

TABLE I

Substance, 2,3-epoxide	Time of reaction, hours	Yield, %	M. p., °C.	Calcd.				Found			Mol. wt. (Rast)
				C	H	OMe	Mol. wt.	C	H	OMe	
Pomiferin trimethyl ether	12	80	159.5	70.27	6.32	19.46	478.5	70.13	6.32	19.48	441
Tetrahydropomiferin trimethyl ether	16	10	150-151	69.69	7.10	19.29		69.77	7.00	19.1	
Isopomiferin dimethyl ether	3	82	200 ^a	69.81	6.08	13.36		69.90	6.08	13.0	
Iso-osajin monomethyl ether	5	63	199.5-200 ^a	71.87	6.03	7.14		72.21	6.04	7.16	

^a Mixed m. p. 180-185°.

methyl ether and produced, with initial separation of the 2,3-epoxide, anisic acid (m. p. 180°, mixed m. p. unchanged) in a yield of 0.5 g. from 1.7 g. of starting material. Likewise, osajin monomethyl ether yielded anisic acid (m. p. 180°, mixed m. p. unchanged) in a yield of 0.3 g. from 1.7 g. of substance oxidized.

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Summary

1. The 2,3-epoxides (ketoxides) of pomiferin trimethyl ether, tetrahydropomiferin trimethyl ether, isopomiferin dimethyl ether and iso-osajin monomethyl ether have been prepared.

2. Pomiferin trimethyl ether 2,3-epoxide produces veratric acid on further oxidation.

3. Isopomiferin dimethyl ether and iso-osajin

monomethyl ether produce veratric and anisic acids, respectively, on oxidation.

4. Pomiferin dimethyl ether and osajin monomethyl ether produce veratric and anisic acids, respectively, on oxidation.

5. The above facts (1) are in harmony with the previous assignment of an isoflavone structure to osajin and pomiferin; (2) show that the isoflavone nucleus is not reduced in tetrahydropomiferin; (3) prove that neither the isoflavone double bond (2, 3) nor the side chain hydroxyls (4' in osajin and 3',4' in pomiferin) is involved in the acid isomerization characteristic of these pigments; and (4) allocate the methoxyl groups in pomiferin dimethyl ether and osajin monomethyl ether to the 3',4' positions for the former and to the 4' position for the latter.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE GEORGIA SCHOOL OF TECHNOLOGY]

Chlorination of Propyl Trichloroacetates

By C. W. GAYLER¹ AND HOWARD M. WADDLE

The work of Waddle and Adkins² on the chlorination of the butyl esters of trichloroacetic acid and the work of Maxwell³ on the chlorination of *n*-propyl and *i*-propyl trichloroacetates led the authors to a further study of the chlorination of the propyl trichloroacetates.

By the chlorination of *n*-propyl trichloroacetate and the subsequent rectification of the products, Maxwell³ isolated a fraction thought to be α -chloro-*n*-propyl trichloroacetate. Due to the inconclusive results, it was thought best to repeat this early work. Also work by Waddle and Ad-

kins² revealed no such stable α -chloro substituted product in chlorinated *n*-butyl *s*-butyl, and *i*-butyl trichloroacetates.

Preparation of Esters.—The esters were prepared by refluxing two moles of trichloroacetic acid, Merck U. S. P., with four moles of the alcohol for a period of four hours. The excess alcohol was removed by distillation. The residue was washed successively with 10% sodium carbonate solution and water, dried over solid calcium chloride, and distilled under reduced pressure. The yields obtained were roughly 57% of the theoretical.

Chlorination of Esters.—The esters were chlorinated in the presence of the light from a 150-watt unfrosted bulb at 120° in a manner identical with that described by Waddle and Adkins.² Chlorine was passed into the esters until the gain in weight corresponded to monosubstitution, a 34.5-g. increase for each molecular weight of ester chlorinated. The chlorinated esters were fractionated, using a total reflux, partial take-off, packed column. The apparatus and technique used are described by Waddle and Adkins.²

(1) This work was presented for the degree of Master of Science in Chemistry at the Georgia School of Technology by Mr. Gayler, whose present address is University of Texas, Austin, Texas.

(2) Howard M. Waddle and Homer Adkins, *THIS JOURNAL*, **61**, 3361 (1939).

(3) T. A. Maxwell, Senior Thesis, Georgia School of Technology, 1933.

TABLE I

Trichloroacetic ester of	Mole of ^a ester	ANALYTICAL DATA AND PHYSICAL CONSTANTS					M_D		Chlorine, %	
		°C.	B. p.	Mm.	d^{20}_4	n^{20}_D	Calcd.	Found	Calcd.	Found
Propanol-1		69	10		1.3170 ^b	1.4508 ^b	41.83	41.93		
Propanol-2		65	10		1.2987 ^b	1.4440 ^b	41.83	42.01		
2-Chloropropanol-1	0.30	94	8		1.4505	1.4766	47.8	46.61	59.12	59.50
3-Chloropropanol-1	.28	107	8		1.4732	1.4830	47.8	46.50	59.12	59.20
2-Chloropropanol-2	.25	72	8		1.4183	1.4640	47.8	46.8	59.12	59.61
3-Chloropropanol-2	.31	93.5	8		1.4590	1.4760	47.8	48.2	59.12	59.60

^a Mole of ester produced by chlorination of 1 mole of ester. ^b Taken at 20°.

Characterization of the Monochloro Derivatives.—One mole of *n*-propyl trichloroacetate treated as outlined above gave 0.25 mole of unchlorinated ester; 0.02 mole of a compound thought to be the trichloroacetate of 1-chloropropanol-1 (I); 0.30 mole and 0.28 mole of the trichloroacetates of 2-chloropropanol-1 (II) and 3-chloropropanol-1 (III), respectively. Fraction I reacted with water in the cold, and liberated hydrogen chloride. The 2,4-dinitrophenylhydrazone of the dried hydrolysis product melted at 162°. This did not correspond to the 2,4-dinitrophenylhydrazone of propionaldehyde. Sufficient material was not available for further work on this fraction. Fraction II was subjected to saponification with aqueous potassium hydroxide at 30°. From this was obtained a fraction having the following constants: b. p. 134°; n^{20}_D 1.4370; d^{20}_4 1.100; m. p. 3,5-dinitrobenzoate 76.5°. The melting point is not lowered when mixed with the 3,5-dinitrobenzoate of a sample of 2-chloropropanol-1. Beilstein⁴ gives the following constants of 2-chloropropanol-1; b. p. 133–134°; n^{20}_D 1.4363; d^{20}_4 1.103. Fraction III was saponified with aqueous potassium hydroxide at 35°. From this was obtained a fraction having the following constants: b. p. 165°; n^{20}_D 1.4469; d^{20}_4 1.1318; α -naphthyl urethan melting at 76.5°. The melting point was not lowered when mixed with the α -naphthyl urethan of a sample of 3-chloropropanol-1. Beilstein⁴ gives the following constants for 3-chloropropanol-1: b. p. 160–162°; d^{17}_4 1.320.

Bickel and French⁵ reported the melting point of the α -naphthyl urethan of 3-chloropropanol-1 as 76°.

One mole of isopropyl trichloroacetate treated as referred to above gave 0.14 mole of unchlorinated ester, 0.25 mole and 0.31 mole of the trichloroacetate of 2-chloropropanol-2 (IV) and 3-chloropropanol-2 (V), respectively.

Fraction IV was saponified readily at 30° with aqueous potassium hydroxide, requiring two moles for one of the ester. The reaction proceeded as fast as the base was added. From this mixture was isolated a fraction boiling at 56°, the 2,4-dinitrophenylhydrazone of which melted at 126°. This corresponds to the 2,4-dinitrophenylhydrazone of acetone as given by Shriner and Fuson.⁶

Fraction V did not respond to saponification in the cold. A sample of this fraction was refluxed for twenty-four hours with 25% potassium hydroxide. From this drastic treatment a fraction was obtained the phenyl urethan of which melted at 152°. Beilstein⁷ gives the melting point of bis-phenyl urethan of propylene glycol as 153°. The mixed melting point of the bis-phenyl urethan prepared from fraction V and that prepared from an authentic sample of propylene glycol was 152°.

Prior to the analysis for chlorine by use of the Parr bomb, all the samples were washed with 3% sodium carbonate solution, water, dried over calcium chloride and distilled.

The analytical results and physical constants are summarized in Table I.

Summary

1. The action of chlorine on *n*-propyl and *i*-propyl trichloroacetates has been studied.

2. The α - and β -chloro-*n*-propyl trichloroacetates and *i*-propyl trichloroacetates have been prepared by the above method and their properties reported.

ATLANTA, GEORGIA

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(4) Beilstein, 4th ed., Vol. I, p. 356.

(5) Bickel and French, *THIS JOURNAL*, **48**, 747 (1926).

(6) Shriner and Fuson, "Identification of Organic Compounds," 1st ed., John Wiley and Sons, Inc., New York, N. Y., p. 109.

(7) Beilstein, Supplement. Vol. I, p. 246.