from ethanol gave 1.70 g. (96%) of the pure product, m.p. 212–213°.

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.60; H, 4.96; N, 6.89.

Other Attempted Friedel–Crafts Reactions.—When the dibenzimide was added to a suspension of anhydrous aluminum chloride in carbon disulfide, the yellow diimide color bleached immediately with the formation of 2-chloro-*p*-phenylenedibenzamide in good yield. A similar reaction using dry thiophene-free benzene bleached very slowly (19 hours) and gave a mixture of products which could not be separated by repeated recrystallization from ethanol or ethyl acetate. The mixture gave a very good Beilstein test and sodium fusion confirmed the presence of halogen. Attempts to treat benzene or anisole with the diimide in the presence of small amounts of boron fluoride led only to the formation of a brown amorphous material which could not be crystallized.

Reaction of *p*-Quinonedibenzimide and Sulfuric Acid in Benzene Solution.—An attempt to use concentrated sulfuric acid as a Friedel–Crafts type catalyst led to an unexpected result. A solution of 0.50 g. of *p*-quinonedibenzimide in 20 ml. of dry thiophene-free benzene was added to a suspension of 0.5 ml. of concentrated sulfuric acid in 10 ml. of benzene and the mixture shaken for 5 minutes. The yellow color disappeared and a black tar formed in the acid layer. After standing at room temperature for 40 hours there was no apparent change. Addition of 100 ml. of water caused the precipitation of a product which was recrystallized from ethanol and then from toluene to give 0.21 g. of white crystals. An analytical sample was prepared by recrystallization from chloroform–petroleum ether, m.p. 199–200°.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.58; H, 4.27; N, 9.00.

The analysis checks for 2-phenyl-6-benzamidobenzoxazole. The melting point of a pure sample of that compound was not depressed when mixed with the above product. The infrared spectrum revealed that the product was a mixture, consisting mainly of the benzoxazole. Continued recrystallization from chloroform–petroleum ether and then from methylcyclohexane gave a solid, m.p. 200–201°. This material did not depress the melting point of 2-phenyl-6-benzamidobenzoxazole but the infrared spectra revealed that the mixture was being resolved and the compound being retained was not the benzoxazole. The impurity was not identified, but the infrared spectra ruled out the possibility of its being 2-hydroxy-*p*-phenylenedibenzamide which could be formed by hydrolysis of the benzoxazole.

2-Phenyl-6-benzamidobenzoxazole.—2-Hydroxy-*p*-phenylenedibenzamide[3] was dehydrated by heating the melted substance at 300° in an evacuated tube (30 mm. press.). The vigorous boiling at the start of the heating subsided after 5 minutes. The cooled melt from 0.30 g. of the phenol was dissolved in hot chloroform and then petroleum ether (b.p. 80–110°) added to form a solvent pair. Upon cooling, 0.28 g. (99%) of white product precipitated, m.p. 199–200°.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.51; H, 4.35; N, 9.21.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XXIV. *o*-Quinonemonoimides

BY ROGER ADAMS AND JOHN MORROW STEWART[1]

RECEIVED JULY 21, 1952

Acetyl, benzoyl and benzenesulfonyl derivatives of certain *o*-aminophenols have been subjected to oxidation with lead tetraacetate. The *o*-quinone monoimides in most cases are unstable and cannot be isolated before decomposition or polymerization occurs. Substituents in the benzene ring in the position para to the amide function tend to induce stabilization in the products and isolation is then possible. The following monoimides were isolated: 4-methyl-*o*-quinone-1-benzimide, 4,6-dimethyl-*o*-quinone-1-benzimide (an oil), 5-chloro-4,6-dimethyl-*o*-quinone-1-benzimide, 1,2-naphthoquinone-1-benzimide. The monoimides add hydrogen chloride to give the corresponding monochloro amides. The monobenzimides are more stable than the acetyl or benzenesulfonyl analogs.

Previous papers have described researches involving the synthesis and reactions of *p*-quinone diimides,[2] *o*-quinone diimides[3] and *p*-quinone monoimides.[4] The preparation of *o*-quinone monoimides has now been undertaken.

Oxidation of *o*-aminophenol results in the formation not of *o*-quinonemonoimine, but of a dimer, aminophenoxazone.[5a] On the other hand, with substituents present in the ring, the *o*-quinone monoimines are sometimes stable. Henrich and his co-workers were successful in preparing 4-methoxy-6-methyl-*o*-quinone-1-imine[5b] and 3-methyl-6-methoxy-*o*-quinone-1-imine.[5c] *o*-Quinone monochloroimines, where the hydrogen on the nitrogen is substituted by a chlorine, are slightly more stable, and several *o*-benzoquinone monochloroimines[5d,e] and 1,2-naphthoquinone monochloroimines[5f,g] have been described. The oxidation of N-(2-nitro-4-chlorophenylsulfenyl)-*o*-aminophenol yields a yellow, amorphous substance for which the authors have proposed an *o*-quinone monoimine structure.[5h]

More complex quinone monoimines, some of which are relatively stable, have been synthesized by condensation reactions, rather than by oxidation of *o*-aminophenols. *m*-Fluorophenol, when treated with nitrous acid or nitrosylsulfuric acid, gives compounds of the indophenol type with an ortho configuration.[5i] The condensation of substituted 1-naphthols with aryl amines leads to substituted 1,2-naphthoquinone-2-amines.[5j] 9,10-Phenanthraquinone reacts with ammonia to form 9,10-phenan-

(1) An abstract of a thesis submitted by John Morrow Stewart to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Eastman Kodak Fellow, 1951–1952.

(2) R. Adams, *et al.*, THIS JOURNAL, **72**, 4601, 5154 (1950); **73**, 131, 1149, 1152, 2219 (1951); **74**, 2593, 2597, 2603, 2608 (1952).

(3) R. Adams and C. N. Winnick, *ibid.*, **73**, 5687 (1951).

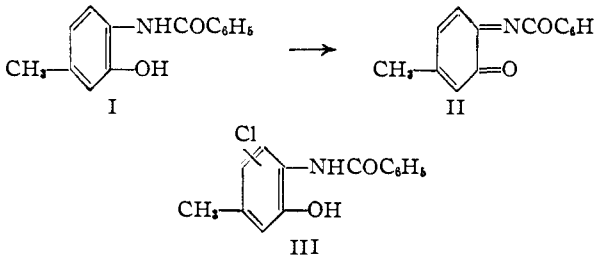
(4) R. Adams, *et al.*, *ibid.*, **73**, 1145 (1951); **74**, 2605 (1952).

(5) (a) O. Fischer and O. Jonas, *Ber.*, **27**, 2784 (1894); (b) F. Henrich and W. Herold, *ibid.*, **61**, 2343 (1928); (c) F. Henrich and O. Fleischmann, *ibid.*, **63**, 1335 (1930); (d) Z. Blaszkowska, *Roczniki Chem.*, **15**, 350 (1935); (e) E. Noelting and G. Thesmar, *Ber.*, **35**, 628 (1902); (f) P. Friedländer and O. Reinhardt, *ibid.*, **27**, 240 (1894); (g) W. Swietoslawski, *et al.*, *Rocsniki Chem.*, **11**, 40 (1931); (h) E. Gebauer-Fulnegg and E. Riesz, *Monatsh.*, **49**, 31 (1928); (i) H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 1405 (1939); 205 (1940); (j) V. Tulagin, U. S. Patent 2,445,252 (1948); (k) J. Schmidt and J. Söll, *Ber.*, **41**, 3679 (1908); (l) T. Zincke and P. Jörg, *ibid.*, **44**, 614 (1911).

thraquinonemonoimine,[5k] and with amines to form N-substituted 9,10-phenanthraquinonemonoimines.[5l]

o-Benzenesulfonamidophenol, *o*-acetamidophenol and *o*-benzamidophenol were oxidized instantaneously by lead tetraacetate in chloroform, benzene or acetic acid at room temperature but yielded only tars and amorphous materials; equally unsatisfactory were the results when active lead dioxide[6] was used as oxidant, or when the temperature was held at 0°. A previously described attempt to oxidize *o*-phenylenedibenzenesulfonamide failed and it was postulated that the monoimide probably underwent an intermolecular Diels–Alder reaction resulting in an amorphous product.[3]

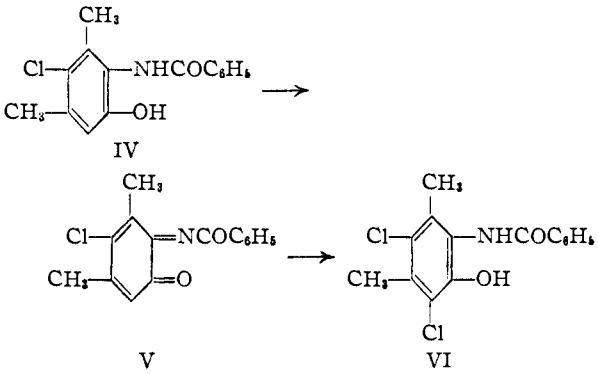
The presence of substituents on the quinoid nucleus induced added stability in *o*-quinonedibenzenesulfonimides so that they could be isolated and their reactions studied. Substituted *o*-amidophenols were, therefore, examined. A comparison of the acetyl, benzenesulfonyl and benzoyl derivatives of 6-amino-*m*-cresol, where the methyl is meta to the hydroxyl and para to the amido group, was made for preliminary information regarding the relative usefulness of these groups for stabilization of the quinoid system. While the first two of these did not give stable products, oxidation of 6-benzamido-*m*-cresol (I) by lead tetraacetate in chloroform at 0° gave 4-methyl-*o*-quinone-1-benzimide (II), which was stable at room temperature for about a day. With hydrogen chloride, II gave a monochlorinated 6-benzamido-*m*-cresol (III) (m.p. 162°) which might have one of



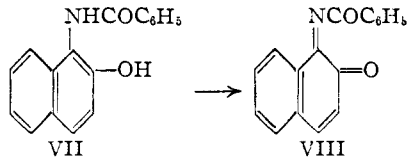
three possible isomeric structures. In the study of *p*-quinonemonobenzenesulfonimides,[4] it was found that hydrogen chloride added exclusively 1,4 to the imide function resulting in an amide with the chlorine exclusively meta to the amide nitrogen and ortho to the hydroxyl. The anticipated structure of the hydrogen chloride adduct to II was, therefore, either 4-chloro-6-benzamido-*m*-cresol or 2-chloro-6-benzamido-*m*-cresol. The former was synthesized by benzoylation of the known 4-chloro-6-amino-*m*-cresol and found not to be identical (m.p. 232°). The chlorine atom is therefore probably in the 2-position.

The oxidation of certain 4-substituted and 4,6-disubstituted 2-aminophenols took place readily but the quinone monoimides were not stable enough for isolation and characterization. In dry chloroform at room temperature with lead tetraacetate, all of these compounds gave an immediate yellow or orange colored solution (presumably due to the quinone monoimide), which after a period of time changed to a dark red or brown (decomposition or polymerization of the quinone monoimide). If the length of time before the change of color was taken as an indication of the stability of the quinone monoimide, then the order of increasing stability follows: for the 4-substituted, 2-benzenesulfonamido-*p*-cresol, immediate brown; 2-benzamido-*p*-cresol, 15 seconds; 2-benzamido-4-chlorophenol, 10 minutes; 2-benzamido-4-phenylphenol (3-benzamido-4-hydroxybiphenyl), 25 minutes; for the 4,6-disubstituted, 2-benzamido-4,6-dimethylphenol, 5 minutes; 2-benzamido-4,6-dichlorophenol, stable color and the crystalline product obtained was stable for about one hour. These experiments confirmed the earlier ones that the benzimide derivatives are more stable than the benzenesulfonimides.

The 3,5-disubstituted 2-benzamidophenols formed more stable monoimides. 2-Benzamido-3,5-dimethylphenol, when oxidized by lead tetraacetate in chloroform at room temperature, gave a stable, orange, oily product, which added hydrogen chloride to yield 2-benzamido-4-chloro-3,5-dimethylphenol (IV), identical with the compound formed by benzoylation of the known 2-amino-4-chloro-3,5-dimethylphenol. Oxidation of IV gave a stable product, 5-chloro-4,6-dimethyl-*o*-quinone-1-benzimide (V), which added hydrogen chloride to form 2-benzamido-4,6-dichloro-3,5-dimethylphenol (VI).



1-Benzamido-2-naphthol (VII), which may be looked upon as a 4,5-disubstituted 6-benzamidophenol, was oxidized to the stable 1,2-naphthoquinone-1-benzimide (VIII). With hydrogen chloride VIII formed an adduct in which the position of the chlorine was not determined. The facile oxidation of VII was unexpected in view of the earlier reported failure of an attempt to oxidize 1-benzenesulfonamido-2-naphthol.[7]



Experimental

All melting points are corrected.

6-Acetamido-*m*-cresol.—To a solution of 1.6 g. of 6-amino-*m*-cresol hydrochloride[8] in 20 ml. of water at 50°, 1.05 g. of acetic anhydride was added and stirred until all was dissolved. A solution of 1.5 g. of sodium acetate trihydrate in 10 ml. of water was then added all at once, with

(6) R. Kuhn and I. Hammer, *Ber.*, **84**, 91 (1951).

(7) R. Adams and R. A. Wankel, THIS JOURNAL, **73**, 2219 (1951).

(8) F. Henrich, *Ber.*, **54**, 2508 (1921).

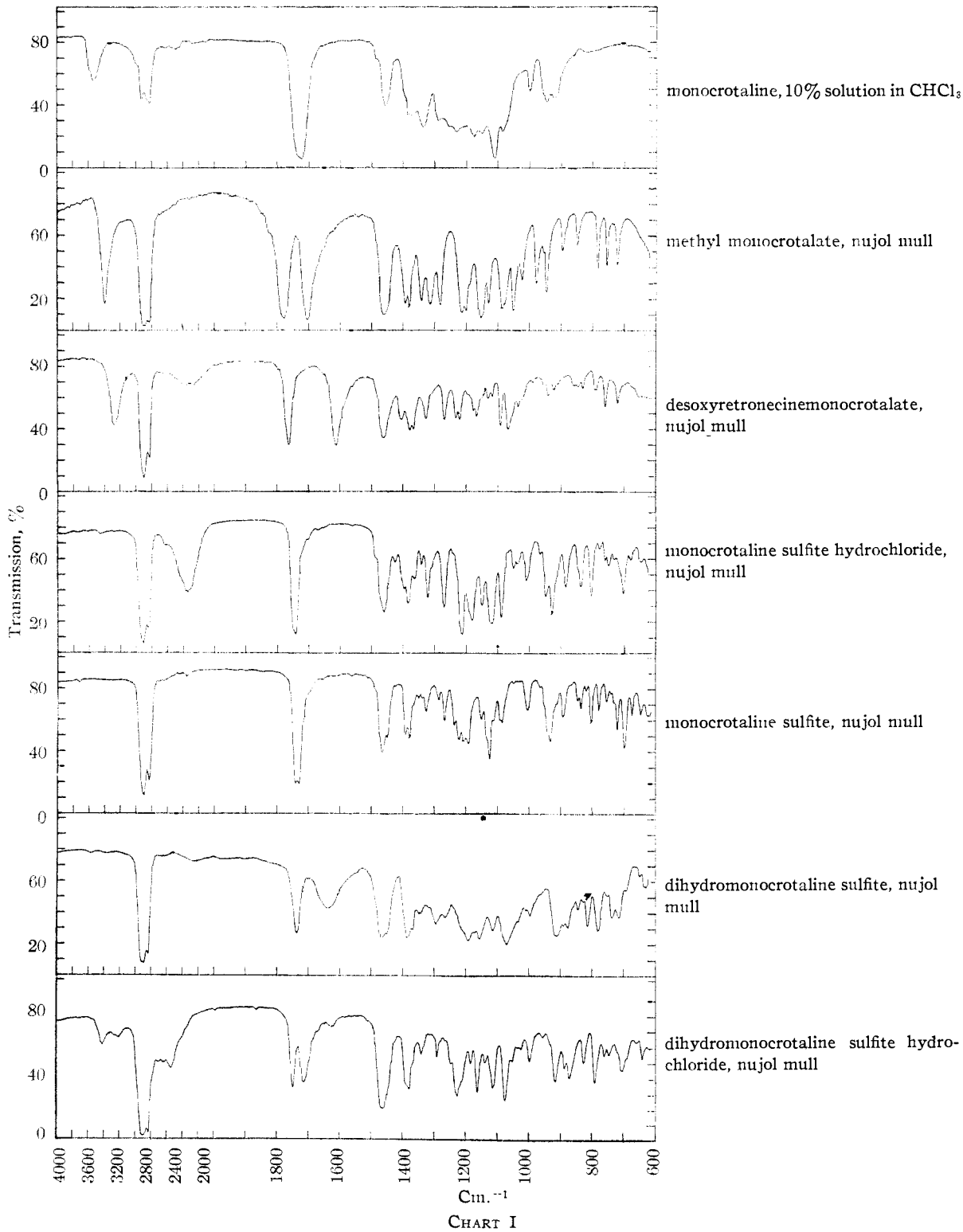


CHART I

rapid stirring. The product was collected by filtration and weighed 1.2 g. (75%). Purification from toluene (Darco) gave lustrous plates which sublime readily, m.p. 169–170°.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71. Found: C, 65.70; H, 6.84.

6-Benzenesulfonamido-*m*-cresol.—A solution of 1.6 g. of 6-amino-*m*-cresol hydrochloride in 30 ml. of α-picoline was cooled in an ice-bath and 1.8 g. of benzenesulfonyl chloride added dropwise, with stirring. After 15 minutes, the solution was poured into cracked ice and hydrochloric acid to precipitate the product. The crude 6-benzenesulfonamido-*m*-cresol weighed 1.7 g. (65%), and was purified by recrystallization from toluene (Darco); colorless prisms, m.p. 139.5–140.5°.

Anal. Calcd. for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98. Found: C, 59.38; H, 4.85.

2-Benzenesulfonamido-*p*-cresol.—A solution of 12.3 g. of 2-amino-*p*-cresol[9] in 200 ml. of pyridine was cooled in an

(9) P. Wagner, *Ber.*, **7**, 1270 (1874).

ice-bath and 18 g. of benzenesulfonyl chloride added dropwise, with stirring. After working up as above, 26.0 g. (98%) of a crude product was obtained, but many recrystallizations from toluene were necessary to obtain a pure product; colorless prisms, m.p. 147.5–148.5°.

Anal. Calcd. for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98. Found: C, 59.46; H, 4.97.

General Method for Synthesis of *o*-Benzamidophenols: 2-Benzamido-4-chlorophenol.—A solution of 7.0 g. (0.05 mole) of benzoyl chloride in 20 ml. of pyridine was added slowly, with stirring, to a solution of 9.0 g. (0.05 mole) of 2-amino-4-chlorophenol hydrochloride[10] in 50 ml. of pyridine at room temperature. After standing 4 hours at room temperature, the solution was poured into ice and hydrochloric acid. The precipitated crude product was collected, washed with water and treated with 300 ml. of 5% aqueous sodium hydroxide. The undissolved material (1.05 g., presumed to be the dibenzoyl derivative) was removed by filtration; acidification of the filtrate with hydrochloric acid gave 8.4 g. (68%) of 2-benzamido-4-chlorophenol. Recrystallization from 95% ethanol gave colorless prisms, m.p. 223.5–224°.

Anal. Calcd. for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07. Found: C, 63.19; H, 4.01.

2-Benzamido-4,6-dichlorophenol and 2-Benzamido-4,6-dichlorophenyl Benzoate.—When 6.4 g. of 2-amino-4,6-dichlorophenol hydrochloride[11] was benzoylated as above, the product consisted of 1.75 g. (21%) of the desired 2-benzamido-4,6-dichlorophenol, soluble in alkali, and 3.65 g. of 2-benzamido-4,6-dichlorophenyl benzoate, insoluble in alkali. The yield of the desired product was not improved by conducting the benzoylation at 0°.

The 2-benzamido-4,6-dichlorophenol was purified by recrystallization from 95% ethanol; colorless needles, m.p. 215–216°.

Anal. Calcd. for $C_{13}H_9Cl_2NO_2$: C, 55.35; H, 3.22. Found: C, 55.34; H, 3.30.

The 2-benzamido-4,6-dichlorophenyl benzoate was purified from 95% ethanol to give very fine needles, m.p. 170.5–171°.

Anal. Calcd. for $C_{20}H_{13}Cl_2NO_3$: C, 62.20; H, 3.39 Found: C, 62.34; H, 3.58.

4-Methyl-*o*-quinone-1-benzimide.—A suspension of 1.14 g. of 6-benzamido-*m*-cresol in 90 ml. of dry chloroform was stirred at 0° while 2.22 g. of dry lead tetraacetate was added in small portions. A yellow color appeared immediately, and darkened somewhat as the oxidation proceeded. All of the oxidant was added during 25 minutes; the reaction was stirred for 5 minutes longer, filtered, and the dark yellow-brown filtrate evaporated *in vacuo*. The residue remainng from the evaporation was extracted with a minimum amount of hot ethyl ether and the solution chilled in acetone–Dry Ice to give 0.55 g. (49%) of orange needles. The 4-methyl-*o*-quinone-1-benzimide was recrystallized five times by dissolving in a minimum amount of dry ether at room temperature and chilling in an acetone–Dry Ice mixture, m.p. 65.6–66°.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.66; H, 4.92. Found: C, 74.79; H, 5.09.

After standing one day at room temperature, the purified product had taken on a dull orange color, and melted at 215–225° (dec.).

x-Chloro-6-benzamido-*m*-cresol.—Hydrogen chloride was passed into the ethereal mother liquors from the purification of 4-methyl-*o*-quinone-1-benzimide; the solution was decolorized, but no precipitate formed. Evaporation of the solvent gave needles which were recrystallized from a chloroform–petroleum ether (b.p. 80–110°) solvent pair, m.p. 161.5–162°.

Anal. Calcd. for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62. Found: C, 63.96; H, 4.81.

4-Chloro-6-benzamido-*m*-cresol.—4-Chloro-6-amino-*m*-cresol[12] was benzoylated by the proeedure given above to give 84% yield of 4-chloro-6-benzamido-*m*-cresol. Purification from ethanol gave colorless plates, m.p. 231–232°.

Anal. Calcd. for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62. Found: C, 64.32; H, 4.72.

Oxidation of 2-Benzamido-3,5-dimethylphenol.—A suspension of 1.2 g. of 2-benzamido-3,5-dimethylphenol[13] in 50 ml. of dry benzene was stirred with 2.2 g. of lead tetraacetate at room temperature for 20 minutes. After filtration, the solvent was evaporated *in vacuo* and 30 ml. of petroleum ether (b.p. 30–60°) added to the residue; a red-orange oil separated. Attempts to crystallize this oil from chloroform–petroleum ether were unsuccessful, and the oil did not solidify even when chilled in acetone–Dry Ice.

2-Benzamido-4-chloro-3,5-dimethylphenol. (**A**).—The chloroform–petroleum ether solution obtained above of the oily oxidation product of 2-benzamido-3,5-dimethylphenol was saturated with hydrogen chloride; the orange color disappeared and a white precipitate separated, weighing 1.26 g. (92%). Purification by recrystallization from toluene gave colorless needles, m.p. 224–225.5°.

Anal. Calcd. for $C_{15}H_{14}ClNO_2$: C, 65.33; H, 5.09. Found: C, 65.63; H, 5.35.

(**B**).—Benzoylation of 2-amino-4-chloro-3,5-dimethylphenol[14] by the previously described procedure gave 81% yield of 2-benzamido-4-chloro-3,5-dimethylphenol, m.p. 224–225.5°, not depressed upon admixture with the hydrogen chloride adduct of the oxidation product of 2-benzamido-3,5-dimethylphenol.

5-Chloro-4,6-dimethyl-*o*-quinone-1-benzimide.—A suspension of 1.38 g. of 2-benzamido-4-chloro-3,5-dimethylphenol in 75 ml. of chloroform at room temperature was stirred with 2.21 g. of lead tetraacetate for 5 minutes, and then filtered. The orange filtrate was concentrated *in vacuo* to a residue, which was powdered, treated with 50 ml. of ether and transferred to a filter. An additional quantity of product was obtained by concentration and chilling the filtrate. The yield of 5-chloro-4,6-dimethyl-*o*-quinone-1-benzimide was 1.36 g. (99%); purification from ether gave orange needles, m.p. 133–134°.

Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.81; H, 4.42. Found: C, 65.64; H, 4.50.

2-Benzamido-4,6-dichloro-3,5-dimethylphenol.—Hydrogen chloride was passed into a solution of 0.5 g. of 5-chloro-4,6-dimethyl-*o*-quinone-1-benzimide in 50 ml. of chloroform until decolorization was complete. Concentration of the chloroform to 15 ml. and addition of 50 ml. of petroleum ether (b.p. 30–60°) precipitated 0.54 g. (95%) of 2-benzamido-4,6-dichloro-3,5-dimethylphenol. Purification from a chloroform–petroleum ether (b.p. 80–110°) solvent pair gave colorless, very fine needles, m.p. 213–213.5°.

Anal. Calcd. for $C_{15}H_{13}Cl_2NO_2$: C, 58.08; H, 4.22. Found: C, 57.93; H, 4.44.

1,2-Naphthoquinone-1-benzimide.—A suspension of 2.63 g. of 1-benzamido-2-naphthol[15] (prepared by the general method above from Eastman 1-amino-2-naphthol hydrochloride) in 75 ml. of chloroform was stirred with 4.43 g. of lead tetraacetate at room temperature for one hour. After filtration, the orange solution was evaporated *in vacuo* and the residue transferred to a filter with the aid of 50 ml. of petroleum ether. The crude 1,2-naphthoquinone-1-benzimide weighed 2.48 g. (94%), and was purified from a chloroform–petroleum ether (b.p. 80–110°) solvent pair; orange needles, m.p. 190–190.5°.

Anal. Calcd. for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24. Found: C, 78.22; H, 4.31.

x-Chloro-1-benzamido-2-naphthol.—When hydrogen chloride was passed into a solution of 1,2-naphthoquinone-1-benzimide in a minimum amount of chloroform, a quantitative yield of x-chloro-1-benzamido-2-naphthol was obtained. Purification from toluene (Darco) gave colorless needles, m.p. 235°.

Anal. Calcd. for $C_{17}H_{12}ClNO_2$: C, 68.58; H, 4.06. Found: C, 68.78; H, 4.17.

The following is a summary of the results of other oxidations tried which gave products too unstable to isolate. The benzamidophenols were prepared by the general method given above, and the oxidations were by lead tetraacetate in dry chloroform.

(10) A. Faust and E. Saame, *Ann.*, **7**, (Supp.), 193 (1870).

(11) F. Fischer, *ibid.*, **7** (Supp.), 189 (1870).

(12) R. F. v. Walther and W. Zipper, *J. prakt. Chem.*, [2] **91**, 414 (1915).

(13) K. v. Auwers and E. Borsche, *Ber.*, **48**, 1711 (1915).

(14) K. v. Auwers, *et al.*, *Fortschr. Chem. Physik u. physik. Chem.*, **18**, 22 (1924).

(15) J. Scheiber and P. Brandt, *J. prakt. Chem.*, [2] **78**, 92 (1908).

o-Benzamidophenol[16]: an amorphous, purple product, not reducible to *o*-benzamidophenol; did not react as expected with hydrogen chloride; apparently polymeric.

o-Benzenesulfonamidophenol[17]: tar.

o-Acetamidophenol (Eastman): tar.

6-Acetamido-*m*-cresol: at room temperature, the initial orange color of the solution lasted 2 minutes, then turned brown; at 0°, the orange color persisted, but the product decomposed when the solvent was removed.

6-Benzenesulfonamido-*m*-cresol: at room temperature, an immediate dark brown solution formed from which only amorphous, yellow, high-melting material was obtained; at 0°, the initially yellow solution began to turn brown in 3 minutes.

4-Chloro-6-benzamido-*m*-cresol: the orange solution obtained at room temperature appeared to be stable; the reaction was worked up after 5 minutes; the orange needles obtained were stable at room temperature for only about 10 minutes.

2-Benzenesulfonamido-*p*-cresol: an immediate dark brown solution formed which contained only brown, amorphous materials.

2-Benzamido-*p*-cresol[18]: at room temperature, the initial orange color lasted 15 seconds, then turned magenta; at −5°, the orange solution had become red in about 15 minutes; the purple product appeared to be polymeric.

2-Benzamido-4-chlorophenol: at room temperature, the orange color lasted for 10 minutes, then darkened; at 0°, the oxidation was slower, and after one hour only half of the amide had been oxidized; a few orange needles were isolated which were stable at room temperature for 5 minutes, and then decomposed to a yellow, amorphous solid.

3-Benzamido-4-hydroxybiphenyl[19]: at room temperature, the orange color was stable for 25 minutes; the reaction, when worked up after 5 minutes, gave orange needles, m.p. about 90°; the product was not sufficiently stable to recrystallize from ether.

2-Benzamido-4,6-dichlorophenol: at room temperature, an immediate orange color developed which appeared to be stable; a few orange crystals, m.p. 111–117°, were isolated which decomposed in about one hour at room temperature.

6-Benzamido-2,4-dimethylphenol[20]: at room temperature, the initially yellow solution darkened in a few minutes; at 0°, the yellow color appeared stable, but the product decomposed when the solvent was removed.

(16) J. H. Ransom, *Am. Chem. J.*, **23**, 17 (1900).

(17) C. B. Pollard and L. H. Amundsen, THIS JOURNAL, **57**, 357 (1935).

(18) K. v. Auwers and F. Eisenlohr, *Ann.*, **369**, 224 (1909).

(19) L. C. Raiford and J. C. Colbert, THIS JOURNAL, **47**, 1454 (1925).

(20) K. v. Auwers, H. Bundesmann and F. Wieners, *Ann.*, **447**, 196 (1926).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE UNIVERSITY]

Oxidative Ring Cleavage Reactions of Propylene Sulfide

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Reactions of propylene sulfide with chlorine and bromine in various solvents, and with 30% hydrogen peroxide have been studied, and the mode of ring opening has been shown by proving the structure of the products formed. Addition of chlorine and bromine to propylene sulfide in anhydrous solvents caused ring cleavage at the primary carbon–sulfur bond to give bis-(1-methyl-2-haloethyl) disulfides. Reversing the manner of addition and adding the propylene sulfide to liquid chlorine or bromine gave 1-halo-2-propanesulfenyl halides plus more highly halogenated compounds. Aqueous chlorine also cleaved the sulfide ring at the primary carbon to give 1-chloro-2-propanesulfonyl chloride. In the reactions of 30% hydrogen peroxide with propylene sulfide small yields of 2-hydroxy-1-propanesulfonic acid, formed by ring cleavage at the secondary carbon–sulfur bond, were obtained, and sulfuric acid was also identified as a chief product in these reactions. Derivatives of these compounds were prepared and compared to compounds made by unequivocal methods.

Introduction

In the few studies which have been made on the structure of the addition products of unsymmetrical olefin sulfides, it has been found that amines open the isobutylene sulfide ring mainly at the primary carbon[1]; mercaptans with isobutylene sulfide and either acidic (boron trifluoride) or basic (sodium ethoxide) catalysis give mixtures of products resulting from opening of the ring at either the tertiary or primary carbon[2]; alcohols with isobutylene sulfide and acidic (boron trifluoride) catalysis give mainly ring opening at the tertiary carbon[2]; hydrochloric acid in methanol, and acid chlorides with either propylene sulfide or chloropropylene sulfide open the rings mainly at the secondary carbon.[3,4]

Most of the previously published investigations of the reactions of olefin sulfides have led to products which were mercaptans or esters of mercaptans. In this work propylene sulfide has been treated with oxidizing types of reagents to yield products other than mercaptans, and the direction of cleavage of the sulfide ring has been shown by proof of the structure of these products.

(1) H. R. Snyder, J. M. Stewart and J. B. Ziegler, THIS JOURNAL, **69**, 2672 (1947).

(2) H. R. Snyder, J. M. Stewart and J. B. Ziegler, *ibid.*, **69**, 2675 (1947).

(3) W. Davies and W. E. Savige, *J. Chem. Soc.*, 317 (1950).

(4) W. Davies and W. E. Savige, *ibid.*, 774 (1951).

Discussion

Addition of either chlorine or bromine to propylene sulfide in an anhydrous solvent such as chloroform gave excellent yields of bis-(halopropyl) disulfides. The structure, as shown in the accompanying diagram of reactions (Fig. 1), is for the isomer proved to be the main product—the cleavage of the sulfide ring proceeding at the primary carbon to give bis-(1-methyl-2-chloroethyl) disulfide (I) or the corresponding bromine compound. Using a solution of bromine in carbon tetrachloride of known concentration, a solution of propylene sulfide in the same solvent could be titrated to a color endpoint, and the reaction was found to be quantitative.

Compound I, or its bromine analog, on treatment with excess piperidine gave bis-(1-methyl-2-piperidinoethyl) disulfide, isolated as the dihydrochloride salt. The amine was desulfurized with Raney nickel and the only new amine isolated from the reaction was proved through the melting point of