each reaction, for each 1.00 mole of ester there was used 1.00 mole of sodium, 666 ml. of ethanol and 1.11 moles of alkyl halide.[11] The reaction was allowed to reflux until the mixture was neutral to moist universal indicator paper, except in the case of cyclopentyl bromide where the mixture remained alkaline. Data are summarized in Table I.

2-Alkylfumaric Acids.—A modification of the previously reported[6-8] procedure was used. For a 0.5-mole run 150 ml. of absolute ether was used. The initial reaction of the added bromine was very vigorous, but the second half-mole could be added all at once. The final mixture was then refluxed for 4.5 to 5 hr. Here an improvement in procedure involved the addition of 500 ml. of water, separation and return of the *lower* ethered layer *via* a dropping funnel to the reaction flask, now charged with 135 g. of potassium hydroxide pellets in 150 ml. of ethanol. Complete solution of the hydroxide was found unnecessary, and the mixture was vigorously stirred and cooled at 0–5° by an ice-bath. After working up essentially as described[7] the red residual slurry was triturated with hot chloroform. The crystallized acids were recrystallized from aqueous ethanol (Norit) at least three times. Additional crops for recrystallization were available by concentrating the chloroform and aqueous mother liquors. Data are summarized in Table II.

2-Alkylmaleic Anhydrides.—The procedure of Tanatar[9] was used wherein the appropriate 2-alkylfumaric acid (0.05 mole) and 0.05 mole of phosphorus pentoxide were intimately mixed in the reaction flask which was then arranged for low pressure distillation and placed in an oil-bath heated to 100°. The temperature was gradually raised until distillation commenced. It was found essential to rinse the reaction flask with glacial acetic acid, followed by acetone (before charging it), to effect very complete mixing of the reagents, to use very slow initial heating and to submerge the reaction flask completely in the oil-bath. The crude products were subsequently twice distilled from 1–2 g. of phosphorus pentoxide using a small Vigreux column and then were fractionated through a 20-plate column. Data are summarized in Table III.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

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[9] S. Tanatar, *Ann.*, **268**, 255 (1892).

[10] A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 465.

[11] When cyclohexylmethyl bromide was employed, a liquid, b.p. 120–122° (20 mm.), was the only product. It gave a negative ferric chloride test. Cyclohexylmethyl iodide gave satisfactory results.

The Chemistry of Perfluoro Ethers. II. Ether Cleavage with Simultaneous Replacement of α-Fluorine by Chlorine[1a]

BY GEORGE VAN DYKE TIERS

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In Part I of this series[1b] the first known chemical reaction undergone by a perfluoro ether was re-

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[1] (a) Presented at the 126th Meeting of the American Chemical Society, New York, 1954, Abstracts, p. 27-M; (b) G. V. D. Tiers, THIS JOURNAL, **77**, 4837 (1955).

ported. Members of a series of perfluoro (α-alkyl) cyclic ethers were treated with aluminum chloride to give simple replacement of the three alpha fluorine atoms by chlorine.

A quite different result was obtained when perfluoro di-(*n*-alkyl) ethers were similarly treated. No α,α,α′,α′-tetrachlorofluoro ethers were found, but instead the cleavage products corresponding to them were isolated, as illustrated by the equation

$$R_fCF_2OCF_2R_f \xrightarrow{AlCl_3} (R_fCCl_2OCCl_2R_f) \longrightarrow R_fCOCl + R_fCCl_3$$

The absence of partially-reacted ethers or their cleavage products lends support to the postulation of the tetrachloro ether as a reaction intermediate. Although under these conditions the cyclic α,α,α′-trichloroperfluoro ethers were stable,[1b] decachlorodiethyl ether on heating splits spontaneously to CCl_3COCl and C_2Cl_6.[2]

The reaction of $(n\text{-}C_4F_9)_2O$ with aluminum chloride gave known products. The acyl chloride, $n\text{-}C_3F_7COCl$,[3-5] and the trichloride, $n\text{-}C_3F_7CCl_3$,[6] were identified by boiling points and infrared spectra. The acyl chloride $n\text{-}C_5F_{11}COCl$,[5] from cleavage of the ether $(n\text{-}C_6F_{13})_2O$, was similarly identified. The trichloride, $n\text{-}C_5F_{11}CCl_3$, is a new compound.

It is now possible to characterize perfluoro ethers and determine their structure by cleavage followed by preparation of a suitable derivative of the resulting perfluoroacyl chloride or chlorides. In the examples described here the amides were prepared. By mixed melting point determination with authentic samples of $n\text{-}C_3F_7CONH_2$[3-5] and $n\text{-}C_5F_{11}CONH_2$[5] these amides were shown to have the normal structure.

This work verifies that the perfluoro ethers have retained the normal structure of the hydrogen-containing ethers from which they were obtained by electrochemical fluorination.[7,8]

Experimental

Perfluoro Ethers.—The perfluoro ethers $(n\text{-}C_4F_9)_2O$ and $(n\text{-}C_6F_{13})_2O$ used in this work had been prepared in these laboratories by electrochemical fluorination[8] of the corresponding ethers, $(n\text{-}C_4H_9)_2O$ and $(n\text{-}C_6H_{13})_2O$.[9] Their boiling points, refractive indices and infrared spectra indicated the absence of impurities.

Reactions with Aluminum Chloride.—Reactions and processing were very similar to those previously described.[1b] Minor differences are noted below.

Reaction of $(n\text{-}C_4F_9)_2O$.—Twenty grams of the perfluoro ether $(n\text{-}C_4F_9)_2O$ and the theoretical amount of aluminum chloride (8.0 g.) were heated together at 175° for 16 hours in a rocking autoclave of 43-ml. volume. The autoclave was chilled and opened: volatile materials were caught in a liquid air trap on warming and partial evacuation. There was obtained 2.3 g. of material boiling above room temperature, with n^{25}D 1.2880 (reported[3] for $n\text{-}C_3F_7COCl$, n^{25}D 1.288). Infrared analysis showed this material to be fairly pure $n\text{-}C_3F_7COCl$. The amide, prepared by direct reaction with ammonia gas and recrystallized from CCl_4, did not depress the melting point of an authentic sample of $n\text{-}C_3F_7CONH_2$.[5] *Anal.* Calcd. for $C_4H_2F_7NO$: N, 6.57. Found: N, 6.64.

Distillation of the filtered reaction product gave several fractions, b.p. 87–98°, which contained both unreacted $(n\text{-}C_4F_9)_2O$ and $n\text{-}C_3F_7CCl_3$. By refractive indices and infrared spectra the amounts were determined to be 6.0 and 2.8 g., respectively. From this the ether conversion is calculated as 70%, and the yields of $n\text{-}C_3F_7COCl$ and $n\text{-}C_3F_7CCl_3$ are each 30% (based upon ether not recovered). In an otherwise identical reaction, run at 150° for 13 hours, the conversion was 45% but the yield of $n\text{-}C_3F_7CCl_3$ was only 8%; $n\text{-}C_3F_7COCl$ was not recovered. Some hexachloroethane was found in the distillation residues.

Reaction of $(n\text{-}C_6F_{13})_2O$.—The ether $(n\text{-}C_6F_{13})_2O$, 110 g. and aluminum chloride, 35 g. (120% of theory) were heated at 230° for 15 hours. Upon distillation of the filtered reaction mixture there was obtained $n\text{-}C_5F_{11}COCl$, b.p. 87–93°, n^{25}D 1.2992 (reported[5] for $n\text{-}C_5F_{11}COCl$, b.p. 90°, n^{25}D 1.310) yield 20.6 g. (43%). Infrared analysis showed this to be pure $n\text{-}C_5F_{11}COCl$. *Anal.* Calcd. for $C_6ClF_{11}O$: Cl, 10.7. Found: Cl, 10.8.

The amide, recrystallized from CCl_4, did not depress the melting point of an authentic sample of $n\text{-}C_5F_{11}CONH_2$.[5] *Anal.* Calcd. for $C_6H_2F_{11}NO$: N, 4.47; F, 66.8. Found: N, 4.40; F, 66.7.

There was also obtained a fraction which proved to be fairly pure $n\text{-}C_5F_{11}CCl_3$: it had b.p. 140–144°, n^{25}D 1.3403 and weighed 28.5 g. (51%). It was, however, contaminated by some hexachloroethane; this was removed by means of the purification procedure previously described for the cyclic α,α,α′-trichloroperfluoro ethers.[1b] Twenty grams of pure $n\text{-}C_5F_{11}CCl_3$, b.p. 143°, n^{25}D 1.3383, was obtained. *Anal.* Calcd. for $C_6Cl_3F_{11}$: C, 18.6; Cl, 27.5. Found: C, 18.6; Cl, 27.5.

Sixteen grams (15%) of unreacted $(n\text{-}C_6F_{13})_2O$ was recovered. Yields are based on ether not recovered.

The reaction of 25 g. of $(n\text{-}C_6F_{13})_2O$ and 8 g. of $AlCl_3$ at 185° for 14 hours went to the extent of 77%. The yields of $n\text{-}C_5F_{11}COCl$ and $n\text{-}C_5F_{11}CCl_3$ were 51 and 63%, respectively.

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CONTRIBUTION NO. 100 FROM THE
CENTRAL RESEARCH DEPARTMENT
MINNESOTA MINING & MANUFACTURING COMPANY
ST. PAUL 6, MINNESOTA

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[3] Technical Bulletin, "Heptafluorobutyric Acid," Minnesota Mining and Manufacturing Company, New Products Division, St. Paul 6, Minnesota, 1949.

[4] D. R. Husted and A. H. Ahlbrecht, Abstracts, 116th A.C.S. Meeting, September, 1949, p. 10K.

[5] A. H. Ahlbrecht, D. R. Husted, T. S. Reid and G. H. Smith, Jr., THIS JOURNAL, **78**, in press (1956).

[6] G. V. D. Tiers, H. A. Brown and T. S. Reid, *ibid.*, **75**, 5978 (1953).

[7] J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 414.

[8] J. H. Simons, U. S. Patent 2,500,388 (March 4, 1950).

The Chemistry of Perfluoro Ethers. III. Synthesis of ω-Trichloromethylperfluoroacyl Chlorides by Cleavage of Cyclic Perfluoro Ethers[1]

BY GEORGE VAN DYKE TIERS

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Perfluoro (α-alkyl) cyclic ethers have been found to react with aluminum chloride to give simple substitution of the three α-fluorine atoms by chlorine.[2a] Alpha substitution also occurred with perfluoro di-(*n*-alkyl) ethers, but was then followed by cleavage of the ether.[2b]

This study has now been extended to two cyclic perfluoroethers which do not bear an α-perfluoroalkyl group. These ethers split very much as had

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[1] Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, Abstracts, p. 27-M.

[2] (a) Part I, G. V. D. Tiers, THIS JOURNAL, **77**, 4837 (1955); (b) Part II, *ibid.*, **77**, 6703 (1955).