cules since the atoms must first have reached equilibrium by (12) and this preliminary exchange itself cannot be much faster than the competitive

$$I + I_2^* \rightleftarrows I^* + I_2 \qquad (12)$$

removal by (13) because of the similarity of concentrations and estimated activation energies.[15] It is

$$R + I_2^* \longrightarrow RI^* + I \qquad (13)$$

very probable, therefore, that methyl radicals recombine with iodine molecules rather than iodine atoms in the liquid state at 2537 Å. It appears from the recent work of Noyes[16] on the photolysis of iodine and recombination of iodine atoms in solution that primary recombination might occur with methyl iodide under more favorable conditions where less energy is given to the radical formed in photolysis.

Acknowledgment.—The authors are grateful to Dr. R. R. Williams, Jr., for helpful discussions of this work. One of us (R. H. S.) is indebted to the Peter C. Reilly Foundation for a fellowship.

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[15] J. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

[16] R. M. Noyes, *ibid.*, **18**, 999 (1950).

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[CONTRIBUTION FROM THE STERLING–WINTHROP RESEARCH INSTITUTE]

Chlorinated 3-Trifluoromethylphenols

BY ARAM MOORADIAN, T. J. SLAUSON AND S. J. MARSALA

4-Chloro- and 6-chloro-3-trifluoromethylphenols have been prepared through the corresponding chloro-3-trifluoromethylanilines. By further chlorination of these phenols, 2,4- and 2,6-dichloro-3-trifluoromethylphenols have been isolated and identified. A new series of compounds incidental to the preparation and characterization of these phenols is described.

In the early work of Swarts,[1] *m*-trifluoromethylphenol was prepared by diazotizing *m*-trifluoromethylaniline. It was originally our[2] intention to prepare both alkylated and chlorinated derivatives of this phenol. In our attempts at alkylation, direct alkylation with *t*-butyl alcohol in the presence of aluminum chloride was unsuccessful as were attempts at condensation of lower aldehydes with the phenol in acetic acid solution containing dissolved hydrogen chloride. Rearrangement of ethers and esters in the presence of the usual agents such as sulfuric acid–acetic acid, boron trifluoride, aluminum chloride,[3] heat, heat and diethylaniline were all unsuccessful, the best yield obtained being on the order of 5–10%. The intermediates used in this work are shown in Table I.

TABLE I

$3\text{-}CF_3\cdot C_6H_4OR$

R	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl[a]	50	76	23	1.4442	$C_9H_9F_3O$	56.84	56.46	4.75	4.81		
i-Propyl	51	80–82	21	1.4400	$C_{10}H_{11}F_3O$	58.83	59.23	5.43	5.64		
n-Butyl	57	105–108	23	1.4440	$C_{11}H_{13}F_3O$	60.54	60.12	6.00	6.33		
Allyl	79	90–91	22	1.4547	$C_{10}H_9F_3O$	59.42	59.26	4.48	4.67		
n-Butanoyl	56	110–113	16	1.4415	$C_{11}H_{11}F_3O_2$	56.89	57.03	4.78	4.99		
Carbamyl	25	M.p. 109–111			$C_8H_6F_3NO_2$	46.84	46.83	2.95	2.94	6.82	6.74

[a] E. T. McBee, R. O. Bolt, P. J. Graham and R. F. Tebbe, THIS JOURNAL, 69, 947 (1947).

4-Chloro-3-trifluoromethylphenol and 2-chloro-5-trifluoromethylphenol were prepared by diazotizing the corresponding anilines. These as well as derivatives and intermediates are listed in Table II. In our chlorination studies *m*-trifluoromethylphenol was chlorinated with the intention of introducing three chlorine atoms, but the predominating product was 2,6-dichloro-3-trifluoromethylphenol melting at 54°. Along with this, another dichloride was formed in lesser amounts for, though we were not then able to isolate the pure dichloride, it was possible to prepare a pure *p*-nitrobenzyl ether from the uncrystallized fraction of the chlorination product. In order to establish the structures of these materials, the two monochlorides described above were further chlorinated. When 4-chloro-3-trifluoromethylphenol was chlorinated, a mixture resulted. From this mixture 2,4-dichloro-3-trifluoromethylphenol, m.p. 33–34°, was obtained; the *p*-nitrobenzyl ether of this corresponded to that obtained from the uncrystallizable residue described above.

When 2-chloro-5-trifluoromethylphenol was chlorinated, chlorination proceeded with much greater difficulty. 2,6-Dichloro-3-trifluoromethylphenol was isolated.

The structures of these dichlorides were established by the sulfuric acid hydrolytic procedure of Le Fave.[4] Hydrolysis of the 54° isomer gave 2,4-dichloro-3-hydroxybenzoic acid. This was shown by making the methyl ether which melted at 162–163° as reported in the literature.[5] The 33–34° isomer, on hydrolysis, gave 2,6-dichloro-3-hydroxybenzoic acid. This as well as its methyl ether were compared with authentic samples prepared as de-

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[1] F. Swarts, *Bull. classe sci., Acad. roy. Belg.*, 241 (1913), *Chem. Zentr.*, **84**, II, 760 (1913).

[2] This work was undertaken at the suggestion of Dr. C. M. Suter and Dr. E. J. Lawson.

[3] A. L. Henne and M. S. Newman, THIS JOURNAL, **60**, 1697 (1938).

[4] G. M. Le Fave, *ibid.*, **71**, 4148 (1949).

[5] H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, **129**, 152 (1926).

TABLE II

CHLORINATED PHENOLS, DERIVATIVES AND INTERMEDIATES

Compound	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{25}D$	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
4-Chloro-3-trifluoromethylaniline[a]	82	132	27	36.5–38	1.5131	$C_7H_5ClF_3N$							7.15	7.08
4-Chloro-3-trifluoromethylphenol	69	120–122	27	44–45	1.4873	$C_7H_4ClF_3O$	42.77	42.79	2.05	2.24	18.05	17.72		
4-Chloro-3-trifluoromethylanisole	80	113	39		1.4727	$C_8H_6ClF_3O$					16.84	16.99		
4-Chloro-3-trifluoromethylphenoxyacetic acid	61			133–134.5		$C_9H_6ClF_3O_3$	42.45	42.43	2.36	2.78	13.92	14.07		
4-Chloro-3-trifluoromethylphenyl-4′-nitrobenzyl ether	76			130–131.5		$C_{14}H_9ClF_3NO_3$					10.71	10.43	4.23	3.93
2-Chloro-5-trifluoromethylaniline[7]	96	103–104	25			$C_7H_5ClF_3N$							7.15	7.04
2-Chloro-5-trifluoromethylphenol	20	87–88	38		1.4702	$C_7H_4ClF_3O$	42.77	42.62	2.05	2.31	18.05	18.21		
2-Chloro-5-trifluoromethylanisole	50	100–101	38		1.4717	$C_8H_6ClF_3O$					16.84	16.60		
2-Chloro-5-trifluoromethylphenoxyacetic acid	46			105–106		$C_9H_6ClF_3O_3$	42.45	42.49	2.36	2.60				
2-Chloro-5-trifluoromethylphenyl-4′-nitrobenzyl ether	70			131–132.5		$C_{14}H_9ClF_3NO_3$					10.71	10.50	4.23	4.31
2-Chloro-5-trifluoromethylphenyl 4-nitrobenzoate				109–110		$C_{14}H_7ClF_3NO_4$	48.64	48.96	2.04	1.88				
2,4-Dichloro-3-trifluoromethylphenol				34–36	1.5105	$C_7H_3Cl_2F_3O$					30.69	30.90		
2,4-Dichloro-3-trifluoromethylanisole	90	134–135	20		1.5088	$C_8H_5Cl_2F_3O$					28.94	28.95		
2,4-Dichloro-3-trifluoromethylphenyl-4′-nitrobenzyl ether	74			176.5–178		$C_{14}H_8Cl_2F_3NO_3$					19.37	19.56	3.94	3.86
2,6-Dichloro-3-trifluoromethylphenol		114–115	29	53–54	1.5004 (35°)	$C_7H_3Cl_2F_3O$	36.39	36.57	1.31	1.61	30.69	30.27		
2,6-Dichloro-3-trifluoromethylanisole	80	105–107	20		1.4859	$C_8H_5Cl_2F_3O$					28.94	29.13		
2,4-Dichloro-3-hydroxybenzoic acid	80			211–212		$C_7H_4Cl_2O_3$	40.61	40.68	1.95	2.11	34.25	34.35		
2,6-Dichloro-3-trifluoromethylphenyl-4′-nitrobenzyl ether	52			95–96		$C_{14}H_8Cl_2F_3NO_3$					19.37	19.30	3.94	3.86

[a] French Patent 745,293 (1933).

scribed in the literature. At no stage in the chlorination studies was any 2,4-dichloro-5-trifluoromethyl phenol isolated or indications of it found. Since this would probably be a higher melting material than either of the isomers isolated, it evidently was not formed in any appreciable proportion.

A continued study of the monochlorination of *m*-trifluoromethylphenol indicated that all three possible monochlorides result. 2-Chloro-3-trifluoromethylphenol and 2-chloro-5-trifluoromethylphenol are separated as a mixture which boils at least 40° lower than either 4-chloro-3-trifluoromethylphenol or the higher chlorination products. The nature of this mixture was established also by sulfuric acid hydrolysis to a mixture of 2-chloro-3-hydroxy and 4-chloro-3-hydroxybenzoic acids. Further chlorination of this mixture of two chlorophenols gave only 2,6-dichloro-3-trifluoromethylphenol. The presence of 4-chloro-3-trifluoromethylphenol in the monochlorination mixture can be inferred from the formation of 2,4-dichloro-3-trifluoromethylphenol which apparently is derived only from the 4-chlorophenol.

The absence of appreciable amounts of 2,4-dichloro-5-trifluoromethylphenol in these chlorinations ties in well with similar studies on *m*-hydroxybenzaldehyde and *m*-nitrophenol. Groves[6] in his work on dichlorination of *m*-nitrophenol says that the main if not only product was 2,4-dichloro-3-nitrophenol. Hodgson and Beard[5] state that the chlorination of *m*-hydroxybenzaldehyde gives mainly 2,6-dichloro-3-hydroxybenzaldehyde, 4,6-dichloro-3-hydroxybenzaldehyde being formed only to the extent of 10%. Further, chlorination of 4-chloro-3-hydroxybenzaldehyde gives a good yield of 2,4-dichloro-3-hydroxybenzaldehyde.

Experimental

4-Chloro-3-trifluoromethylphenol and 2-chloro-5-trifluoromethylphenol were prepared from 2-chloro-5-nitrobenzotrifluoride and 4-chloro-3-nitrobenzotrifluoride (Hooker) respectively. The steps involved in the preparation of the former compounds are described below. The latter compound was prepared similarly.

4-Chloro-3-trifluoromethylaniline.—2-Chloro-5-nitrobenzotrifluoride was reduced in the usual way with stannous chloride in concentrated hydrochloric acid. The tin chloride complex which precipitates may be decomposed with 35% sodium hydroxide.

4-Chloro-3-trifluoromethylphenol.[7]—To a stirred solution of 570 ml. of water and 72 ml. of concentrated sulfuric acid at 60–70° was added 80.5 g. of 2-chloro-5-aminobenzotrifluoride. This solution was then cooled with stirring to 0 to 5° to give a homogeneous suspension. To this suspension was added 31.3 g. of sodium nitrite in 50 ml. of water at such a rate that the temperature did not exceed 5°, external cooling being used. After addition was complete, the solution was stirred for one hour at 0 to 5°. It was then added dropwise to 300 ml. of 25% sulfuric acid contained in a steam distillation set-up. The product was removed with steam as it was formed. About four liters of distillate were collected. This distillate was extracted with ether and the ether extract distilled. The crude yield was 59 g., b.p. 119–126° at 27 mm. Redistillation gave 55 g. (69%) b.p. 120–122° at 27 mm. The product can be made to crystallize and after recrystallization from Skellysolve A melts at 44–45°.

The methyl ether was made in the usual way with dimethyl sulfate. The reaction occurred rapidly. The reaction mixture was extracted with ether and the extract washed with sodium carbonate solution. Distillation gave

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[6] L. G. Groves, E. E. Turner and G. I. Sharp, *J. Chem. Soc.*, **132**, 512 (1929).

[7] E. J. Lawson and C. M. Suter, U. S. Patent 2,489,423.

an 80% yield of 4-chloro-3-trifluoromethylanisole, b.p. 113° at 39 mm.

4-Chloro-3-trifluoromethylphenoxyacetic Acid.—A mixture of 3.93 g. of 4-chloro-3-trifluoromethylphenol and 3.78 g. of chloroacetic acid was dissolved in a solution of 2.4 g. of sodium hydroxide in 25 ml. of water. This was heated eight hours on a steam-bath, acidified with dilute hydrochloric acid and extracted with ether. The ether extract was then extracted with sodium bicarbonate solution and the bicarbonate solution acidified; yield 3.05 g., m.p. 133–134.5° from benzene.

2-Chloro-5-trifluoromethylphenol.—This phenol, its intermediates and derivatives listed in Table II were made in a similar fashion.

2,6-Dichloro-3-trifluoromethylphenol.—The chlorination of 2-chloro-5-trifluoromethylphenol did not occur at an appreciable rate in carbon tetrachloride at room temperature. To a suspension of 6.3 g. of 2-chloro-5-trifluoromethylphenol in 250 ml. of concentrated hydrochloric acid was added a solution of 1.35 g. of potassium chlorate in 25 ml. of water. Shaking the stoppered flask vigorously seemed to result in complete absorption of the chlorine formed. After 15 minutes the reaction mixture was diluted with two parts of water and extracted with ether. Distillation of the ether extract gave a small fraction, b.p. 85–98° at 20 mm., and about 4 g., b.p. 98–110° at 20 mm. A small amount of Skellysolve A was added to the higher boiling fraction and extensive cooling with a Dry Ice–methylene chloride-bath was resorted to. The solid which precipitated amounted to 2.1 g., m.p. 53–54°. Hydrolysis of this phenol with concentrated sulfuric acid gave 2,4-dichloro-3-hydroxybenzoic acid whose properties are indicated in Table II. Methylation of this phenol in the ordinary way with dimethyl sulfate gave 2,4-dichloro-3-methoxybenzoic acid,[3] m.p. 162–163°.

2,4-Dichloro-3-trifluoromethylphenol.—A solution of 20 g. of 4-chloro-3-trifluoromethylphenol in 250 cc. of carbon tetrachloride was prepared and chlorine was bubbled through the solution for three hours at room temperature. The chlorine saturated solution was allowed to stand three hours more and was then distilled under reduced pressure. There resulted 21.5 g. of product, b.p. 119–121° at 34 mm., $n^{25}\mathrm{D}$ 1.5094. This oil was chilled till it crystallized and then filtered cold. The resultant crystals were recrystallized from Skellysolve A to give 10 g. of large well-shaped crystals, m.p. 33–34°, $n^{25}\mathrm{D}$ 1.5105. From the uncrystallized portion of the product a nitrobenzyl ether, m.p. 176.5–178°, of more 2,4-dichloro-3-trifluoromethylphenol was prepared. The oil was evidently contaminated with the isomeric compound preventing further crystallization.

Chlorination of 3-Trifluoromethylphenol.—Chlorine gas was passed into a solution of 210 g. of 3-trifluoromethylphenol in 400 cc. of carbon tetrachloride quite rapidly until an excess of gas had been added. The reaction mixture was allowed to stand a few hours then distilled under reduced pressure. There resulted 256 g. of crude product, b.p. 97–130° at 29 mm. This was carefully fractionated and a 140-g. cut, b.p. 114–116° at 29 mm., taken. On standing, more than one-half of this crystallized in large crystals m.p. 54° from Skellysolve A. This was identical with the 2,6-dichloro-3-trifluoromethylphenol described above.

The uncrystallized portion was converted to a *p*-nitrobenzyl ether and a small amount of 2,4-dichloro-3-trifluoromethylphenyl-4′-nitrobenzyl ether, m.p. 176–177°, resulted.

In a similar fashion, 3-trifluoromethylphenol was treated with only one mole of chlorine. The reaction was not clean cut since some dichlorinated material and some unchlorinated material resulted; a cut boiling at 70–72° at 13 mm., $n^{25}\mathrm{D}$ 1.4770 was taken. This fraction analyzed well for monochloro-3-trifluoromethylphenol (Cl, calcd. 18.04; found 17.89%) but was evidently a mixture of two isomers. Hydrolysis with sulfuric acid gave 4-chloro-3-hydroxybenzoic acid,[8] m.p. 220° and another material, m.p. 153–157° which resisted further purification. This is undoubtedly 2-chloro-3-hydroxybenzoic acid,[9] m.p. 157–158°. This mixture was treated with sodium hydroxide and chloroacetic acid and a clean-cut product, m.p. 135–136°, resulted (*Anal.* Calcd.: C, 42.45; H, 2.36. Found: C, 42.71; H, 2.56). However a mixed melting point with 4-chloro-3-trifluoromethylphenoxyacetic acid showed a sharp depression (m.p. 108–112°), and neither was it identical with 2-chloro-5-trifluoromethylphenoxyacetic acid, m.p. 105–106°. Hence this derivative must be 2-chloro-3-trifluoromethylphenoxyacetic acid.

Acknowledgment.—The authors are indebted to Mr. M. E. Auerbach and Mr. K. D. Fleischer and co-workers for the analyses reported.

(8) P. H. Beyer, *Rec. trav. chim.*, **40**, 621 (1921).

(9) G. Mazzara and V. Bertozzi, *Gazz. chim. ital.*, **30**, II, 84 (1900).

RENSSELAER, N. Y. RECEIVED DECEMBER 26, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Reactions of Some Triarylsilanes with Methyllithium and Phenylisopropylpotassium

BY ROBERT A. BENKESER AND FRANK J. RIEL

The reaction of tri-*p*-chlorophenylsilane, tris-(*p*-trifluoromethylphenyl)-silane, tri-*p*-tolylsilane and tri-*p*-anisylsilane, with methyllithium was investigated. In all cases the corresponding triarylmethylsilane was formed. Tri-*o*-tolylsilane reacts with phenylisopropylpotassium in a manner similar to tri-*o*-tolylmethane in that all three methyl groups are metalated. When the metalated product is carbonated, a silane tricarboxylic acid is formed. The acid can be esterified to form a triethyl ester. Treatment of the metalated product with methyl iodide forms tri-*o*-ethylphenylsilane. When tri-*p*-tolylsilane and triphenylsilane are treated with phenylisopropylpotassium, disproportionation occurs with the formation of tetra-*p*-tolylsilane and tetraphenylsilane, respectively. On the other hand tri-*p*-tolylmethylsilane reacts with phenylisopropylpotassium to form tri-*p*-ethylphenylmethylsilane upon treatment of the metalated product with methyl iodide.

In attempting the preparation of a compound containing a silicon–metal bond, Gilman[1] and Meals[2] independently discovered that triethylsilane will react with methyl- or *n*-butyllithium according to the equation

$$\mathrm{Et_3SiH + R'Li \longrightarrow Et_3SiR' + LiH}$$

This reaction was later extended by Gilman[3] to triphenylsilane and various other organolithium compounds.

The formation of lithium hydride in this reaction indicates that the silicon–hydrogen bond is broken with the elimination of a hydride ion.[4] This suggests that if electron attracting groups were attached to the silicon atom the electron pair making up the silicon–hydrogen bond might be sufficiently displaced toward the silicon atom that the hydride ion would no longer be formed in this reaction. To investigate this hypothesis the reactions of tri-*p*-chlorophenylsilane and tris-(*p*-trifluoromethylphenyl)-silane with methyllithium were studied. For the purpose of comparison, the reactions of tri-*p*-tolylsilane, and tri-*p*-anisylsilane with methyllithium were also investigated. All of the para substituted silanes reacted with methyl-

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(1) H. Gilman and S. P. Massie, THIS JOURNAL, **68**, 1128 (1946).

(2) R. N. Meals, *ibid.*, **68**, 1880 (1946).

(3) H. Gilman and H. W. Melvin, Jr., *ibid.*, **71**, 4050 (1949).

(4) F. P. Price, *ibid.*, **69**, 2600 (1947).