

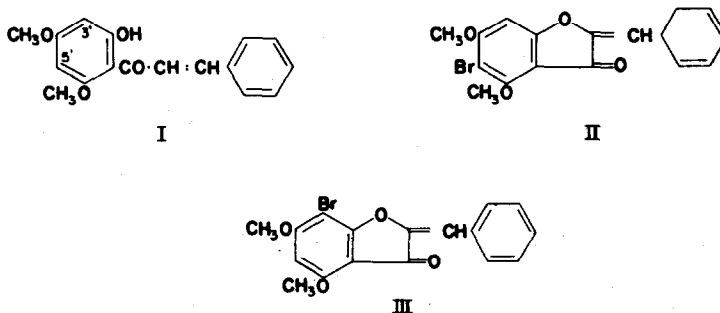
NUCLEAR BROMINATION IN PHLOROGLUCINOL DERIVATIVES

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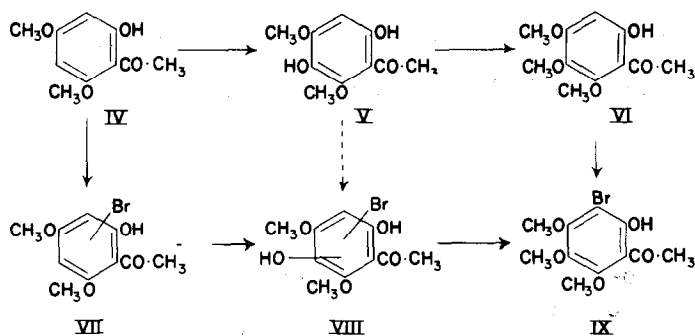
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SINCE Kostanecki and Tambor<sup>1</sup> reported nuclear substitution in the bromination of chalcones derived from phloroglucinol (e.g., I), workers<sup>2,3,4</sup> have assumed that it occurs in the 5'-position to form a tribromide which gives the 5-bromoaurone (II) with aqueous ethanolic potassium hydroxide.



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- <sup>1</sup> St. v. Kostanecki and J. Tambor, Ber. **32**, 2260 (1899).
  - <sup>2</sup> N. M. Cullinane and D. Philpott, J. Chem. Soc. 1761 (1929).
  - <sup>3</sup> D. R. Nadkarni and T. S. Wheeler, J. Univ. Bombay, **6**, 107 (1937).
  - <sup>4</sup> W. A. Hutchins and T. S. Wheeler, J. Chem. Soc. 91 (1939).

It has now been found that the halogen atom enters in fact the 3'-position, so that the compounds previously formulated as in II are actually of type III. Wheeler (this department) has suggested that the resulting steric effects on the 2'-hydroxyl group facilitate the hitherto inexplicable formation of aurone rather than of the corresponding flavone from the so-called 5'-(actually 3'-)bromochalcones.



The monobrominated compound<sup>5</sup> (VII), obtained from 2-hydroxy-4,6-dimethoxyacetophenone (IV), gave VIII, m.p. 147-149° (ethanolic ferric colour - green), when treated with alkaline potassium persulphate. Compound VIII on further methylation yielded IX which was identical (mixed melting point) with authentic 3-bromo-2-hydroxy-4,5,6-trimethoxyacetophenone (IX), m.p. 89-90° (ethanolic ferric colour - green), prepared by

<sup>5</sup> A. R. Penfold, J. Proc. Roy. Soc. N.S.W. 61, 184 (1927).

brominating 2-hydroxy-4,5,6-trimethoxyacetophenone (VI).<sup>6</sup> Bromination of 2,5-dihydroxy-4,6-dimethoxyacetophenone (V),<sup>6</sup> for comparison with VIII, was unsuccessful.

3'-Bromo-2'-hydroxy-4',6'-dimethoxychalcone,<sup>7</sup> m.p. 185-187°, prepared from VII, and benzaldehyde was identical with the chalcone obtained by treating the tribrominated product of I with potassium iodide in acetone.

Satisfactory analyses were obtained for compounds VIII and IX.

The author wishes to thank Professor T. S. Wheeler for his interest and advice.

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<sup>6</sup> V. D. N. Sastri and T. R. Seshadri, Proc. Indian Acad. Sci. 23, 262 (1946).

<sup>7</sup> N. R. Bannerjee and T. R. Seshadri, Proc. Indian Acad. Sci. 36, 134 (1952).