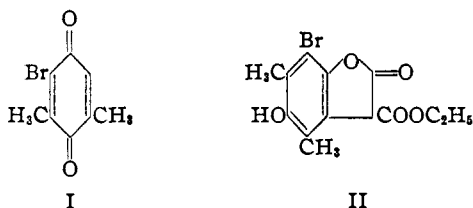


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Quinones and Metallic Enolates. XXI.¹ Bromo-*m*-xyloquinone and Sodio Ethyl Malonate

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Theoretically² a quinone such as bromo-*m*-xyloquinone I, in which there remains one "open" position in the nucleus, may react with a metallic enolate in any of three ways: (a) by replacement of the bromine atom, leading to the halogen-free quinonylmalonic ester; (b) by attack at either of



the methyl groups, leading to one or both of the two possible coumarins; and (c) by 1,4-addition at the "open" position, resulting in a hydroquinone with a malonic ester side chain, or some derivative of this compound. No simple benzoquinones of the type of I have hitherto been investigated with reference to their behavior toward sodio malonic ester; the work described herein is a report of the behavior of I toward sodio ethyl malonate. The reaction followed course (c), and the only product isolated was 3-carbethoxy-4,6-dimethyl-5-hydroxy-7-bromoisocoumaranone, II. The quinone I therefore behaved in the same manner toward the enolate as does the halogen-free trimethylquinone.³

Experimental

Bromo-*m*-xyloquinone, I.—The hydroquinone¹ (5.6 g.) was steam distilled in the presence of ferric sulfate (58 g.), water (200 cc.) and hydrochloric acid (20 cc.). The distillate was extracted several times with ether, the combined

(1) Paper XX, *THIS JOURNAL*, **68**, 887 (1946).

(2) Smith, Arnold and Nichols, *ibid.*, **65**, 2131 (1943), and other papers in this series.

(3) Smith and MacMullen, *ibid.*, **58**, 629 (1936)

extracts were dried (sodium sulfate), and the solvent was removed. The residue, crystallized from ethanol, weighed 4.7 g. (84%) and formed glistening yellow plates which melted at 57–58°.

Anal. Calcd. for C₈H₇O₂Br: C, 44.65; H, 3.26. Found: C, 45.23; H, 3.53.

3-Carbethoxy-4,6-dimethyl-5-hydroxy-7-bromoisocoumaranone, II.—A solution of ethyl malonate (4.6 g., 0.028 mole) in dry, peroxide-free dioxane (25 cc.) was refluxed with sodium (0.47 g., 0.02 gram atom) until the metal dissolved. The solution of the enolate was cooled to room temperature and rapidly added to a well-stirred solution of bromo-*m*-xyloquinone (2.2 g., 0.01 mole) in dioxane (75 cc.). A purple color appeared at once; the mixture was stirred for five hours at room temperature and then filtered. A small portion (2 cc.) of the filtrate, acidified with acetic acid, gave no precipitate with aqueous silver nitrate. The remainder of the filtrate was acidified with hydrochloric acid (10%), diluted with water (400 cc.) and extracted several times with ether. The solvent was removed from the combined extracts and the residue was heated under reduced pressure at 50° for one hour. It was then dissolved in aqueous ethanol (50%, 20 cc.) and the solution was cooled. An oil separated; the supernatant liquid was decanted and this oil was dissolved in ethanol (95%, 5 cc.) and cooled to –10°. The solution slowly (several hours) deposited a white solid (0.9 g., 26%, m. p. 131–136°) which was removed and crystallized from ethanol. It then melted at 147.5–148.5°.

Anal. Calcd. for C₁₃H₁₃O₅Br: C, 47.42; H, 3.95. Found: C, 47.61; H, 3.82.

The yield of II was low, and the remainder of the product could not be isolated in a pure form. It is possible that open-chained compounds related to II were present, but it is unlikely that any coumarins (high-melting, relatively insoluble) were present, and it is certain that no compound derived by replacement of the bromine atom was present.

Summary

Bromo-*m*-xyloquinone reacts with sodio ethyl malonate by a 1,4-addition at the "open" position, the reaction leading to an isocoumaranone. No ionic bromine is liberated during the reaction.

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(4) Original manuscript received April 3, 1945.