102°, n^{20}_D 1.4112; (3) b.p. 102–103°, n^{20}_D 1.4131; (4) residue, n^{20}_D 1.4131. Reported[3] values for 2,4,4-trimethyl-2-pentene are b.p. 101°, n^{20}_D 1.4082; for 2,4,4-trimethyl-2-pentene, b.p. 104.5°, n^{20}_D 1.4158. The alkaline, aqueous phase was acidified. The precipitate was collected and recrystallized to give 6.13 g. (96.7%) of *p*-ethylbenzenesulfonamide, m.p. 108°, identified by the method of mixed melting points with an authentic sample prepared as previously described.[4]

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[3] C. O. Tongberg, J. D. Picken, M. R. Fenske and F. C. Whitmore, This Journal, **54**, 3706 (1932).

[4] R. Fricke and G. Spilker, *Ber.*, **58**, 1595 (1925).

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Infrared Spectra of Magnesium and Bismuth 8-Quinolinolates

BY K. G. STONE

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The insolubility of magnesium 8-quinolinolate dihydrate in chloroform has been noted[1,2] in the literature, but why this inner complex compound should be insoluble whereas others such as the bismuth and ferric compounds are soluble has not been explained. Miller and McLennan[3] have reported the decomposition of the dihydrate on drying at 160° as being

$$Mg(OQ)_2 \cdot 2H_2O \longrightarrow MgO + Q_2O + 2H_2O$$

where OQ represents the 8-quinolinolate ion. This behavior is similar to the hydrolysis observed on heating hydrated magnesium chloride and suggests that the inner complex character of magnesium 8-quinolinolate dihydrate may be less than usually ascribed to the compound.

Infrared spectra of 8-quinolinol, magnesium 8-quinolinolate dihydrate, anhydrous magnesium 8-quinolinolate, bismuth 8-quinolinolate monohydrate and anhydrous bismuth 8-quinolinolate were recorded in the rock salt and calcium fluoride regions using Nujol mulls. As may be seen in Figs. 1 and 2 there is a marked difference between the spectrum of 8-quinolinol and the spectra of the salts, but only slight differences between the spectra of the magnesium and bismuth salts. The removal of the hump at about 3 μ and the decrease in the peak at about 8.3 μ on drying indicate the removal of water.[4] If the hydrated magnesium salt contained magnesium hydroxide, a peak at 6.7–6.8 μ[5] should disappear on drying the salt. If this peak is present, it is covered by an 8-quinolinolate peak and cannot be observed.

From the evidence presented here it must be concluded that magnesium 8-quinolinolate and bismuth 8-quinolinolate have essentially the same

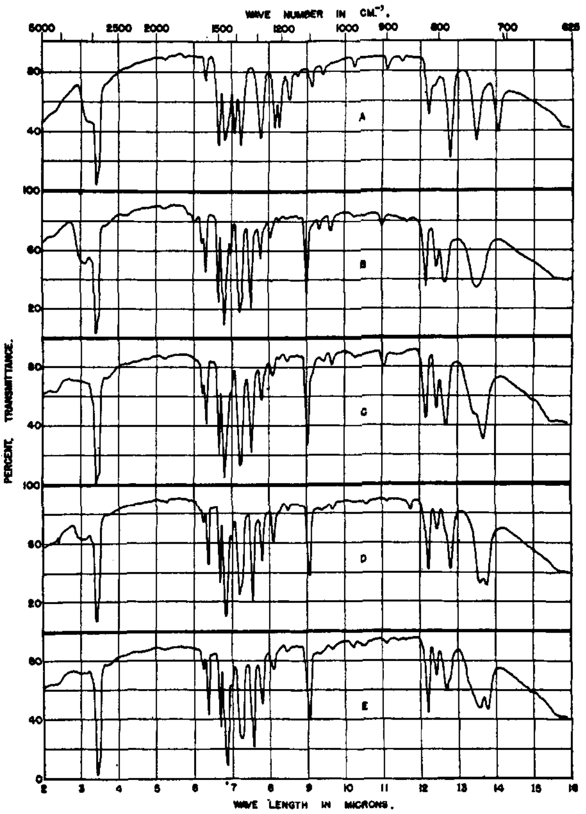

Fig. 1.—Infrared spectra with NaCl prism: A, 8-quinolinol; B, magnesium 8-quinolinolate dihydrate; C, magnesium 8-quinolinolate; D, bismuth 8-quinolinolate monohydrate; E, bismuth 8-quinolinolate.

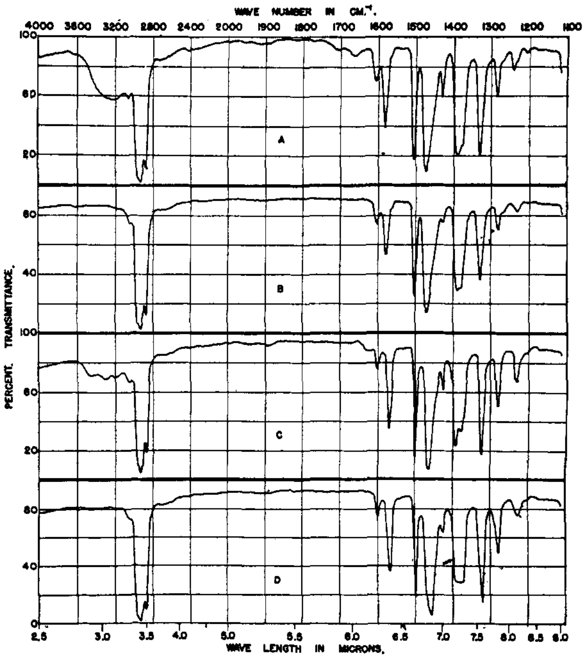

Fig. 2.—Infrared spectra with CaF₂ prism: A, magnesium 8-quinolinolate dihydrate; B, magnesium 8-quinolinolate; C, bismuth 8-quinolinolate monohydrate; D. bismuth 8-quinolinolate.

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(1) M. Arnoux, *Compt. rend. soc. biol.*, **116**, 436 (1934).

(2) C. P. Sideris, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 232 (1940).

(3) C. C. Miller and I. C. McLennan, *J. Chem. Soc.*, 656 (1940).

(4) W. Lyon and E. L. Kinsey, *Phys. Rev.*, **61**, 482 (1942); H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 234.

(5) C. Duval and J. Lecomte, *Bull. soc. chim.*, **8**, 713 (1941).

types of bonding, and some other reason must account for the lack of solubility of the magnesium salt in chloroform.

Experimental

Bismuth 8-quinolinolate was precipitated by the method of Berg[6] and air-dried to yield the monohydrate. The anhydrous bismuth salt was prepared by drying the hydrate at 145° to constant weight. The loss was 3.41% compared to 2.78% calculated.

Anal.,[10] Calcd. for $C_{27}H_{20}O_4N_3Bi$: C, 49.18; H, 3.06; N, 6.37; Bi_2O_3, 35.34. Found, C, 48.93, 48.88; H, 3.11, 3.10; N, 6.33, 6.30; Bi_2O_3, 35.13, 35.00. Calcd. for $C_{27}H_{18}O_3N_3Bi$: C, 50.56; H, 2.83; N, 6.55; Bi_2O_3, 36.33. Found: C, 50.69, 50.47; H, 3.09, 2.93; N, 6.84, 6.83; Bi_2O_3, 35.70, 35.73.

Magnesium 8-quinolinolate was precipitated by the method of Berg[7] and dried to the dihydrate at 80° as recommended by the Duvals[8] and more strongly by Duval.[9] The anhydrous magnesium salt was prepared by drying the dihydrate at 145° as recommended by Duval.[9] The loss was 10.73% compared to 10.33% calculated. There was some decomposition as shown by elemental analysis.

Anal.,[10] Calcd. for $C_{18}H_{16}O_4N_2Mg$: C, 62.01; H, 4.63; N, 8.04;, MgO, 11.83. Found: C, 61.71, 61.73; H, 4.72, 4.84; N, 8.00, 8.07; MgO, 12.16, 12.16. Calcd. for $C_{18}H_{12}O_2N_2Mg$: C, 69.15; H, 3.87; N, 8.96; MgO, 12.90. Found: C, 67.71, 67.52; H, 4.11, 3.87; N, 8.83, 8.73; MgO, 14.26, 14.14.

8-Quinolinol was recrystallized from aqueous ethyl alcohol and melted at 73°.

Infrared spectra of Nujol mulls of the samples were taken on a Baird Associates Infrared spectrophotometer using both a sodium chloride prism and a calcium fluoride prism.

Acknowledgment.—The author expresses appreciation to Dr. A. W. Baker of the Dow Chemical Company for recording the infrared spectra.

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[6] R. Berg, "Analytische Verwendung von o-Oxychinolin und seiner Derivate," Ferdinand Enke Verlag, Stuttgart, 1938, p. 68-69.

[7] Ref. 6, pp. 28-29.

[8] T. Duval and C. Duval, *Anal. Chim. Acta*, **2**, 45 (1948).

[9] C. Duval, *Anal. Chem.*, **23**, 1283 (1951).

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Some Observations on the Mechanism of the Reimer–Tiemann Reaction

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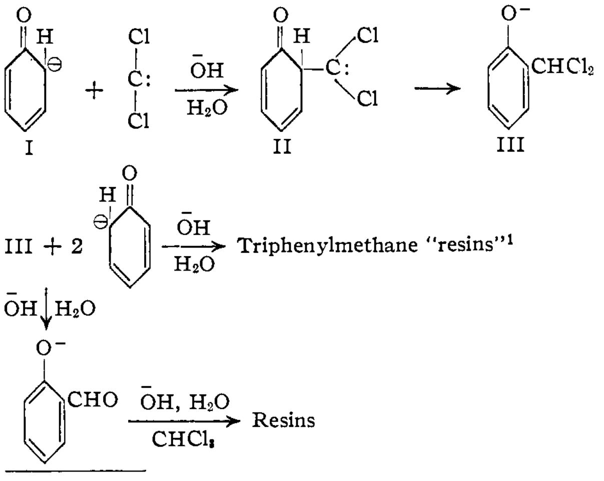
The relatively low yields obtained in Reimer–Tiemann reactions, as well as the fact that starting phenols are frequently recovered, have led many authors to follow Armstrong and Richardson's[1] original suggestion that a diaryl acetal intermediate is formed.

A re-examination of existing experimental data as well as new evidence have led us to the conclusion that a diaryl acetal, if formed at all, does not appear to be the main path by which the aldehyde is formed: (1) Armstrong and Richardson's[1] evidence for the existence of a diaryl acetal rests upon the isolation in 3–6% yield of unstable and unanalyzed oils. (2) The work of Pauly[2] has shown that dialkyl acetals are unstable in the presence of aqueous alkali; Armstrong also notes the instability of his oils in the presence of aqueous sodium bicarbonate. (3) It has now been established that 2-hydroxy-3,6-dimethylbenzaldehyde can be isolated directly from the *alkaline* reaction mixture resulting from the reaction between 2,5-dimethylphenol, aqueous alkali and chloroform. (4) By increasing the amount of alkali, and chloroform in a Reimer–Tiemann reaction (which according to Armstrong's optimum conditions yielded 15% aldehyde and 80% recovered phenol), the amount of recovered phenol was nearly halved, while resin formation increased accordingly.

Points 1 and 2 establish the instability of acetals of hydroxybenzaldehydes in aqueous alkaline media. It appears highly improbable that any such intermediate would exist for any appreciable time under the normal Reimer–Tiemann reaction conditions. Point 3 confirms this observation for one particular reaction, even though the yield of aldehyde is low (see Experimental). Point 4 allows the general conclusion that, if any acetal is formed at all, its importance in tying up starting material becomes a function of the relative concentrations of the reactants.

A slight modification of the exact mechanism of the remaining steps in the over-all reaction is furthermore considered desirable in view of the following considerations. Hine[3] has presented reasonable kinetic evidence that carbon dichloride is the reactive species rather than chloroform itself. This viewpoint is somewhat strengthened by the steric requirements of a nucleophilic attack upon chloroform; certain highly hindered abnormal Reimer–Tiemann products[4] could hardly be formed unless carbon dichloride were the reacting species. The fate of *o*- and *p*-hydroxybenzaldehydes in the presence of aqueous alkali and chloroform remains to be elucidated. Although no Cannizzaro reaction appears to take place with *o*- and *p*-hydroxybenzaldehydes[5] and as a consequence it might be expected that the carbonyl group in these compounds would be too unreactive to undergo base-catalyzed addition of chloroform, nevertheless salicylaldehyde reacts rapidly with alkali and chloroform under normal Reimer–Tiemann reaction conditions with the formation of black resins.

The following scheme is therefore proposed



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[1] D. E. Armstrong and D. H. Richardson, *J. Chem. Soc.*, 496 (1933).

[2] H. Pauly and R. F. von Buttler, *Ann.*, **383**, 230 (1911).

[3] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[4] Hans Wynberg, Ph.D. Thesis, University of Wisconsin, 1952. An account of this and related work will be the subject of another communication.

[5] G. Lock, *Ber.*, **62**, 1177 (1929),