Synthesis of Fluoro-aryloxy Fatty Acids and Their Mono-mercurated Derivatives

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A considerable amount of work has been done in recent years on pest control chemicals, but comparatively very little work has been done on aromatic fluorine compounds which may act as potential pest control chemicals. The synthesis of several fluoro-aryloxy fatty acids and their mercury derivatives has been reported earlier.[1] Some of these compounds have been investigated for their toxicity against "Alternaria solani" with encouraging results.[2] The present investigation deals with the synthesis of some flourine substituted aryloxy fatty acids and their mercury derivatives as possible antifungal agents.

The condensation of 2-chloro-4-fluorophenol and 2-bromo-4-fluorophenol with halogenated fatty acids in sodium hydroxide solution[3] provides a good method for preparation of fluorine substituted aryloxy fatty acids. The fluoroaryloxy fatty acids have been mercurated

1) K. C. Joshi and S. C. Bahel, *J. Ind. Chem. Soc.*, **37**, 365 (1960).

2) K. C. Joshi et al., *J. Sci. Ind. Res.*, **21c**, 315 (1962).

3) N. V. Hayes and G. E. K. Branch, *J. Am. Chem. Soc.*, **65**, 1555 (1943).

TABLE I

Sample No.	α-Fluoro-aryloxy fatty acid	B. p. °C/mmHg	Yield %	Neut. equiv.		C, %		H, %	
				Found	Calcd.	Found	Calcd.	Found	Calcd.
1	2-Chloro-4-FP propionic acid	144/0.2	60	218.0	218.5	49.00	49.40	3.60	3.66
2	2-Chloro-4-FP butyric acid	154/1	64	232.1	232.5	51.20	51.60	4.25	4.30
3	2-Chloro-4-FP valeric acid	143.5/0.1	48.5	246.0	246.5	53.00	53.54	4.80	4.86
4	2-Chloro-4-FP caproic acid	150.5/1	52	260.8	260.5	54.80	55.27	5.30	5.37
5	2-Chloro-4-FP caprylic acid	169/0.1	48	288.1	288.5	57.60	58.20	6.20	6.23
6	2-Chloro-4-FP capric acid	175/0.05	55	315.9	316.5	60.20	60.66	6.88	6.95
7	2-Bromo-4-FP propionic acid	141/0.05	60	262.4	263.0	40.80	41.06	2.95	3.04
8	2-Bromo-4-FP butyric acid	170/3	56.5	276.5	277.0	43.10	43.32	3.54	3.61
9	2-Bromo-4-FP valeric acid	166/1	56	290.9	291.0	44.90	45.30	4.10	4.12
10	2-Bromo-4-FP caproic acid	180/4	52.5	304.2	305.0	47.00	47.21	4.55	4.59
11	2-Bromo-4-FP caprylic acid	197/1	51	332.4	333.0	50.40	50.48	5.35	5.40
12	2-Bromo-4-FP capric acid	208/1	52	360.2	361.0	52.90	53.18	5.96	6.09

FP Fluorophenoxy

TABLE II

Sample No.	Mercury derivative $XFC_6H_2(OCHR\cdot CO_2)Hg$ X	R	M. p.	Hg, % Found	Hg, % Calcd.	C, % Found	C, % Calcd.	H, % Found	H, % Calcd.
1	Cl	CH_3	—	47.6	48.0	25.7	25.9	1.4	1.44
2	Cl	C_2H_5	—	46.0	46.45	27.4	27.8	2.0	2.03
3	Cl	C_3H_7	—	44.5	45.0	29.2	29.6	2.2	2.24
4	Cl	C_4H_9	—	43.8	43.4	30.9	31.3	2.54	2.61
5	Cl	C_6H_{13}	224°C	40.6	40.11	34.25	34.46	3.25	3.28
6	Cl	C_8H_{17}	—	39.2	38.91	37.0	37.26	3.85	3.88
7	Br	CH_3	250°C (+)	42.9	43.4	23.20	23.39	1.28	1.30
8	Br	C_2H_5	—	41.9	42.1	25.10	25.23	1.65	1.68
9	Br	C_3H_7	—	41.6	41.0	26.8	26.98	2.00	2.04
10	Br	C_4H_9	302°C	39.9	39.80	28.35	28.59	2.35	2.38
11	Br	C_6H_{13}	—	37.3	37.73	31.45	31.60	2.98	3.00
12	Br	C_8H_{17}	—	35.55	35.84	34.0	34.31	3.55	3.57

— Solid did not melt. (+) decomposed.

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Further work on these compounds, viz. their suitability as fungicides against a wide range of fungi, is in progress.

Experimental

2-Chloro-4-fluorophenol was conveniently prepared by passing chlorine gas (40 g.) into *p*-fluorophenol (135 g.) in presence of iron fillings at room temperature for 7~8 hr., b. p. 60.5~61.5°C/0.1~1 mmHg. Finger et al.[4] reported b. p. 88°C/40 mmHg (Mol. wt., Found : 148.8. Calcd. : 146.55). 2-Bromo-4-fluorophenol was prepared by treating *p*-fluorophenol (50 g.) with bromine (72 g.) in carbon disulphide, b. p. 58~60°C/0.5 mmHg. Finger etal.[4] reported b. p. 89°C/1 mmHg. (Mol. wt., Found : 192.5. Calcd. : 191.01).

α-Fluoro-aryloxy fatty acids were prepared by the method of Joshi et al.[1] The compounds were characterized by the determination of their neutralization equivalents and are listed in Table I.

Preparation of Mercury Derivatives.—The α-fluoro-aryloxy fatty acids were mercurated by the method of Joshi.[1] A mixture of equimolecular quantities of fluoro-aryloxy fatty acids in ethyl alcohol and yellow mercuric oxide in acetic acid was treated for 4 to 6 hr., till a sandy powder separated. The powder was washed with hot water, hot dilute acetic acid and hot ethyl alcohol. The results of elementary analyses are recorded in Table II. It is evident that mono-mercurated derivatives are formed.

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4) G. C. Finger et al., ibid., **81**, 94, (1959).