prepared by the method of Doering and Hoffmann.[9] We were not able to demonstrate whether VI was formed by a dichlorocarbene–olefin addition or a two-step addition-elimination reaction of the mercurial with the olefin. With the goal of obtaining a product which would yield dichlorocyclopropanes when mixed with olefins at room temperature or below, several attempts were made to prepare trichloromethyl derivatives of other metals, including Pb, Cu, Ag, and Zn, using the trichloroacetate pyrolysis procedure. All these attempts were unsuccessful.

Experimental

The inorganic mercuric salts used in this study were commercial materials, reagent grade. The monoglyme (1,2-dimethoxyethane) was obtained from Matheson, Coleman and Bell. Purification was achieved by refluxing over lithium aluminum hydride, followed by distillation and subsequent storage over sodium ribbon. Sodium trichloroacetate was prepared by the careful neutralization of commercial trichloroacetic acid, followed by freeze-drying until no more water could be removed. This product was then forced through a 100-mesh sieve and thoroughly mixed, under nitrogen, to ensure uniformity.

The potassium *t*-butoxide was used as received from the MSA Research Corporation.

All melting points are uncorrected and were obtained in open capillary tubes on a MEL-Temp apparatus.

Trichloromethylmercuric Bromide (II) *via* Haloform–Base Route.—Into a 500 ml., three-necked flask equipped with stirrer, thermometer, and condenser were placed 150 ml. of benzene, 108.1 g. (0.3 mole) of mercuric bromide, and 11.9 g. (0.1 mole) of chloroform. While stirring rapidly, 11.2 g. (0.1 mole) of potassium *t*-butoxide was added in small portions through Gooch tubing over a period of 30 min. while cooling with an ice bath. Stirring was continued an additional 50 min. before pouring the mixture into 1 l. of water. The water was then extracted with diethyl ether and the ether was subsequently washed with water, dried, and evaporated on a rotary evaporator to give 0.5 g. (1.2% yield) of product, m.p. 160–161°, after recrystallization from chloroform. As indicated in Table I, mercury and chlorine analyses, and molecular weight determinations were in satisfactory agreement with calculated values. The mother liquor was carefully examined for other organomercurials but none were found.

Preparation of II *via* Sodium Trichloroacetate Route.—Into a flask equipped with reflux condenser and exit tube were placed mercuric bromide, 36.04 g. (0.1 mole), 18.5 g. (0.1 mole) of III, and 150 ml. of monoglyme. The exit tube led to an inverted graduated cylinder used to measure carbon dioxide evolution by water displacement. Heat was applied with a mantle and in 15 min., 2.5 l. of carbon dioxide had been collected from the refluxing solution. Reflux was continued an additional 1 hr., but no further gas evolution could be detected. The contents of the flask were then poured into water to give a heavy brown oil that was separated by ether extraction. The extract was water-washed, dried over magnesium sulfate, and the solvent removed on a rotary evaporator. Recrystallization from chloroform gave 17.8 g. (44.5%) of product, m.p. and m.m.p. with II above, 160–161°.

Use of a 2:1 ratio of III/mercuric bromide gave the same product in 69% yield (recrystallized).

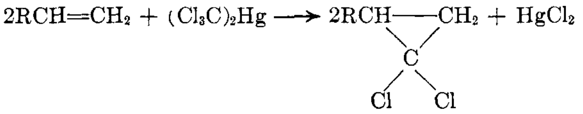
Bis(trichloromethyl)mercury (IV) from Mercuric Chloride and III.—Into the same apparatus as described above was placed 27.2 g. (0.1 mole) of mercuric chloride, 37.0 g. (0.2 mole) of III and 150 ml. of monoglyme. The solution was refluxed for 1 hr. and 4.3 l. of gas was collected (4 l. in first 25 min.). The contents of the flask were poured into 1 l. of water to give a dense white oil which was separated by ether extraction and treated as described above. Recrystallization from chloroform gave 31.2 g. (71.5%) of product, m.p. 140–141°.

The same product was obtained in 54% yield (recrystallized) by an identical procedure utilizing 31.9 g. (0.1 mole) of mercuric acetate in place of mercuric chloride.

All other mercurials were obtained by identical procedures and the pertinent data is shown in Table I.

Preparation of IV from I and Sodium Trichloroacetate.—Into the same apparatus as described previously were placed 8.9 g. (0.025 mole) of I, 4.6 g. (0.025 mole) of sodium trichloroacetate, and 100 ml. of monolyme. After 1 hr. of reflux, 1 l. of gas had been collected. Product isolation as described above gave 7.5 g. (67.5% yield) of IV, m.p. and m.m.p. with IV above, 140–141°.

Preparation of 1,1-Dichlorocyclopropanes from Olefins and I or IV.—Into a nitrogen-flushed 100-ml. flask equipped with condenser and magnetic stirring bar were placed 4.37 g. (0.01 mole of IV and 16.8 g. (0.1 mole) of 1-dodecene. This mixture was heated in an oil bath at 170–190° for 2.5 hr. Petroleum ether (50 ml.) was added to precipitate unchanged IV and I (identified by recrystallization and m.p. comparison with known I) and this filtered, clear layer was water-washed, dried, and distilled to separate 1-dodecene from the product fraction, b.p. 98–120° (0.5 mm.). The dichlorocyclopropane product was identified by comparisons with the same compound[8] prepared from chloroform, potassium *t*-butoxide, and olefin.[9] The yield of product was 24%, by gas chromatographic analysis, based on the following stoichiometry.



$$2RCH{=}CH_2 + (Cl_3C)_2Hg \longrightarrow 2RCH\text{—}CH_2 + HgCl_2$$

A 25% yield of dichloronorcarane was obtained by heating IV with cyclohexene for 15 min. at 200° in an autoclave.

Heating I with cyclohexene for 15 min. at 250° in an autoclave gave a 36% yield of dichloronorcarane.

Acknowledgment.—The author is indebted to Dr. K. T. Knapp for the X-ray fluorescence analysis of these compounds.

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[9] Wm. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

A New Synthesis of Perfluoroalkylmagnesium Halides

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Although perfluoroalkyl Grignard reagents have been known for some time, direct formation of the organometallics from the corresponding halides and magnesium has been possible only with perfluoroalkyl iodides. Perfluoropropylmagnesium bromide was prepared[2] by a metathetical reaction of phenylmagnesium bromide with perfluoropropyl iodide and not by the conventional Grignard technique. 1,1,2,2,3,3,3-Heptafluoropropane was obtained[3] upon hydrolysis of the reaction mixture between perfluoropropyl bromide and magnesium in ether; thus it is possible that a Grignard reagent was present, although no other reactions were described. The experimental difficulties connected with the preparation of trifluoromethylmagnesium iodide[4] and the ready availability of trifluoromethyl bromide led us to explore the feasibility of converting the latter into the corresponding Grignard reagent.

No reaction occurred upon treatment of the bromide with sublimed magnesium in anhydrous ether. How-

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[1] Taken from part of a thesis submitted by Robert D. Battershell to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] O. R. Pierce, A. F. Meiners, and E. T. McBee, *J. Am. Chem. Soc.*, **75**, 2516 (1953).

[3] T. J. Brice, W. H. Pearlson, and J. H. Simons, *ibid.*, **68**, 969 (1946).

[4] R. N. Haszeldine, *J. Chem. Soc.*, 1273 (1954).

TABLE I

REACTION OF TRIFLUOROMETHYL BROMIDE, MAGNESIUM AMALGAM, AND ACETONE[a]

Temp., °C.	−20	−20	−20	−20	−20	−20	25	25	25	25	25
Hg, g.	1	3.5	5	10	5	60	None	5	30	300	380
Conversion, %[b]	8	7[c]	11	19[c]	9	8[d]	0	9[e]	10	9	18

[a] With the noted exceptions, 0.2 g.-atom of magnesium and 0.2 mole of acetone were used; acetone and I, the latter in a continuous stream, were added simultaneously after Grignard formation commenced. [b] Based on acetone. [c] Metalation for 3 hr. prior to addition of acetone. [d] 0.5 mole of magnesium used. [e] Ethylene bromide added at "entraining agent."

ever, in the presence of commercial magnesium turnings activated with a small amount of mercury a reaction began almost immediately, leading to the formation of a reagent which reacted with dry acetone to produce 2-trifluoromethyl-2-propanol. For reasons unknown, the reaction ceased after 20 to 30% of the theoretical amount of magnesium had been consumed. Neither the addition of fresh magnesium during the reaction nor the use of ethylene dibromide as "entraining agent"[5] to renew the surface of the metal caused a significant increase in conversion. The optimum experimental conditions required reaction of CF_3Br at −20° with a magnesium amalgam prepared from approximately equal weights of magnesium and mercury in anhydrous ether (Table I). In some cases small amounts of 2-propanol were isolated.[6] In one experiment, 2-butanone and tetrahydrofuran solvent were used under the general condition at −20°; conversion was 5%.

Several experiments were carried out using trifluoromethyl iodide, with no improvement in yield. As expected, the Grignard reagent prepared from heptafluoropropyl iodide and magnesium amalgam when treated with acetone afforded a better yield of the corresponding alcohol (Table II).

TABLE II

REACTION OF PERFLUOROALKYL IODIDES, MAGNESIUM AMALGAM, AND ACETONE

Iodide	Mole	Mg, mole	Hg, g.	Temp., °C.	Yield,[a] %
CF_3I	0.14	0.14	400	25	9
CF_3I	.20	.20	25	−65	14
C_3F_7I	.10	.15	15	0	37

[a] Based on iodide.

Trifluoromethylmagnesium iodide is thermally unstable and decomposes to give tetrafluoroethylene and fluorocarbon polymers.[4] On the suggestion[7] that difluorocarbene may be an intermediate in the decomposition of perfluoromethylmetallics, several reactions were carried out using cyclohexene in attempts to trap any carbene present during the reaction of trifluoromethyl iodide with magnesium amalgam. However, no 7,7-difluorobicyclo[4.1.0]heptane could be isolated; instead, 1-iodo-2-trifluoromethylcyclohexane was produced in 43% yield. When the reaction was carried out in the absence of ether, the product formed in 27% yield. Although attempts have not been made to obtain optimum reaction conditions or to extend the reaction to other olefinic systems, this method appears to be useful for addition of perfluoroalkyl iodides to olefins under very mild conditions. It bears some resemblance to the addition of bromotrichloromethane to olefins which Kharasch, *et al.*,[8] found to be catalyzed by magnesium turnings and a trace of iodine.

Experimental[9]

Starting Materials.—Trifluoromethyl bromide was obtained from the Du Pont de Nemours Co. and used without purification. Trifluoromethyl and heptafluoropropyl iodide were prepared according to Hauptschein and Grosse.[10]

Preparation of Perfluoroalkylmagnesium Halides and Reaction with Acetone. General Procedure (See Also Tables I and II).—A 500-ml. three-necked flask was equipped with a Dry Ice condenser vented through a Dry Ice trap, a Trubore stirrer with teflon paddle, and a close-circuit addition funnel. A gas inlet tube extending below the surface of the flask contents was affixed for reactions with the volatile halides. The apparatus was swept for about 15 min. with a stream of high purity nitrogen, magnesium turnings were added, and the apparatus was flamed while the nitrogen sweep was continued. Upon cooling, triple-distilled mercury was added and the mixture was stirred rapidly until the amalgam formed. Anhydrous ether (200 ml.) was added and this was followed by the halide. When reaction commended, as evidenced by the evolution of heat and darkening of the metallic surface, the reaction mixture was cooled to the designated temperature and the dropwise addition of acetone was begun, with continued addition of the halide. In the reactions with trifluoromethyl bromide and iodide, addition was terminated when the halide was no longer absorbed. Upon hydrolysis with 10% aqueous hydrochloric acid, the ether layer was separated and the aqueous layer (containing fluoride ion) was extracted several times with ether. The combined ether solution was dried over sodium sulfate and distilled to give the respective alcohol, 2-trifluoromethyl-2-propanol, or 2-methyl-3,3,4,4,5,5,5-heptafluoro-2-pentanol. The alcohols were identified by infrared spectral and vapor phase chromatographic comparison with authentic materials.[11]

1-Iodo-2-trifluoromethylcyclohexane.—(a) In the presence of ether: a magesium amalgam was prepared under a nitrogen atmosphere from 4.8 g. (0.2 g.-atom) of magnesium and 250 g. of mercury. The amalgam was covered with a solution of 25 g. (0.3 mole) of cyclohexene in 200 ml. of dry ether, whereupon 40 g. (0.2 mole) of trifluoromethyl iodide was allowed to distil slowly into the mixture. The latter was stirred for 4 hr. without heating and was hydrolyzed with 10% cold aqueous hydrochloric acid; the ether layer was separated and the aqueous layer (containing fluoride ion) extracted twice with 100 ml. of ether. The combined ether solution was dried over sodium sulfate and distilled to give 23.5 g. (43%) of product, b.p. 42–43° (2.6 mm.), n^{20}_{D} 1.4818, d^{20}_{4} 1.7442.

Anal. Calcd. for $C_7H_{10}F_3I$: C, 30.23; H, 3.62; I, 45.64, M_D, 45.36. Found: C, 30.15; H, 3.89; I, 45.39; M_D, 45.42.

(b) In the absence of ether: the magnesium amalgam was prepared as above and treated with the iodine and 100 ml. of cyclohexene. Work-up as before gave 15 g. (27%) of product.

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(5) D. E. Pearson, D. Cowan, and J. D. Becker, *J. Org. Chem.*, **24**, 504 (1959).

(6) The reduction of carbonyl compounds by perfluoroalkyl Grignard reagents in ether has been described by E. T. McBee, C. W. Roberts, and S. C. Curtis, *J. Am. Chem. Soc.*, **77**, 6387 (1955).

(7) E. Bergman, *J. Org. Chem.*, **23**, 476 (1958).

(8) M. S. Kharasch, O. R. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

(9) All temperatures are uncorrected. Analyses were performed by Dr. C. S. Yeh, Purdue University. Infrared spectra were obtained by Mrs. W. Dilling, Purdue University, on a Perkin-Elmer, Model 21, spectrophotometer. Vapor phase chromatography was carried out on a Perkin-Elmer, Model 154-B, fractometer, using Carbowax on firebrick and helium as the carrier gas.

(10) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 2461 (1951).

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

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Decomposition of Tetrabutylphosphonium Acylates[1]

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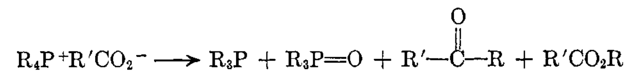
Letts and Collie[2] reported that tetraethylphosphonium acetate and benzoate decompose according to the following general equation. Although they were able



$$R_4P^+R'CO_2^- \longrightarrow R_3P + R_3P{=}O + R'{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R + R'CO_2R$$

to identify the various products of these decompositions, no attempt was made to establish the yields or the best reaction conditions. It did appear, though, that the ketones were formed in considerably greater yield than the esters.

It seemed worthwhile to reinvestigate this decomposition with the view of establishing more completely the nature of the reaction. Tetrabutylphosphonium butyrate, benzoate, and acetate were prepared and pyrolyzed. In general the course of the reaction was found to be that suggested by Letts and Collie. Temperatures of 300–340° are required to obtain optimum yields of ketone. The best yields of ketone were obtained when the reaction was conducted under reduced pressure. This is probably due to more rapid removal of the ketone from the hot reaction mixture so that there is less chance for condensation reactions, etc., to occur. Under these conditions tetrabutylphosphonium benzoate gave valerophenone in 39% yield and n-butyl butyrate in 12% yield. Table I contains the data obtained from various pyrolysis reactions of this salt. Tetrabutylphosphonium butyrate similarly gave 4-octanone in 39% yield. The ester yield was not determined. In all cases other products were formed in small amount as was shown by gas–liquid chromatographic analysis. These were not identified. The pyrolysis of tetrabutylphosphonium acetate was investigated briefly. Under the conditions used, 325° and atmospheric pressure, 2-hexanone and acetone were the major products. Acetone undoubtedly was formed by condensation of acetate ions.

These reactions may have some value in synthesis. Although the yields of ketone are not high they may be satisfactory for some purposes. The mechanism of the formation of ketone is of interest and may well involve a pentacovalent phosphorus compound as an intermediate. Further work on this aspect of the problem is in progress. The formation of ester undoubtedly involves a typical nucleophilic displacement process.[3]

Table I

Temp., °C.	Pressure, mm.	Time, hr.	Valerophenone, %	Butyl benzoate, %
270	0.05	20	8	2
270	58	8	11	6
	+0.05	24		
300	760	8	22	2
340	760	8	21	16
340	94	1.5	39	12
400	760	15 min.	19	22

Experimental

Preparation of Tetrabutylphosphonium Salts.—Tetrabutylphosphonium bromide, m.p. 107–108° (lit.,[4] 99–101°), 17.0 g. (0.05 mole), in 100 ml. of dry methanol was added with stirring to a suspension of the silver salt of the acid (0.055 mole) in 300 ml. of dry methanol. The mixture was stirred for 24 hr. and filtered with Filter Aid. The filtrate was concentrated *in vacuo* at room temperature. The semicrystalline solid residues were used as such without further treatment.

Pyrolysis of Tetrabutylphosphonium Benzoate.—The pyrolysis reactions were conducted in a distilling flask with a short distillation path. Times are measured from immersion in the hot bath. The yields were calculated on the basis of g.l.c. data. Standard curves were constructed from known samples. The distillates were chromatographed and the percentages of ketone and ester were estimated by comparison with the known chromatograms. Other products found were butyl bromide, tributylphosphine, and tributylphosphine oxide. The infrared spectra of valerophenone and n-butyl benzoate obtained on samples isolated by g.l.c. were identical to those of known samples.

Pyrolysis of Tetrabutylphosphonium Butyrate and Acetate.—Essentially the same technique was used. 4-Octanone was identified by collection from a gas–liquid chromatogram and inspection of the infrared spectrum. The yields of ketone and conditions were: 250° (28 mm.) for 10 hr., 28%; 300° (26 mm.) for 2 hr., 39%; 350° (760 mm.) for 30 min., 32%.

Pyrolysis of tetrabutylphosphonium acetate at 325° yielded a distillate which was shown by g.l.c. to be composed of methanol (from the salt preparation), acetone, and 2-hexanone. The ketones were characterized by conversion of fractions from gas-liquid chromatography to 2,4-dinitrophenylhydrazones; thus acetone 2,4-dinitrophenylhydrazone, m.p. 124–126° (lit.,[5] m.p. 126°), and 2-hexanone 2,4-dinitrophenylhydrazone, m.p. 106–108° (lit.,[5] m.p. 106°), were obtained.

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(1) Research supported by the National Science Foundation.

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Hydrolysis of Fluorinated Ethers

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The hydrolysis of ethers containing the $—CF_2O—$ group by sulfuric acid has been used for the synthesis of the esters of various fluorinated acids[1] and for the determination of the direction of addition of alcohols to fluorinated olefins.[2] Optimum conditions[1a] call for

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