[Contribution from the Chemical Laboratory of the University of Mississippi]

DI-IODOTHYMOL AND THE DECOMPOSITION OF ITS SALTS[1]

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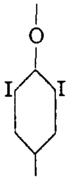
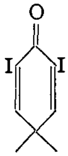
Colored products obtained by the action of iodine and alkali upon phenols have been described by various investigators.[2] The deep red product formed from common phenol[2d] has been shown to consist largely of material having a high apparent molecular weight and quinonoid characteristics. Its formation from phenol takes place according to the equations

$$C_6H_5OH + 4NaOH + 3I_2 = C_6H_2I_3ONa + 3NaI + 4H_2O \qquad (I)$$

$$n\ C_6H_2I_3ONa + I_2 = (C_6H_2I_2O)_n + n NaI + I_2 \qquad (II)$$

During the action represented by Equation II, divalent radicals such as  or  or the ortho isomers are probably formed, the final product being made by their polymerization. Substances of this type are amorphous, soluble in carbon disulfide or bromoform, and insoluble in alcohol, water and ligroin, lose their color on reduction and regain it upon re-oxidation. They will be referred to here as chromo-resinoids.

Probably the best known of these substances is the one obtained from thymol, as it is, in an unpurified state, used as the pharmaceutical now called thymol iodide. The similarity in preparation and properties strongly suggest for the thymol chromo-resinoid a genesis similar to that of its phenol analog. This would require the formation and subsequent decomposition of di-iodothymol. Previous work[3] also pointed in this direction. As no description of a di-iodothymol could be found in the literature, an attempt was made to prepare it.

Willgerodt and Kornblum[4] and later Rasik Lal Datta and Nogendra Prosad[5] have iodinated phenols in ammoniacal solution, the former using alcohol as a solvent and the latter the alkali salts of the phenols.

It was found possible to introduce a second iodine atom into *p*-iodothymol by a modification of these methods using no solvent other than the

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[1] A portion of this work formed part of a thesis presented to the Faculty of the Graduate School of the University of Mississippi by Carl H. Everett in partial fulfilment of the requirements for the degree of Master of Science.

[2] (a) Lautemann, *Ann.*, 120, 309 (1861); (b) Kämmerer and Benzinger, *Ber.*, 11, 557 (1878); (c) Messinger and Vortmann, *ibid.*, 22, 2312 (1889); (d) Hunter and Woollett, This Journal, 43, 135 (1921); (e) Vortmann, *Ber.*, 56, 234 (1923); and others.

[3] Woollett, This Journal, 43, 553 (1921).

[4] Willgerodt and Kornblum, *J. prakt. Chem.*, [2] 39, 290 (1889).

[5] Rasik Lal Datta and Nogendra Prosad, This Journal, 39, 441 (1917).

ammonia solution. The di-iodothymol made thus is a straw-colored liquid which did not solidify at −17°. It forms a crystalline benzoate (m. p. 112°). The second iodine atom is presumably ortho to the hydroxyl. Because of the repeated reports of dimolecular structures for iodothymol derivatives, the molecular weight of the benzoate was taken and found to be normal.

Di-iodothymol decomposes spontaneously, giving the expected red resinoid when treated with sodium hydroxide solution. The decomposition appears to start at the surface of undissolved droplets of the phenol and once initiated goes a great way toward completion. As alcohol, acetone, sulfites or other substances which react easily with iodine prevent the decomposition, and as free iodine in catalytic quantity will cause decomposition in undecomposed alkaline solutions, the spontaneous decomposition is believed to be due to traces of free iodine in the di-iodothymol.

Potassium ferricyanide also will cause the formation of a chromo-resinoid apparently identical with the above. The action in this case is not catalytic but requires molecular quantities of ferricyanide and will take place in the presence of considerable antagonistic material such as sulfites.

As might be expected from its method of preparation, U. S. P. thymol iodide contains a demonstrable amount of di-iodothymol, as shown by the action of potassium ferricyanide on alcoholic extracts from it.

While tri-iodophenol seldom decomposes on mere contact with alkali, its behavior otherwise is remarkably like that of di-iodothymol.

Experimental

Preparation of *p*-Iodothymol.—Eight hundred cc. of 0.25 molecular sodium thymolate and 0.25 molecular I_2–KI solution were run slowly and at approximately equal rates into a 12-cm. funnel filled with cracked ice. The funnel discharged into a 3-liter beaker containing cracked ice and 500 cc. of water, mechanically stirred.

When about one-tenth of the reactants had been added, the product was seeded with iodothymol and addition was interrupted until crystallization started. Excess of iodine present at the end was removed by sodium bisulfite.

The white crystalline *p*-iodothymol (51.5 g.) was filtered off and purified by dissolving twice in alkali, treating with norit, and precipitating by dilute sulfuric acid; then by twice dissolving in alcohol, treating with norit, filtering and precipitating by water; and finally by two crystallizations from heptane (m. p. 69°). Willgerodt[4] gives the melting point as 69°.

Preparation of Di-iodothymol.—One gram of pure *p*-iodothymol was dissolved in 800 cc. of concd. ammonia. To this was added rapidly and with shaking 20 cc. of 0.2 *M* iodine–potassium iodide solution. After one minute 1 cc. of 20% sodium bisulfite was added and the mixture was poured into a previously prepared bottle containing 500 cc. of ice water and 150 cc. of ether. The di-iodothymol was extracted twice and the ether allowed to evaporate spontaneously. Steam was passed through the remaining yellowish oil to remove iodothymol. The non-volatile residue was taken up in a small amount of acetone and then added to 200 cc. of water containing 5 cc. of 4 *N* sodium hydroxide, boiled to remove acetone, cooled, 1 g. of norit added and filtered. The filtrate contained nearly pure di-iodothymol, which was precipitated by dilute sulfuric acid, extracted with ether and dried over sodium sulfate. After evaporation of the ether, a light yellow oil was left which failed to solidify after several days at −17°; average yield, 0.63 g. or 43%.

Anal. (Carius). Calcd. for $C_{10}H_{12}I_2O$: I, 63.17. Found: I, 62.92, 62.85, 62.92.

Preparation of Di-iodothymol Benzoate.—A solution of 2 g. of di-iodothymol was made as above, cooled and shaken with 20 cc. of benzoyl chloride and 70 cc. of 4 *N* alkali. The insoluble material was washed with alkali and water, dried and crystallized three times from alcohol and four times from heptane. The last two crystallizations gave colorless crystals of constant melting point (112°).

Anal. (Carius). Calcd. for $C_{17}H_{16}I_2O_2$: I, 50.18. Found: I, 50.03, 49.97. *Mol. wt.* (cryoscopically in benzene). Calcd. for $C_{17}H_{16}I_2O_2$: 506.05. Found: 429, 447.

Decomposition by Alkali.—Samples I to IV of di-iodothymol were stirred up with sodium hydroxide solution. They turned red and became semi-solid. Water was then added, and the precipitates were filtered off, washed, dried and extracted with alcohol to remove undecomposed di-iodothymol. The chromo-resinoid, alcoholic extract and silver iodide precipitated from the filtrate with silver nitrate were all weighed. The chromo-resinoid was analyzed for iodine.

TABLE I

No.	Sample, g.	Undecomposed, g.	Amount decomposed, g.	Iodine removed, g.	%	Chromo-resinoid $(C_{10}H_{11}IO)_n$ formed, g.	%	Iodine in resinoid (Carius), %
I	0.7626	0.1230	0.6392	0.1507	33.4	0.4515	70.8	47.34
II	1.7615	.1574	1.6041	0.5006	31.21	1.0962	68.3	44.26
III	0.6794	...	0.5002 (calcd.)	0.1655	33.1	0.341		44.93
IV	0.9796	...	0.6734 (calcd.)	......		0.4537		46.35
Calculated values..................					31.58		68.17	46.32

Decomposition by Other Means.—Samples V to VIII of di-iodothymol were put in solution in alkali using acetone as a protective agent. This was later removed by boiling. The resinoids formed were not extracted to remove undecomposed di-iodothymol.

TABLE II

Samples V and VI were caused to decompose by adding small amounts of iodine in solution.

No.	Sample, g.	Iodine added, g.	Chromo-resinoid $(C_{10}H_{11}IO)_n$ formed g.	%	Iodine in resinoid (Carius), %
V	0.6667	0.05	0.4800	72.00	47.17
VI	1.0343	.29	.7271	70.30	...

Samples VII and VIII were treated with $K_3Fe(CN)_6$ solution.

		$N/10$ $K_3Fe(CN)_6$, cc.			
VII	0.5631 (0.00140 mole)	14.8 (0.00148 mole)	0.3777	67.08	46.36
VIII	1.1515 (0.00286 mole)	31.1 (0.00311 mole)	0.8245	71.60	47.73

Di-iodothymol from U. S. P. Thymol Iodide.—A sample was extracted with methanol. Water and a little sodium bisulfite were added to the alcoholic extract and steam was passed through to remove methanol, thymol and iodothymol. The residue was dissolved in 5 cc. of acetone and dilute sodium hydroxide added. The acetone was removed by boiling, the alkaline solution treated with norit and filtered. A solution containing 2 g. of potassium ferricyanide was added to the cold filtrate and the typical red resinoid was filtered off, dried and weighed: sample, 4.372 g.; chromo-resinoid 0.113 g., corresponding to 3.7% di-iodothymol.

Anal. (Carius). Calcd. for $(C_{10}H_{11}IO)_n$: I, 46.32. Found: I, 44.75.

Summary

Di-iodothymol and its benzoate have been prepared.

Di-iodothymol salts have been shown to be precursors of the chromo-resinoid formed when iodine acts on alkaline solutions of thymol according to the equation $nC_{10}H_{11}I_2ONa = (C_{10}H_{11}IO)_n + n\ NaI$.

Di-iodothymol has been shown to be present in U. S. P. thymol iodide.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE POLYMERIZATION OF ASYMMETRICAL DIPHENYLETHYLENE. THE PREPARATION OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

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Bergmann and Weiss, in a paper recently published,[2] have shown that the saturated dimer of asymmetrical diphenylethylene is 1,1,3-triphenyl-3-methylhydrindene and not tetraphenylcyclobutane, as previously supposed, and have stressed the importance of this fact in connection with the views of Staudinger and others on the mechanism of polymerization and the structure of high molecular weight compounds. In a study of the properties of this saturated dimer in this Laboratory, its identity has been established, independently, from its oxidation products. Our investigation, which is still in progress, is concerned chiefly with the mechanism of the reaction by which triphenylmethylhydrindene and other indenes are formed, but the work has paralleled that of Bergmann and Weiss in many respects and therefore it is considered advisable to publish the results which have been obtained at this time.

Polymerization of asymmetrical diphenylethylene (I) by the use of catalysts yields two dimeric compounds, one unsaturated (III) and the other saturated (XII). The unsaturated dimer, m. p. 113°, was prepared first by Hildebrand[3] and shown by Lebedev[4] to be 1,1,3,3-tetraphenyl-1-butene,

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[1] This paper represents part of a dissertation to be submitted to the Graduate School by Mr. Ryan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Bergmann and Weiss, *Ann.*, 480, 49 (1930).

[3] Dissertation by Hildebrand, Strassburg, 1909.

[4] Lebedev, Andreevskii and Matiushkina, *Ber.*, 56, 2349 (1923).