(72%) of 4,4′-difluorobiphenyl, m.p. 86° (after steam distillation) was obtained.

Anal. Calcd. for $C_{12}H_8F_2$: C, 75.7; H, 4.2; F, 20.1. From: C, 75.9; H, 4.5; F, 19.2.

2,2′-Difluoro-6,6′-dimethylbiphenyl. *dl*-2,2′-Diamino-6,6′-dimethylbiphenyl (VI) was prepared according to Dethloff;[27] it melted after recrystallization from alcohol at 133–134°. The resolution, carried out according to Meisenheimer,[28] gave the (+) −form, m.p. 153–155°; $[\alpha]_D^{20}$ −34.0°, and the (−) −form, m.p. 152°, $[\alpha]_D^{20}$ +33.1° (both in dilute (3.5%) hydrochloric acid, $c = 0.995$ and 1.006, respectively).

At −10°, a solution of 9 g. of the (−)-form in 40 ml. of concd. hydrochloric acid and 90 ml. of water was diazotized with 7.0 g. of sodium nitrite in 15 ml. of water. Addition of 40 ml. of 55% fluoroboric acid precipitated the tetrazonium bisfluoroborate, 13 g. (75% yield) (dec. pt. 93–96°). At this stage, no appreciable racemization had taken place. $[\alpha]_D^{25}$ −38.5° (acetone; c 0.3).

A solution of 13 g. of the salt in 150 ml. of acetone was refluxed for 3 hr. in the presence of 0.25 g. of cupric fluoride. The acetone was distilled and the residue, after addition of 50 ml. of water, subjected to steam distillation. The product (1.6 g.; 20.5%) had m.p. 40°. $[\alpha]_D^{20}$ −0.45° (in chloroform, c, 1.940).

Anal. Calcd. for $C_{14}H_{12}F_2$: F, 17.4. Found: F, 16.8.

1-Fluoroanthraquinone. A solution of 11.2 g. of 1-aminoanthraquinone in 20 ml. of concd. sulfuric acid was diluted with 40 ml. of water and at 10° diazotized with a solution of 8 g. of sodium nitrite in 12 ml. of water. The product was filtered and cooled to 0° and 20 ml. of fluoroboric acid (60%) added. The diazonium fluoroborate was filtered and washed with water, methanol and ether; yield, 14 g. (87.5%); dec. pt. 142°. By normal decomposition of 8 g. of this salt, 4.0 g. (71%) of 1-fluoroanthraquinone was obtained. It was purified by sublimation and melted at 193–194°.

Anal. Calcd. for $C_{14}H_7FO_2$: C, 74.3; H, 3.1; F, 8.4. Found: C, 73.7; H, 3.1; F. 8.3.

2-Fluoroanthraquinone. To a solution of 11.2 g. of 2-aminoanthraquinone in a mixture of 40 ml. of glacial acetic acid, 35 ml. of concd. hydrochloric acid, and 10 ml. of water, a solution of 8 g. of sodium nitrite in 20 ml. of water was added at 20°. The solution was cooled to 0° and the diazonium fluoroborate (13.5 g.; 84%; dec. pt. 188–200°) precipitated by addition of 20 ml. of 60% fluoroboric acid. Thermal decomposition of 8 g. of this salt gave 2.7 g. (47%) of 2-fluoroanthraquinone, m.p. 203–204° after sublimation. A mixture of the two quinones melted at 184–186°.

Anal. Calcd. for $C_{14}H_7FO_2$: C, 74.3; H, 3.1; F, 8.4. Found: C, 74.6; H, 3.4; F, 8.3.

ADDED IN PROOF: While this paper was in press, a similar synthesis of 2,5-difluorostyrene was reported by T. V. Talalaeva, G. V. Kazennikova and K. A. Kocheshkov, *Fhur. Obshchei Klim.*, 29, 1593 (1959) [*C.A.*, 54, 8677 (1960)].

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[27] W. Dethloff and H. Mix, *Ber.*, 82, 534 (1949).

[28] J. Meisenheimer and M. Hoering, *Ber.*, 60, 1425 (1927).

[CONTRIBUTION FROM ALCHEM]

Preparation of Trifluoroacetic Acid

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Trifluoroacetic acid has been prepared by the direct oxidation of 1,1,1-trifluoroethane with air and water vapor in a high voltage electric discharge. The reaction was uncomplicated by any side reactions.

The compound 1,1,1-trifluoroethane is readily prepared from vinylidene chloride and hydrogen fluoride (Equation 1). Oxidation of 1,1,1-trifluoroethane is thermodynamically spontaneous but attempts to produce trifluoroacetic acid using oxygen and vanadium oxide were without success (Equation 2). It was decided that oxidation of trifluoroethane might take place readily in a high voltage electric discharge. A reactor of Pyrex glass in the shape of a Dewar cylinder was fabricated and aluminum foil electrodes were wrapped on the outside of the glass (Fig. 1). Electrical power for the reactor was furnished by an Acme neon sign transformer (Model 4611397–484393) using 110 volts a.c. primary and delivering 15,000 volts a.c. open circuit at its secondary terminals. Initial experiments of passing air and trifluoroethane through the operating reactor at atmospheric pressures did not produce any trifluoroacetic acid, but rather de-

$$CH_2{=}CCL_2 + 3HF \longrightarrow CF_3CH_3 + 2HCL \qquad (1)$$

$$CF_3CH_3 + 1^1/_2O_2 \longrightarrow CF_3CO_2H + H_2O \qquad (2)$$

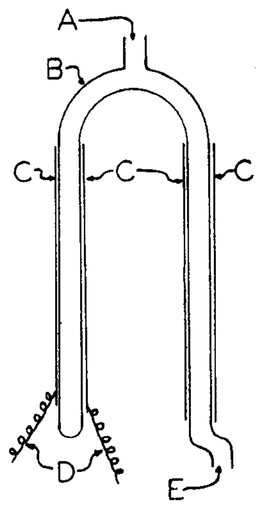

Fig. 1. Reactor used to prepare trifluoroacetic acid. *A.* Port of entry for gaseous mixture of air, 1,1,1-trifluoroethane, and water vapor. *B.* Reactor vessel having the shape of a Dewar cylinder and constructed of Pyrex glass tubing. *C.* Aluminum foil wraps for electrodes. *D.* Electrical leads for application of 15,000 volts a.c. to electrodes. *E.* Exit port for gaseous mixture leaving reactor.

TABLE I

Experimental Results Trifluoroacetic Acid Preparation

	Run Number							
	A	B	C	D	E	F	G	H
Annular spacing, mm.	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Electrode area, cm.^{2}	610	610	610	610	610	610	610	610
Mole ratio, air:MF[a]	8	12	14	12	10	12	10	12
Residence time, min.	1.0	1.0	1.0	1.5	1.0	1.3	1.0	2.0
Reactor temperature°	75	75	75	75	75	75	30	75
Air rate, cc./min.	139	145	146	96	142	42	164	72
MF[a] rate, cc./min.	17.3	12.0	10.5	8.0	14.3	3.5	16.4	6.0
Total operating time, min.	120	120	120	120	120	120	30	120
% H_2O saturation at 30°	100	100	100	100	100	100	100	0
Total MF[a] passed, g.	7.01	4.87	4.26	3.25	5.84	1.42	1.65	2.07
TFA[b] produced, g.	2.286	2.078	1.222	1.536	1.935	0.949	0.268	None
TFA[b] theory, g.	9.52	6.61	5.78	4.41	7.93	1.93	2.25	MF[a] decomp.
% Yield per pass	24.0	31.5	21.2	34.8	24.5	49.2	11.9	H_2SiF_6 in trap

	Run Number							
	I	J	K	L	M	N	O	P
Annular spacing, mm.	3.0	5.5	3.0	3.0	3.0	3.0	3.0	3.0
Electrode Area c.m.^{2}	610	610	305	610	610	610	610	610
Mole ratio, air:MF[a]	10	10	10	10	10	10	10	12
Residence time, min.	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0
Reactor temperature°	30	45	45	45	75	75	75	75
Air rate, cc./min.	327	260	156	156	142	142	72	72
MF[a] rate, cc./min.	33	26	16	16	14	14	6.0	6.0
Total operating time, min.	30	150	150	300	150	300	120	120
% H_2O saturation at 30°	100	100	100	100	100	100	50	50
Total MF[a] passed, g.	3.30	13.18	8.01	16.02	7.30	14.60	2.44	2.44
TFA[b] produced, g.	0.194	1.570	0.660	2.210	2.001	3.243	Traces of TFA[b]	
TFA[b] theory, g.	4.50	17.88	10.86	21.72	9.91	19.82	considerable H_2SiF_6	
% Yield per pass	4.3	8.8	6.1	10.2	20.2	16.4		

[a] 1,1,1-Trifluoroethane. [b] Trifluoroacetic acid.

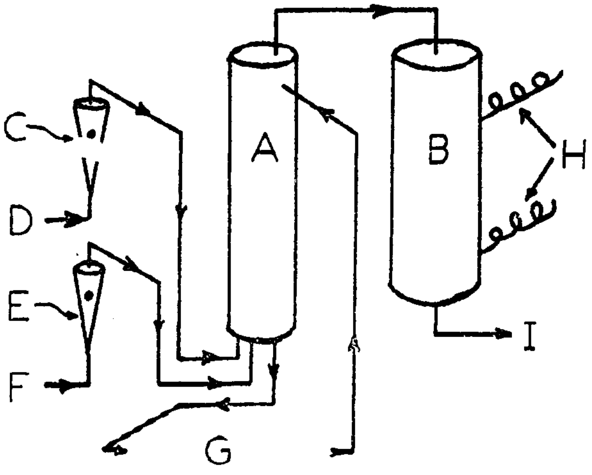

Fig. 2. Flowsheet of apparatus used in the study of the preparation of trifluoroacetic acid. *A*. Insulated humidifier filled with pieces of glass. The glass chips provide evaporating surfaces for the water. *B*. Insulated reactor (see Fig. 1). The temperatures cited in Table I refer to gross temperature of reactor during operation. *C*. Rotameter for the measurement of 1,1,1-trifluoroethane flow. *D*. Point of entry of 1,1,1-trifluoroethane into system. *E*. Rotameter for measurement of air flow. *F*. Point of entry of air into system. *G*. Recycle path for water used to humidify gaseous mixture of air and trifluoroethane. *H*. Electrical connections for admittance of 15,000 volts a.c. into reactor. *I*. Point of exit of gaseous mixture leaving reactor

composed the trifluoroethane and caused fluoride etching of the inside glass reactor walls. When water vapor was added to the air-trifluoroethane mixture and this three-component system passed through the operating reactor, trifluoroacetic acid was produced (Equation 3). The system shown in Fig. 2,

$$CF_3CH_3 + 1^1/_2O + xH_2O + [\text{electric discharge}] \longrightarrow CF_3CO_2H + yH_2O \quad (3)$$

constructed of Pyrex glass, was set up to study the influence of water vapor, temperature, electrode area, electrode spacing, air-to-trifluoroethane mole ratios, and residence time on the reaction (Equation 3). Table I presents several of the experimental results of this study.

DISCUSSION OF RESULTS

The presence of water vapor, that is saturation of the air-trifluoroethane reactants mixture at 30°, permits synthesis of trifluoroacetic acid without degradation of unreacted trifluoroethane or decomposition of trifluoroacetic acid product. The gross temperature of the reactor is a major system variable with the yield of trifluoroacetic acid per pass increasing directly with the temperature over the ranges studied. An optimum air-to-trifluoroethane ratio was noted at 12 moles air to 1 mole trifluoroethane. The yield of trifluoroacetic acid is directly related to the operating electrode area, an increase in electrode area causing a directly proportional increase in the amount of trifluoroacetic acid produced per pass over the variable limits studied. The residence time of the reactants mixture in the operating reactor directly influences the yield of trifluoroacetic acid produced.

Because no undesirable decomposition of either trifluoroacetic acid or of trifluoroethane was noted when the gas mixtures were saturated with water vapor at 30°, independent of the residence times of the reactants in the operating reactor, the chemical reaction shown by Equation 3 is concluded to be highly specific.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Preparation and Thermal Rearrangement of Poly(trimethylsilyl)phenols

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Phenols having a single trimethylsilyl group on the ring are conveniently prepared by the hydrolysis of the corresponding aryloxytrimethylsilane:

$$(CH_3)_3SiC_6H_4OSi(CH_3)_3 \xrightarrow[H^+ \text{ or } OH^-]{H_2O} (CH_3)_3SiC_6H_4OH + (CH_3)_3SiOSi(CH_3)_3.$$

Previous attempts to prepare phenols having more than one *ortho-* or *para-*trimethylsilyl substituent have failed because of aryl-silicon cleavage during hydrolysis.[4] It has been found that the aryloxytrimethylsilanes can be converted to the phenols without appreciable silicon-carbon cleavage by treating them with a concentrated solution of sodium methoxide in anhydrous methanol, diluting with water, and extracting the phenol with pentane. Phenols having trimethylsilyl substituents in the 2,4-, 2,6-, and 2,4,6-positions have been prepared in this manner.

Both *o-* and *p-*(trimethylsilyl)phenol are known to rearrange to phenoxytrimethylsilane at 200–250°:[4]

$$(CH_3)_3SiC_6H_4OH \longrightarrow C_6H_5OSi(CH_3)_3.$$

The poly(trimethylsilyl)phenols undergo the same rearrangement. When both *ortho-* and *para-*trimethylsilyl groups are present the rearrangement is exclusively *ortho*. The strong tendency for *ortho* rearrangement is confirmed by a study of the rearrangement of the monosubstituted phenols; the rates are in the order $o \gg p \gg m$. It is suggested that *ortho* rearrangement occurs predominantly by an intramolecular process while *meta* and *para* rearrangements involve a series of intermolecular desilylation reactions.

During the course of another investigation it became desirable to prepare phenols having one or more positions blocked by groups which could be replaced by hydrogen under mild conditions. The trimethylsilyl group attached to an aromatic ring is readily cleaved by acid,[1-3] particularly when electron-releasing groups such as hydroxyl or alkoxyl are present.

$$ArSi(CH_3)_3 \xrightarrow[H_2O]{H^+} ArH + (CH_3)_3SiOSi(CH_3)_3 \qquad (1)$$

The trimethylsilyl group was therefore selected as the blocking group. The three mono(trimethylsilyl)phenols have been prepared previously,[4,5] but phenols having more than one trimethylsilyl substituent in the ring have not been reported. Attempts to prepare compounds of this type by hydrolysis of the corresponding aryloxytrimethylsilane led to cleavage of aryl-silicon bonds. The purpose of this communication is to describe a method by which trimethylsilyl-substituted aryloxytrimethylsilanes can be converted to the corresponding phenols without appreciable carbon-silicon cleavage and to report the synthesis and thermal rearrangement of a number of poly(trimethylsilyl)phenols.

PREPARATION OF PHENOLS

(Trimethylsilyl)phenoxytrimethylsilanes. Mono(trimethylsilyl)phenols are conveniently prepared by the reaction of the corresponding chlorophenoxytrimethylsilane with sodium and trimethylchlorosilane in refluxing toluene, followed by hydrolysis of the (trimethylsilyl)phenoxytrimethylsilane to the phenol:

$$ClC_6H_4OH + (CH_3)_3SiCl \longrightarrow ClC_6H_4OSi(CH_3)_3$$
$$\xrightarrow[(CH_3)_3SiCl]{Na} (CH_3)_3SiC_6H_4OSi(CH_3)_3$$
$$\xrightarrow[H^+ \text{ or } OH^-]{H_2O} (CH_3)_3SiC_6H_4OH \qquad (2)$$

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(1) H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

(2) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **76**, 6353 (1954).

(3) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(4) J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(5) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 2421 (1953).