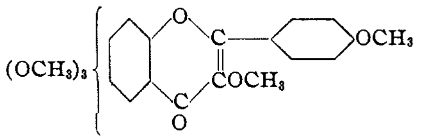
indicate that tangeretin is a substance of the flavonol type of the structure



It seems to be the first instance reported of a fully methylated flavonol occurring in nature.

Tangeretol, formed together with anisic acid by the hydrolysis of tangeretin, is isomeric with gossypitol tetramethyl ether.[3]

Acknowledgments.—G. L. Keenan of the Food and Drug Administration made the optical crystallographic examination; Jos. R. Spies of the Insecticide Division made the microcombustions and nitrogen determinations; and Fred Acree of the same division made the methoxyl determinations.

Summary

A pentamethylflavonol, tangeretin, has been isolated from tangerine peel. On alkaline hydrolysis anisic acid and a tetramethyl keto phenol (tangeretol) were obtained. Tangeretol is isomeric with gossypitol tetramethyl ether.

WASHINGTON, D. C. RECEIVED MARCH 30, 1934

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(3) Perkin, *J. Chem. Soc.*, **103**, 650 (1913).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation and Properties of Substituted Phenylacetylenes and Di-phenylethynyl Mercurys

BY M. M. OTTO

In some research work it was necessary to have samples of ortho-, meta- and para-halogen and para-alkyl substituted phenylacetylenes. The literature revealed that *p*-methylphenylacetylene,[1] *p*-ethyl- and *p*-isopropylphenylacetylenes,[2] *p*-bromophenylacetylene,[3] and *o*-chlorophenylacetylene,[4] had been prepared. The best methods of preparation were of two distinct types. The first may be illustrated by the reactions

$$C_6H_5COCH_3 + PCl_5 \longrightarrow C_6H_5CCl{=}CH_2 + KOH \xrightarrow{\text{(alc.)}} C_6H_5C{\equiv}CH \quad \text{(I)}$$

The second type is illustrated by the set of reactions

$$C_6H_5CH{=}CHCOOC_2H_5 + Br_2 \longrightarrow$$

$$C_6H_5CHBrCHBr{-}COOC_2H_5 + KOH \xrightarrow{\text{(alc.)}}$$

$$C_6H_5C{\equiv}CCOOH + Cu(C_2H_3O_2)_2 \longrightarrow$$

$$(C_6H_5C{\equiv}CCOO)_2Cu + H_2O \longrightarrow C_6H_5C{\equiv}CH \quad \text{(II)}$$

By the use of either of these two general methods, *o*-, *m*- and *p*-bromo- and chlorophenylacetylene, *p*-methyl-, *p*-ethyl- and *p*-isopropylphenylacetylene were prepared. Their physical properties, together with those of the compounds in the literature, and type procedure are listed in Table I. As a step in making some of these acetylenes, three new phenylpropiolic acids, namely, *m*-chloro-, *m*-bromo- and *o*-bromophenylpropiolic acids were prepared. These were purified and analyzed. The analyses for halogen[5] and the physical properties are given in Table II.

As a means of identifying acetylenes, Johnson and McEwen[6] have shown that the mercury derivative is very useful. All of the acetylenes of Table I were converted to these compounds, melting points determined, and analyses performed.[7] The results are given in Table III.

TABLE I

PROPERTIES OF SUBSTITUTED PHENYLACETYLENES

Phenyl-acetylene	Procedure	B. p., °C. or m. p., °C.		n_D^{25}	d^{25}	MR_D
p-Methyl	1	65–67	18 mm.	1.5447	0.9159	39.14
p-Ethyl	1	72–74	16 mm.	1.5360	.9088	44.62
p-Isopropyl	1	79–81	12 mm.	1.5296	.9037	49.23
p-Chloro[a]	1	M. p. 43.5–44		....	....	...
m-Chloro[a]	11	64–65	12 mm.	1.5610	1.1046	39.11
o-Chloro	11	71	18 mm.	1.5690	1.1249	39.76
p-Bromo	1	M. p. 63.5–63.7		....	....	...
m-Bromo[a]	1	85–86	16 mm.	1.5896	1.4466	43.18
o-Bromo[a]	1	92–93	20 mm.	1.5962	1.4434	42.66

[a] New compounds.

TABLE II

PROPERTIES OF SUBSTITUTED PHENYLPROPIOLIC ACIDS

Phenylpropiolic acid	M. p., °C.	Halogen, % Calcd.	Found
o-Chloro	131–132	19.09	19.19
m-Chloro[a]	140–141	19.09	18.93
o-Bromo[a]	118–119	35.52	35.09
m-Bromo[a]	135–136	35.52	35.29

[a] New compounds.

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(1) (a) Kunckell and Gotsch, *Ber.*, **33**, 2657 (1900); (b) Urbain and Delephine, *Ann. chim.*, **10**, 427 (1931).

(2) Kunckell and Koritzsky, *Ber.*, **33**, 3262 (1900).

(3) Dufraisse and Desquesnes, *Bull. soc. chim.*, **49**, 1880 (1931).

(4) Bergmann and Bondi, *Ber.*, **66**, 278 (1933).

(5) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(6) Johnson and McEwen, THIS JOURNAL, **48**, 471 (1926).

(7) Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

TABLE III

SUBSTITUTED DI-PHENYLETHYNYL MERCURYS

Phenyl-acetylene	Formula	M. p., °C.	Mercury, % Calcd.	Mercury, % Found
.....	$(C_6H_5C{\equiv}C)_2Hg$	124.5–125[b]	...	...
p-Methyl	$(CH_3C_6H_4C{\equiv}C)_2Hg$	199–202[b]	...	...
p-Ethyl[a]	$(C_2H_5C_6H_4C{\equiv}C)_2Hg$	142–143	43.51	44.02
p-Isopropyl[a]	$(C_3H_7C_6H_4C{\equiv}C)_2Hg$	109–110	41.21	40.95
p-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	221–222	42.54	42.56
m-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	138–139	42.54	42.85
o-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	213–214	42.54	42.66
p-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	256–257	35.79	35.88
m-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	143–144	35.79	35.97
o-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	184–185	35.79	35.61

[a] New compound. [b] Johnson and McEwen, Ref. 6.

Summary

1. Four new substituted phenylacetylenes and three new phenylpropiolic acids have been described.

2. Eight mercury derivatives of substituted phenylacetylenes have been prepared, described and analyzed.

3. The properties of *p*-ethyl- and *p*-isopropylphenylacetylene have been reported.

NOTRE DAME, INDIANA RECEIVED APRIL 2, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Hydrolysis of Tertiary Aliphatic Halides. I

BY H. MILTON WOODBURN AND F. C. WHITMORE

Our attention was drawn to this subject by difficulties which we experienced in attempting to prepare tertiary amyl alcohol by the hydrolysis of its chloride. We were further interested in this process by statements made by Ayres regarding the hydrolysis of amyl chlorides.[1] A study of the literature revealed considerable confusion on the subject.[2] In the present work experiments were conducted with tertiary butyl chloride, tertiary amyl chloride and bromide, methyldibutylcarbinyl chloride[3] and tri-*n*-butylcarbinyl chloride.[3] The results of these experiments gave definite results which can be summarized in the following statements.

1. The ease of hydrolysis of a tertiary chloride with hot water or sodium carbonate solution decreases with increasing molecular weight, probably because of decreasing solubility. Comparable experiments with tertiary butyl chloride and tributylcarbinyl chloride with hot water gave 5.7 and 0.05 g. of hydrochloric acid liberated, respectively.

2. The hydrolysis of tertiary chlorides is dependent on their solubility in the hydrolyzing medium. Thus the rate of hydrolysis of tertiary butyl and tertiary amyl chlorides is greater in pure water than in 5% sodium carbonate solution. The rate is still slower with 40% sodium carbonate solution.

3. The hydrolysis of tertiary chlorides with hot water or sodium carbonate solution gives olefins exclusively. With *cold* water or *cold* sodium hydroxide solution, a certain amount of tertiary alcohol is formed along with the olefin.

4. Tertiary halides are more resistant to hydrolysis than is ordinarily supposed.

Experimental

Preparation of the Halides.—Tertiary butyl chloride and tertiary amyl chloride were prepared by the method of Norris.[4] Tertiary amyl bromide was best made by the action of hydrogen bromide gas with trimethylethylene prepared by dehydrating commercial tertiary amyl alcohol[5] with 15% sulfuric acid. The product boiled at 44–47° (80 mm.). The higher tertiary chlorides were available from another research.[3]

Hydrolysis Experiments.—Measured amounts of the halides and water or the aqueous reagents were stirred mechanically in the cold or at the refluxing temperature or were merely refluxed.

The liberated inorganic halide (halogen acid or sodium halide) was determined by titration with standard silver nitrate (0.1058 *N*) and potassium thiocyanate (0.1178 *N*) according to Volhard.

The results of the experiments are summarized in Table I.

TABLE I

Tertiary halide	Cc.	Reagent	Cc.	Conditions	Time, min.	Halogen reacted, %
BuCl	25	Water	50	Shake, cold	2	1.2
BuCl	25	Water	50	Reflux	480	71.0
BuCl	25	5% Na_2CO_3	50	Reflux	480	43.4
AmCl	50	Water	100	Shake, cold	2	0.3
AmCl	50	Water	100	Reflux	540	48.6
AmCl	50	5% Na_2CO_3	100	Reflux	540	44.5
AmCl	50	40% Na_2CO_3	100	Reflux	1020	20.0
AmCl	50	2% H_2SO_4	100	Reflux	540	46.8

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(1) Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929).

(2) Butlerow, *Ann.*, **144**, 6, 33 (1867); Straus, *ibid.*, **370**, 366 (1909); Michael and Leupold, *ibid.*, **379**, 287 (1911); Dobbin, *J. Chem. Soc.*, **37**, 237 (1880); Bauer, *Ann.*, **220**, 158 (1889); Friedel and Silva, *Jahresb.*, 339 (1873); Wislicenus, *Ann.*, **219**, 319 (1889); Slawjanow, *Chem. Zentr.*, 11, 134 (1907); Mereshkowski, *ibid.*, 1, 1814 (1914); Muset, *ibid.*, 1, 1313 (1907).

(3) Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933).

(4) Norris, "Organic Syntheses," 1928, Vol. V111, p. 50.

(5) Supplied by the Sharples Solvents Corp., Philadelphia, Pa.