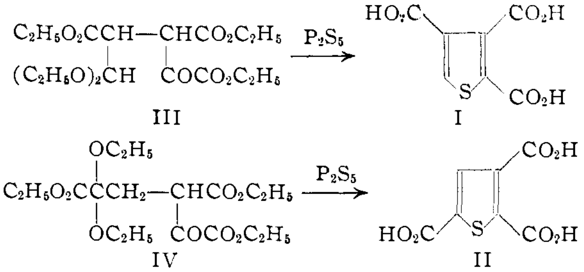
acid (I) and 2,3,5-thiophenetricarboxylic acid (II), appear not to have been synthesized previously. In connection with the preparation of other heterocyclic compounds in this Laboratory, intermediates have become available for the synthesis of I and II.

The acid I was obtained in 26% yield from diethyl α-diethoxymethyl-α′-ethoxalylsuccinate (III)[2] and phosphorus pentasulfide. In like manner II was obtained from diethyl α,α-diethoxy-α′-ethoxalylglutarate (IV),[3] but the yield was very low (4%).



The acids I and II had solubility properties similar to the tricarboxylic acids of benzene, *i.e.*, they were highly soluble in ether and ethyl acetate as well as in water.

Messinger[4] has described an acid obtained by permanganate oxidation of a mixture of dimethylacetylthiophenes. The acid was not purified, but a trimethyl ester melting at 118° was prepared. Hartough[5] has assumed that this product was trimethyl 2,3,5-thiophenetricarboxylate. Its melting point, however, does not correspond with the melting point of either the trimethyl ester of I (87°) or the trimethyl ester of II (83°). It must be concluded, therefore, that Messinger probably did not have in hand a thiophenetricarboxylic acid.

Acknowledgment.—The author is grateful to W. L. Brown, H. L. Hunter, G. M. Maciak and G. Beckmann for the microanalyses.

Experimental

2,3,4-Thiophenetricarboxylic Acid.—A mixture of 90 g. (0.25 mole) of crude diethyl α-ethoxalyl-α′-diethoxymethylsuccinate[2] and 55 g. (0.25 mole) of phosphorus pentasulfide in 350 ml. of toluene was stirred and heated under reflux for two hours. After cooling, the dark toluene solution was decanted and washed successively with 500 ml. of ice-cold 2 *N* sodium hydroxide solution and two 250-ml. portions of water. Evaporation of the toluene solution by warming under reduced pressure left a dark liquid residue. This was distilled under reduced pressure until nothing more came over. There was much decomposition, and a large quantity of resin remained in the flask. The liquid that was collected over the range 130–200° (2–5 mm.) was redistilled to yield 28 g. of red brown liquid, b.p. 140–160° (0.2 mm.). This was saponified upon shaking and heating with a solution of 20 g. of sodium hydroxide in 50 ml. of water and 25 ml. of ethanol. The resulting semi-solid mixture was warmed under reduced pressure to remove alcohol. The residue was taken up in 200 ml. of water, and this solution was acidified with excess hydrochloric acid. After clarification with a little carbon to remove some tar that separated, the water solution was evaporated to dryness by heating under reduced pressure. Three 150-ml. portions of ether were used to extract the solid residue, and after evaporation of the ether solution, a sirup remained that slowly crystallized to a tan powder. This crude acid weighed 18.5 g. (34% yield). It was purified by recrystallization from 50 ml. of glacial acetic acid and obtained as a white powder, m.p. 247–249° (sublimed above 225°). The yield of pure acid was 14 g. (26%).

Anal. Calcd. for $C_7H_4O_6S$: C, 38.90; H, 1.87; S, 14.83. Found: C, 39.11; H, 1.92; S, 14.63.

The acid was readily soluble in water, ether, alcohol, ethyl acetate, etc., but insoluble in petroleum ether.

The trimethyl ester was obtained in 80% yield by esterification with methanol and sulfuric acid. It was purified by recrystallization from petroleum ether and by sublimation under reduced pressure; m.p. 87–87.5°.

Anal. Calcd. for $C_{10}H_{10}O_6S$: C, 46.51; H, 3.90. Found: C, 46.86; H, 4.09.

2,3,5-Thiophenetricarboxylic Acid.—This was prepared in the same way as described above for the synthesis of the 2,3,4-isomer except that diethyl α-ethoxalyl-α′,α′-diethoxyglutarate[3] was used in place of diethyl α-ethoxalyl-α′-diethoxymethylsuccinate. The yield of crude acid was about 10 g. (18%). It was purified with difficulty and with considerable loss by recrystallization from glacial acetic acid in which it appeared to be somewhat more soluble than the 2,3,4-isomer. It was readily soluble in water, ether or alcohol. The yield of pure acid, obtained as a white powder, was 2.3 g. (4%); m.p. 214–216°.

Anal. Calcd. for $C_7H_4O_6S$: C, 38.90; H, 1.87; S, 14.83. Found: C, 39.13; H, 1.97; S, 14.49.

Analytical sample was dried at 120°. When it was dried at 100° for two hours, unlike the 2,3,4-isomer, it still retained one-half mole of water.

The trimethyl ester melted at 82.5–83°.

Anal. Calcd. for $C_{10}H_{10}O_6S$: C, 46.51; H, 3.90. Found: C, 46.80; H, 3.96.

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[3] R. G. Jones, THIS JOURNAL, **77**, 4074 (1955).

[4] J. Messinger, *Ber.*, **18**, 2300 (1885).

[5] H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 399.

Synthesis and Biological Properties of Diaryl-(trifluoromethyl)-carbinols

BY A. KALUSZYNER, S. REUTER AND ERNST D. BERGMANN

RECEIVED MARCH 14, 1955

Previous experiments[1] have shown that ethyl trichloroacetate fails to give with aromatic magnesium—or lithium—organic ompounds the normal diaryl-(trichloromethyl)-carbinols (I); complicated dechlorination reactions take place instead. It seemed, therefore, desirable to study the analogous reaction of ethyl trifluoroacetate, as the C–F bond was likely to be more stable toward metalorganic compounds.[2] In addition, the reaction products II could be expected to have insecticidal properties.[3] The behavior of ethyl mono- and difluoroacetate toward Grignard compounds has remained unexplored, and ethyl trifluoroacetate has only been shown to react normally with methylmagnesium iodide and—partly—with ethylmagnesium bromide, when this investigation was begun.[4–6] Compound II (Ar = C_6H_5), has, however, been ob-

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[1] A. Kaluszyner and S. Reuter, THIS JOURNAL, **75**, 5126 (1953).

[2] For a comparison of the reactivity of C–Cl and C–F bonds, see J. Hine and D. E. Lee, *ibid.*, **74**, 3182 (1952).

[3] A survey of nuclear-fluorinated analogs of DDT has been given by R. Riemschneider and H. D. Otto, *Z. Naturforschung*, **9b**, 95 (1954). 1,1-Di-(*p*-chlorophenyl)-2,2,2-trifluoroethane has been described by S. Kirkwood and J. R. Dacey, *Can. J. Res.*, **24B**, 69 (1946); see S. Kirkwood and P. H. Phillips, *J. Pharmacol. Expt. Therap.*, **87**, 375 (1946).

[4] F. Swarts, *Bull. soc. chim. Belg.*, **36**, 191 (1927) (*C. A.*, **21**, 2658 (1927)).

[5] E. Gryszkiewicz-Trochimowski, *Rec. trav. chim. Pays-Bas*, **66** 427 (1947).

[6] K. N. Campbell, J. O. Knobloch and B. K. Campbell, THIS JOURNAL, **72**, 4380 (1950).

TABLE I

CARBINOLS $Ar_2C(OH)\cdot CF_3$ (II)

Ar	Formula	Yield, %	B.p. m.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl	$C_{14}H_{11}F_3O$	Up to 70	117–119 (3 mm.); 74.5–75[a]				
p-Tolyl	$C_{16}H_{15}F_3O$	79[b]	130–135 (2 mm.); 61–62[c]	68.5	68.2	5.4	5.3
p-Methoxyphenyl	$C_{16}H_{15}F_3O_3$	45	75.5–76.5[d]				[e]
p-Ethoxyphenyl	$C_{18}H_{19}F_3O_3$	47	46–48[f]	63.5	63.9	5.6	5.7[g]
p-Fluorophenyl	$C_{14}H_9F_5O$	24[h]	111-114 (3 mm.)	58.3	58.3	3.1	3.5[i]
p-Chlorophenyl[k]	$C_{14}H_9Cl_2F_3O$	53	150–160 (2.5 mm.)	52.3	52.0	2.8	2.8[l]
p-Bromophenyl	$C_{14}H_9Br_2F_3O$	46[h]	186–190 (5 mm.)[m]	Br, 40.0	40.3	F, 14.0	13.6[n]

[a] From petroleum ether. [b] This is the yield of the distillate, which crystallized and had m.p. 52–56°. Recrystallization to constant m.p. (61–62°) was accompanied by much loss of material (yield 58%). In toluene, the yield of pure material was 61%. [c] From ligroin (b.p. 90–120°). [d] From 95% alcohol. [e] Calcd. OCH_3, 19.9: found 19.9, 19.6. [f] After chromatography on alumina (solvent, petroleum ether; eluent, mixture of ether and petroleum ether). [g] $n^{16}D$ (supercooled) 1.5360. [h] Crude yield (of the distillate). [i] $n^{15}D$ 1.5104. [k] See Expt. Part. [l] $n^{30}D$ 1.5510, d^{30}_4 1.4360, *MR* calcd. 71.45, *MR* found 71.12. [m] The crude carbinol boiled over a wider range; after purification *via* the acetate and alkaline hydrolysis, it had the above b.p. [n] $n^{30}D$ 1.5750, d^{30}_4 1.7600, *MR* calcd. 77.25, *MR* found 77.00.

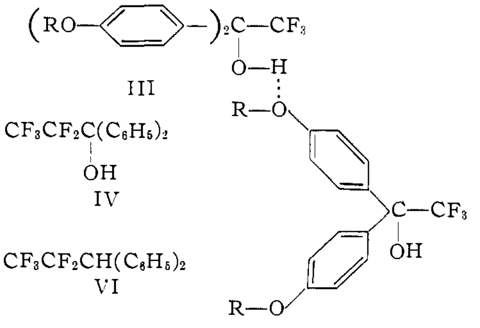
tained from ω-trifluoroacetophenone and phenylmagnesium bromide.[7]

As Table I shows, ethytrifluoroacetate gives with arylmagnesium bromides the expected diaryl-(trifluoromethyl)-carbinols (II), without the formation of fluoride ions.

In view of the biological properties of the di-(*p*-chlorophenyl)-(trifluoromethyl)-carbinol (see below), several variations in its synthesis have been investigated. The Grignard reaction between ethyl trifluoroacetate and *p*-chlorophenylmagnesium bromide in ether gave erratic yields (between 9 and 25%), whilst in toluene as medium a yield of 53% was reproducibly obtained. Following an observation by Swarts,[4] isoamyl trifluoroacetate was tried, at low temperature, but the yield of pure carbinol was only 7%. Reaction of *p*-chloro-ω-trifluoroacetophenone with *p*-chlorophenylmagnesium bromide gave the carbinol in 15% yield. The ketone was obtained in 19% yield from chlorobenzene and trifluoroacetyl chloride, in analogy with observations of Cohen, *et al.*,[8] and Simons and Ramler,[7] and could be identified by its well-defined 2,4-dinitrophenylhydrazone. It could be reduced without difficulty to the corresponding secondary alcohol, by means of aluminum isopropoxide.

$Ar_2C(OH)\cdot CCl_3$
I

$Ar_2C(OH)\cdot CF_3$
II

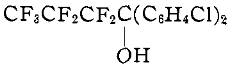


III

$$\underset{\textstyle OH}{CF_3CF_2\overset{}{C}(C_6H_5)_2}$$

IV

$CF_3CF_2CH(C_6H_5)_2$
VI



$$\underset{\textstyle OH}{CF_3CF_2CF_2C(C_6H_4Cl)_2}$$

V

In the infrared spectra of the diaryl-(trifluoromethyl)-carbinols (II), the CF_3 group is responsible for two bands at about 1280 and 1180 cm.$^{-1}$, respectively, which appear to correspond to the antisymmetric and symmetric vibration of the group.[9] No intramolecular hydrogen bonds could be observed, in contradistinction with the findings reported for analogous trichloro compounds.[10] Only in concentrated solutions of the di-*p*-chloro, di-*p*-methoxy and di-*p*-ethoxy compounds (II), hydrogen bonding has been observed (band at 3450 in addition to that at 3600 cm.$^{-1}$), indicating the presence of *inter*molecular hydrogen bonds, possibly with the ether oxygen atoms (as III) or the corresponding chlorine compounds.

The scale model of II shows that the hydrogen atom of the hydroxyl group can either be located outside or inside the angle formed by the two benzene rings; these two positions are not interconvertible without temporary distortion of the *ortho*-hydrogen atoms of the rings. Only in the second of the above two locations, does the hydroxyl hydrogen not interfere with the mobility of the trifluoromethyl group; in this position, it will, indeed, not be able to form a hydrogen bridge.

In the ultraviolet, the diphenyl compound II shows a group of four maxima between 2400 and 2700 Å. which are slightly shifted toward the red in the di-*p*-tolyl derivative and appear also in the spectrum of the di-*p*-fluoro compound. In the dichloro and the dibromo derivative, the fine-structure disappears and a broad band is observed, with a maximum at 2570 Å. (log ε 3.45) and 2600 Å. (3.76), respectively. The spectra of the di-*p*-methoxyphenyl- and di-*p*-ethoxyphenyl-(trifluoromethyl)-carbinol are again practically identical, exhibiting the expected bathochromic shift.

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(7) J. H. Simons and E. O. Ramler, THIS JOURNAL, **65**, 389 (1943).

(8) S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, *ibid.*, **71**, 3439 (1949).

(9) *Cf.* trifluoromethyl hypofluorite: R. T. Lagemann, E. A. Jones and P. J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952); trifluoromethylacetylene: A. L. Henne and M. Nager, THIS JOURNAL, **73**, 1042 (1951); trifluoromethane: National Bureau of Standards Catalogue, No. 979; trifluoroacetaldehyde: D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **74**, 5422 (1952); trifluoroacetic acid: N. Fuson, M. L. Josien, J. R. Lawson and E. A. Jones, *J. Chem. Phys.*, **20**, 1627 (1952); *cf.* R. Suhrmann and H. Luther, *Fortschritte der chemischen Forschung*, **2**, 820 (1953); β-diketones derived from trifluoroacetic acid: J. D. Park, H. A. Brown and J. R. Lacher, THIS JOURNAL, **75**, 4753 (1953).

(10) E. D. Bergmann and S. Pinchas, *ibid.*, **74**, 1263 (1932). *Inter*molecular hydrogen bonding between hydroxyl hydrogen and fluorine has been observed by A. H. Ellison, H. W. Fox and W. A. Zisman, *J. Phys. Chem.*, **57**, 622 (1953).

In studying the chemical properties of the carbinols (II), the nitration of a chloroform solution of the diphenyl compound at −10° was investigated. The infrared spectrum (measured on a Nujol mull) of the product indicated that the nitro group had entered the *para*-positions (absorption at 810 cm.$^{-1}$, none between 770 and 790 or 740 and 750 cm.$^{-1}$).[11] The ultraviolet spectrum resembles that of the *p*-dichloro- and *p*-dibromo analogs; it has a broad maximum at 2610 Å. (4.24).

The hydroxyl group of the carbinols (II) is singularly unreactive. The reduction requires refluxing with phosphorus and hydriodic acid for many days; neither phosphorus trichloride nor pentachloride converts the hydroxyl group into a chlorine atom. Acetylation proved possible, when it was carried out with acetic anhydride in presence of some concentrated sulfuric acid. The refractory behavior of the hydroxyl group in the analogous (trichloromethyl)-dimethylcarbinol has been commented upon before,[12] and McBee, *et al.*,[13] have reported that compounds containing the system $CF_3 \cdot CHOH \cdot CH-$ are unusually difficult to dehydrate.

Biological Properties.—Of the newly prepared substances, only di-(*p*-chlorophenyl)-(trifluoromethyl)-carbinol showed insecticidal properties which, however, did not reach the activity level of DDT or γ-benzene hexachloride. In larvicidal tests, the dichloro compound proved inferior to γ-benzene hexachloride, but superior to di-*p*-(chlorophenyl)-methylcarbinol (DMC). On the other hand, the carbinols (II) have proven to be excellent synergists for DDT.[14] The dichloro derivative, *e.g.*, is 1.5–2.5 times more potent than DMC, di-(*p*-chlorophenyl)-methyl chloride and 1,1-di-(*p*-chlorophenyl)-ethane, the three most active synergists for DDT.[15] Details of this study will be reported elsewhere.

In connection with these experiments, the reaction of aromatic Grignard compounds with ethyl pentafluoropropionate and heptafluorobutyrate was investigated. From the former, pentafluoroethyldiphenylcarbinol (IV) could be obtained with phenylmagnesium bromide in 46% yield and analogously the di-(*p*-chlorophenyl) compound in 54% yield, from the latter with *p*-chlorophenylmagnesium bromide heptafluoropropyl-di-(*p*-chlorophenyl)-carbinol (V) in 55% yield. Reduction of pentafluoroethyldiphenylcarbinol with phosphorus and hydriodic acid gave pentafluoroethyldiphenylmethane (VI) in 55% yield.

Acknowledgments.—In the experimental work, we have been assisted by Mr. S. Cohen and Mr. P. Mozes. For the infrared and ultraviolet spectra, we are indebted to Dr. S. Pinchas (Weizmann Institute of Science, Rehovoth), and Miss H. Weiler (Scientific Department, Ministry of Defence).

Experimental Part[16,17]

Ethyl trifluoroacetate was prepared by refluxing for 30 minutes a mixture of 114 g. of trifluoroacetic acid, 120 ml. of 95% alcohol and 120 ml. of concd. sulfuric acid. The ester was distilled off in a column at 60–62°, dried with phosphorus pentoxide and redistilled; yield 124 g. (87%). When only 86 ml. of (anhydrous) alcohol and 50 ml. of sulfuric acid were used, the yield was 92%. By Gilman's more complicated method,[18] no better yields could be obtained.

Isoamyl trifluoroacetate was prepared analogously from 68.4 g. of trifluoroacetic acid, 88 g. of isoamyl alcohol and 50 ml. of concd. sulfuric acid; b.p. 118–120°, yield 72.5 g. (78.5%).

General Procedure for the Preparation of (Trifluoromethyl)-diarylcarbinols (II).—An ethereal solution of ethyl trifluoroacetate (1 mole) was added to the Grignard solution prepared from 2.5–3 moles of the aryl halide and magnesium. The mixture was refluxed for 90 minutes, kept at room temperature for 12 hours and decomposed with ice and dilute sulfuric acid. The ethereal layer was de-acidified, dried and evaporated and the carbinol isolated by vacuum distillation. It was purified by crystallization or chromatography on active alumina. This latter procedure proved to be the best method for the elimination of the biaryls which boil at approximately the same temperature as the carbinols formed. Thus, *e.g.*, 4,4′-diethoxybiphenyl (m.p. 174–175°), 4,4′-dichlorobiphenyl (m.p. 145°) and 4,4′-difluorobiphenyl (m.p. 88°) have been identified.

All *para*-substituted carbinols give strong color reactions (red to violet) with concentrated sulfuric acid. The di-*p*-chloro compound, *e.g.*, dissolved in a mixture of 95% sulfuric acid and glacial acetic acid, shows a purple color that turns rapidly orange with a maximum at 4950 Å.

For the preparation of di-(*p*-chlorophenyl)-(trifluoromethyl)-carbinol, the following variant of the above procedure proved preferable. From a Grignard solution prepared from 24.3 g. of magnesium turnings and 191.5 g. of *p*-chlorobromobenzene, the ether was distilled off, and a solution of 49.7 g. of ethyl trifluoroacetate in 100 ml. of anhydrous toluene added. When the lively reaction had subsided, the mass was heated at 100° for 90 minutes and worked up as usual. The carbinol boiled at 150–160° (2–3 mm.); yield 60 g. (53%). Chromatography of a petroleum ether solution (elution with a mixture of ether and petroleum ether) gives after a head fraction of some 4,4′-dichlorobiphenyl, the desired carbinol as a slightly yellowish oil. Also for the di-(*p*-tolyl) compound, this procedure has proven advantageous.

Di-(*p*-nitrophenyl)-(trifluoromethyl)-carbinol.—At a temperature of 0 to −10°, a mixture of 20 ml. of nitric acid (d. 1.5) and 5 ml. of concd. sulfuric acid was added, with vigorous agitation, to a solution of 5 g. of diphenyl-(trifluoromethyl)-carbinol in 15 ml. of chloroform. After 4 hours at room temperature, the chloroform layer was separated, washed with water, dried and concentrated. The residue (7 g.) was a light-yellowish resin which could not be induced to crystallize, although it gave correct analytical results.

Anal. Calcd. for $C_{14}H_9F_3N_2O_5$: N, 8.2. Found: N, 8.1.

It was, therefore, converted into the **acetyl derivative** by heating it at 100° for one hour with 28 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid. The acetyl derivative, isolated in the usual way, formed crystals, which melted at 148–150° after recrystallization from alcohol.

Anal. Calcd. for $C_{16}H_{11}F_3N_2O_6$: N, 7.3. Found: N, 7.3, 7.2.

Hydrolysis of the acetate with methanolic potassium hydroxide solution gave di-(*p*-nitrophenyl)-(trifluoromethyl)-carbinol in crystalline form; from acetic acid, m.p. 116°.

Other acetyl derivatives, prepared in the same manner, are listed in Table II.

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[11] See D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

[12] W. Gerrard and P. L. Wyvill, *C. A.*, **44**, 2440 (1950). See ref. 10.

[13] E. T. McBee, J. F. Higgins and O. R. Pierce, This Journal, **74**, 1387 (1952).

[14] Patent application pending.

[15] R. B. March, R. L. Metcalf and L. L. Lewallen, *J. Econ. Entomol.*, **45**, 851 (1952).

[16] All m.p.'s are uncorrected.

[17] The carbon–hydrogen determinations have been carried out by the method recently described by W. Bodenheimer and M. Goldstein (*Bull. Res. Council Israel*, **3**, 53 (1953)), the determinations of fluorine and other halogen by the method of Ch. Eger and A. Yarden (*Anal. Chem.*, in press).

[18] H. Gilman and R. G. Jones, This Journal, **65**, 1458 (1943).

TABLE II

ACETYL DERIVATIVES OF THE CARBINOLS $Ar_2C(OH)\ CF_3$ (II)

Ar	Formula	Yield, %	B.p. °C.	Mm.	Recrystallized from	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl	$C_{15}H_{13}F_3O_2$	60	141	3	Alcohol; pet. ether	96	65.3	65.4	4.4	4.4[a]
p-Tolyl	$C_{18}H_{17}F_3O_2$		150–152	1.5	Pet. ether	59-60[b]	67.1	66.8	5.3	5.3
p-Chlorophenyl	$C_{16}H_{11}Cl_2F_3O_2$	74			AcOH; alcohol	69.5–70	52.9	53.0	3.1	3.5
p-Bromophenyl	$C_{16}H_{11}Br_2F_3O_2$	75	185–200	5.5	Pet. ether; methanol	74.5–75.0	42.5	43.1	2.4	2.6

[a] Mol. wt. calcd., 294; mol. wt. found, 307. [b] The product gives a strong melting point depression with the corresponding carbinol.

TABLE III

DIARYL-TRIFLUOROMETHYL-METHANES, Ar_2CHCF_3

Ar	Formula	Yield, %	B.p. °C.	Mm.	Recrystallized from	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Phenyl	$C_{14}H_{11}F_3$	50	115	8	Ligroin	19–20	71.2	71.7	4.7	4.9
p-Tolyl	$C_{16}H_{15}F_3$		143–148	5	Pet. ether	37.5–38.0				[a]
p-Methoxyphenyl	$C_{16}H_{15}F_3O_2$		165–175	2	Dil. alcohol	48–48.5	64.8	64.7	5.1	5.8
p-Ethoxyphenyl	$C_{18}H_{19}F_3O_2$		195–200	6			66.7	66.5	5.9	61.[b]
p-Chlorophenyl	$C_{14}H_9Cl_2F_3$	82	166	10	Ligroin; methanol	44.5–45.5[c]	55.1	55.5	3.0	3.3
p-Bromophenyl	$C_{14}H_9Br_2F_3$	75	175–185	10	Ligroin; methanol	53–54				[d]

[a] F calcd., 21.6; F found, 21.0. [b] $n^{15}D$ 1.5272. [c] See text. [d] Br calcd., 40.6; Br, found, 40.2. F calcd.: 14.4; F found: 14.3.

Propionate of Diphenyl-(trifluoromethyl)-carbinol.—A solution of 2 g. of the carbinol in 12.5 g. of propionic anhydride, to which 3 drops of concentrated sulfuric acid were added, was kept at room temperature for 12 hours and then refluxed for 2 hours. The reaction product was poured into water and after neutralization with sodium carbonate solution, extracted with ether. The ester is an oil, boiling at 136–138° (3 mm.); $n^{15}D$ 1.5104, yield 1.5 g. (77%).

Anal. Calcd. for $C_{17}H_{15}F_3O_2$: C, 66.2; H, 4.7. Found: C, 65.9; H, 5.1.

1,1-Diphenyl-2,2,2-trifluoroethane.—A mixture of 10 g. of diphenyl-(trifluoromethyl)-carbinol, 4 g. of red phosphorus, 1.5 g. of iodine, 25 ml. of glacial acetic acid and 0.5 ml. of water was refluxed for about 200–250 hours. The hot solution was filtered and diluted with water, and the oily product (7.2 g.) collected and distilled; b.p. 115° (8 mm.). The distillate (5 g., 50%) melted at 19–20°; the product can be recrystallized from ligroin; $n^{20}D$ 1.5230.

Anal. Calcd. for $C_{14}H_{11}F_3$: C, 71.3; H, 4.7. Found: C, 71.7; H, 4.9.

The properties of other diaryl-trifluoromethyl-methanes, which have been prepared analogously, are listed in Table III.

Di-(*p*-chlorophenyl)-trifluoromethylmethane has been described by Kirkwood and co-workers (ref. 3) as crystals of m.p. 64–65°. As the reduction of the corresponding carbinol by the above method gave a well-defined product of m.p. 44.5–45.5° (see Table III), which could not be raised by further recrystallizations, the compound was synthesized by an alternative method which gave the same results.

With vigorous agitation, 4.5 g. of chlorobenzene was suspended in a mixture of 10 ml. of 96% sulfuric acid and 3 ml. of 20% oleum, and at −5°, 4.2 g. of *p*-chlorophenyltrifluoromethylcarbinol added in small portions. After 12 hours, the solution was poured onto ice and the oil which separated, extracted with ether. The residue of the ethereal solution solidified upon cooling and was recrystallized from methanol. Thus, 3.9 g. (80%) of the desired compound was obtained, m.p. 37–40°. Successive recrystallization from petroleum ether and methanol raised the m.p. to 44.5–45°, which did not change upon further crystallization. It was not depressed by admixture of the product obtained by the alternative method.

***p*-Chloro-ω-trifluoroacetophenone.**—In a 500-ml. three-neck flask, mounted with stirrer, thermometer and a gas outlet, 188 g. of benzoyl chloride and 114 g. of trifluoroacetic acid were mixed at −20°. The mixture was slowly heated (50–52°) and the trifluoroacetyl chloride[19] distilled directly into a well-stirred and cooled (0°) mixture of 124 g. of chlorobenzene, 100 ml. of carbon disulfide and 146.5 g. of aluminum chloride. The transformation of the trifluoroacetic acid into its chloride was completed by heating the mixture gradually up to 150°. When the Friedel–Crafts reaction was complete (about 24 hours), the product was decomposed with ice and hydrochloric acid under nitrogen and then the product was extracted with ether and distilled. The fraction boiling at 180–183° (760 mm.) solidified and was recrystallized from petroleum ether; m.p. 26°, yield 40 g. (19%). In spite of repeated purification, no entirely satisfactory analysis was obtained. The ketone is volatile with steam. Potassium hydroxide decomposes it into a gas (fluoroform) and *p*-chlorobenzoic acid. Identification as **2,4-dinitrophenylhydrazone**, yellow crystals from dilute alcohol, m.p. 111°.

Anal. Calcd. for $C_{14}H_8ClF_3N_4O_4$: N, 14.4; F, 14.7; Cl, 9.0. Found: N, 14.1; F, 14.6; Cl, 9.2.

(*p*-Chlorophenyl)-(trifluoromethyl)-carbinol.—The reduction of 10.4 g. of the preceding compound with 20.0 g. of aluminum isopropoxide in 100 ml. of isopropyl alcohol was carried out as usual. The reaction product was decomposed with dilute hydrochloric acid and extracted with ether; b.p. 117–118° (25 mm.), yield 8 g. (76%), d^{19}_{19} 1.410, $n^{19}D$ 1.4827, *MR* calcd. 42.71, *MR* found 42.52.

Anal. Calcd. for $C_8H_6ClF_3O$: C, 45.7; H, 2.9. Found: C, 45.9; H, 3.1.

Ethyl Pentafluoropropionate.—A mixture of 60 g. of perfluoropropionic acid, 50 ml. of alcohol and 20 ml. of concd. sulfuric acid was heated at 100° for two hours. The upper layer was separated, washed three times with 15 ml. of concd. sulfuric acid (until the latter remained colorless) and distilled in presence of phosphorus pentoxide; b.p. 76–77°, $n^{13}D$ 1.3046, in good accord with literature data,[20,21] yield 51.5 g. (73%).

Diphenyl-(pentafluoroethyl)-carbinol (IV).—At 0°, 19.2 g. of the foregoing ester (0.1 mole) in 200 ml. of ether was added to an ethereal solution of 0.26 mole of phenylmagnesium bromide. After 2 hours at 0°, 12 hours at room temperature and 1 hour of refluxing, the mixture was worked up as usual; b.p. 114° (1–2 mm.). The carbinol crystallizes; it is further purified by chromatography and recrystallization from light petroleum ether; m.p. 83°, yield 14 g. (46%).

Anal. Calcd. for $C_{15}H_{11}F_5O$: F, 31.5. Found: F, 31.8.

Pentafluoroethyldiphenylmethane (VI).—Reduction of IV in the above described manner gave VI in 53% yield; $n^{20}D$ 1.5057, d^{20}_{20} 1.29, *MR* calcd. 65.92, *MR* found 65.85.

Anal. Calcd. for $C_{15}H_{11}F_5$: C, 62.9; H, 3.9. Found: C, 62.5; H, 4.1.

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[19] A. L. Henne, R. M. Alm and M. Smook, THIS JOURNAL, **70**, 1968 (1948).

[20] D. R. Husted and A. H. Ahlbrecht, *ibid.*, **75**, 1605 (1953).

[21] R. N. Haszeldine and K. Leedham, *J. Chem. Soc.*, 1548 (1953).

Di-(*p*-chlorophenyl)-pentafluoroethylcarbinol.—From the Grignard solution, prepared with 38.5 g. of *p*-chlorobromobenzene, the ether was distilled off and a solution of 15.4 g. of ethyl pentafluoropropionate in 25 ml. of toluene added. The carbinol is an oil, which boils at 165–175° (4 mm.), and was purified by chromatography; yield 16.0 g. (54%), $n^{25}\text{D}$ 1.5270, $d^{25}{}_4$ 1.4700, *MR* calcd. 77.10, *MR* found 77.57.

Anal. Calcd. for $C_{15}H_9Cl_2F_5O$: C, 48.5; H, 2.4; F, 25.6; Cl, 19.2. Found: C, 48.8; H, 2.4; F, 25.0; Cl, 19.1; ultraviolet spectrum: 227.5 (4.30); 260.0 (3.37).

Ethyl Heptafluorobutyrate.—When a mixture of 90 g. of perfluorobutyric acid, 50 ml. of anhydrous alcohol and 25 ml. of concd. sulfuric acid was refluxed for 2 hours, the ester separated. Upon distillation in presence of phosphorus pentoxide, it boiled at 95–96°; yield 92%.[22]

Di-(*p*-chlorophenyl)-heptafluoropropylcarbinol (V).[23]—A Grignard solution, prepared from 5.3 g. of magnesium turnings and 42 g. of *p*-chlorobromobenzene in 70 ml. of ether was freed from the solvent, and a solution of 24.2 g. of the preceding ester in 25 ml. of toluene added. The mixture was heated at 100° for one hour and worked up as usual. The fraction boiling at 165–175° (5–6 mm.) was subjected to chromatography and the carbinol V obtained as a yellowish oil; yield 23 g. (55%), $n^{22}\text{D}$ 1.5072, $d^{22}{}_{22}$ 1.51, *MR* calcd. 82.2, *MR* found 83.0.

Anal. Calcd. for $C_{16}H_9Cl_2F_7O$: C, 45.6; H, 2.1. Found: C, 46.2; H, 2.5.

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[22] A. L. Henne and W. C. Fiancis, THIS JOURNAL, **75**, 992 (1953).

[23] The chlorine-free carbinol has recently been described by O. R. Pierce, J. C. Siegle and E. T. McBee, *ibid.*, **75**, 6324 (1953).

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The Reactions of Perfluoropropionic Acid and Tetrafluoroethylene with Phenyllithium in Refluxing Ether

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In a previous paper[2] it was reported that the reaction of trifluoroacetic acid with phenyllithium gave none of the expected trifluoroacetophenone. Instead a mixture of the cleavage products, benzoic acid, benzophenone, triphenylmethane and tetraphenylethylene, was obtained. The present report is concerned with the reaction of perfluoropropionic acid with phenyllithium in refluxing ether.

When perfluoropropionic acid was added to three equivalents of an ethereal solution of phenyllithium, only the following three compounds were obtained: benzophenone (52%), *sym*-diphenyldifluoroethylene (37%) and triphenylfluoroethylene (6%).

Elemental analyses and molecular weight determinations were used in elucidating the composition of the olefins. The structure of *sym*-diphenyldifluoroethylene was established further by its oxidation to benzoic acid.

The initially formed lithium perfluoropropionate probably is decarboxylated to give carbon dioxide, which reacts with phenyllithium to give benzophenone and C_2F_5Li, which undergoes β-elimination to give lithium fluoride and tetrafluoroethylene (I). Then I reacts with more phenyllithium to give the olefins II and III.

$$C_2F_5Li \longrightarrow C_2F_4(\text{I}) + LiF \qquad (1)$$

$$\text{I} + 2C_6H_5Li \longrightarrow C_6H_5CF{=}CFC_6H_5(\text{II}) + 2LiF \qquad (2)$$

$$\text{II} + C_6H_5Li \longrightarrow (C_6H_5)_2C{=}CFC_6H_5(\text{III}) + LiF \qquad (3)$$

Support for reaction 1 is available from the work of McBee and co-workers,[3] who found that refluxing an ethereal solution of perfluoro-*n*-propyllithium gave a 97% yield of the olefin, hexafluoropropene. That reactions 2 and 3 are plausible was shown by bubbling tetrafluoroethylene, prepared by the pyrolysis of sodium perfluoropropionate,[4] through three equivalents of phenyllithium and isolating *sym*-diphenyldifluoroethylene (55%) and triphenylfluoroethylene (13%).

Theoretically one can visualize that the fluorinated olefins are formed by two routes: (1) Wurtz–Fittig type coupling and/or (2) successive addition–elimination reactions whereby phenyllithium adds to tetrafluoroethylene to give $C_6H_5CF_2CF_2Li$, which then eliminates lithium fluoride to give α,β,β-trifluorostyrene. This styrene might then react with more phenyllithium to give the fluorinated olefins. We prefer the addition–elimination mechanism since tetrafluoroethylene, which may be regarded as a vinyl halide, would not be expected to function as an alkylating agent.

Recently, Tarrant and Warner[5] have shown that the treatment of trifluorochloroethylene with an equivalent of phenylmagnesium bromide for four days in a reactor packed in Dry Ice gives only one product, 1-chloro-1,2-difluoro-2-phenylethylene in 16.6% yield. It was therefore of interest to treat tetrafluoroethylene with an equivalent and a considerable excess (five equivalents) of phenyllithium to determine the nature of the reaction products. *A priori*, equivalents of this olefin and phenyllithium might be expected to give some α,β,β-trifluorostyrene, while the use of excess phenyllithium might give some tetraphenylethylene and perhaps pentaphenylethane. However, as may be seen in Table I, only *sym*-diphenyldifluoroethylene and triphenylfluoroethylene were obtained. Therefore, if any of the styrene is formed it reacts immediately with more phenyllithium to give the substituted olefins, and apparently triphenylfluoroethylene does not react further with phenyllithium under our experimental conditions.

TABLE I

REACTIONS OF TETRAFLUOROETHYLENE WITH PHENYLLITHIUM

Moles of base per mole of olefin	Products, yield, % *sym*-Diphenyldifluoroethylene	Triphenylfluoroethylene
1	32	10
3	55	13
5	53	17

Experimental

Reaction of Phenyllithium with Perfluoropropionic Acid.—To phenyllithium (0.9 mole in 900 ml. of ether), contained in a 2000-ml., three-neck, round-bottom flask equipped with a mercury-sealed stirrer, a water-cooled reflux condenser and an addition funnel, perfluoropropionic acid (0.3 mole, 67.2 g.), dissolved in 150 ml. of anhydrous ether, was added dropwise with rapid stirring. After the acid was added and the spontaneous refluxing of the ether ceased, the reaction mixture was refluxed for two more hours. After cooling to room temperature, the reaction mixture was quenched by cautiously pouring it onto a mixture of ice and excess con-

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[1] Monsanto Chemical Co. Fellow, 1953–1954.

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[4] J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smitb, *ibid.*, **75**, 4525 (1953).

[5] P. Tarrant and D. A. Worner, *ibid.*, **76**, 1624 (1954).