

quantities of haloketones or aldehydes. This investigation utilized the more reactive bromoketones and by use of five moles of amide and one mole of phosphorus pentasulfide with two to three moles of haloketone great improvements in the yields in the preparation of methylthiazoles have resulted.

When bromopropionaldehyde reacted in the *in situ* procedure, the yields were the same as those obtained when the pure thioamide reacted but a considerable saving in reaction time was achieved. Only 2-methylthiazole was not prepared by the *in situ* procedure. This was prepared by the method of Erlenmeyer⁵ by the reaction of thioacetamide and chloroacetaldehyde hydrate.

Experimental

2,4-Dimethylthiazole.—A mixture of 300 g. (5.1 moles) of acetamide, 225 g. (1.01 moles) of phosphorus pentasulfide and 300 ml. of benzene (dried over sodium wire) in a two-liter three-neck flask was heated on the water-bath. When a black oily lower layer formed, 342.5 g. (2.5 moles) of bromoacetone⁶ was added dropwise at a rate sufficiently fast to maintain refluxing of the benzene. After completion of the addition, the mixture was refluxed for one hour, 100 ml. of water and 20 ml. of concd. hydrochloric acid were added and the mixture heated one hour more. The mixture was steam distilled to remove the benzene, made basic with 50% sodium hydroxide solution and steam distilled. The distillate was extracted with ether, the ether extract was dried over sodium sulfate and the ether removed by distillation at reduced pressure. Fractionation yielded 215 g. (76%) of 2,4-dimethylthiazole, b.p. 70–73° (50 mm.), lit. b.p. 143–145°.³

4,5-Dimethylthiazole.—Phosphorus pentasulfide (67.5 g., 0.32 mole) and 100 ml. of dioxane (refluxed and distilled over sodium wire) were placed in a two-liter three-neck flask fitted with a reflux condenser, dropping funnel and sealed stirrer. Formamide (66 g., 1.47 moles) was added dropwise quite rapidly. When the flask became warm, it was cooled in an ice-water mixture and 151 g. (1.0 mole) of methyl α -bromoethyl ketone⁷ was added dropwise at a rate sufficiently fast to maintain reaction but slow enough to prevent rapid refluxing. After completion of the addition and when the reaction subsided, the mixture was refluxed for one hour, 100 ml. of water and 20 ml. of concd. hydrochloric acid were then added and the mixture refluxed one hour more. The mixture was steam distilled to remove most of the dioxane and any other steam distillable organic materials. The mixture was then made basic with 50% sodium hydroxide solution and steam distilled. The steam distillate was saturated with potassium carbonate, extracted with ether, the ether extract dried over sodium sulfate and the ether removed by distillation at reduced pressure. Fractionation of the residue yielded 81.5 g. (72%) of 4,5-dimethylthiazole, b.p. 75° (47 mm.), lit. b.p. 158°.⁴

2,5-Dimethylthiazole.—This compound was prepared in the same manner as 2,4-dimethylthiazole by the action of 200 g. (3.4 moles) of acetamide and 150 g. (0.71 mole) of phosphorus pentasulfide in 200 ml. of benzene with 150 g. (1.1 moles) of α -bromopropionaldehyde.⁷ The steam distillate containing 2,5-dimethylthiazole was saturated with potassium carbonate, extracted with ether and the ether extract was dried over potassium carbonate. The ether was removed by distillation at reduced pressure and fractionation of the residue yielded 42 g. (30%) of 2,5-dimethylthiazole, b.p. 86° (80 mm.), lit. b.p. 148.9–150.9° (734 mm.).⁸

2,4,5-Trimethylthiazole.—This compound was prepared in the same manner as 2,4-dimethylthiazole by the reaction of 300 g. (5.1 moles) of acetamide and 225 g. (1.01 moles) of phosphorus pentasulfide in 300 ml. of benzene with 403.2 g. (2.67 moles) of methyl α -bromoethyl ketone. The yield of

2,4,5-trimethylthiazole obtained was 240 g. (71%), b.p. 65–67° (20 mm.), lit. b.p. 166.5–167.5° (717.5 mm.).⁹

4-Methylthiazole.—This compound was prepared in the same manner as 4,5-dimethylthiazole by the reaction of 66 g. (1.47 moles) of formamide and 67.5 g. (0.32 mole) of phosphorus pentasulfide in 150 ml. of dioxane with 137 g. (1.0 mole) of bromoacetone. The yield of 4-methylthiazole obtained was 73 g. (73%), b.p. 70° (90 mm.), lit. b.p. 133–134° (760 mm.).¹⁰

5-Methylthiazole.—This compound was prepared in the same manner as 4,5-dimethylthiazole by the reaction of 66 g. (1.47 moles) of formamide and 67.5 g. (0.32 mole) of phosphorus pentasulfide in 150 ml. of dioxane with 137 g. (1.0 mole) of α -bromopropionaldehyde. The yield of 5-methylthiazole obtained was 30 g. (30%), b.p. 57° (32 mm.), lit. b.p. 70–72° (41 mm.).¹¹

2-Methylthiazole.—This compound was prepared by the reaction of thioacetamide¹ and chloroacetaldehyde hydrate in the presence of benzene and acetic anhydride.⁵ The chloroacetaldehyde hydrate used was obtained by addition of anhydrous calcium chloride, with cooling and stirring, to a 40% aqueous solution of chloroacetaldehyde (Dow). A separation into two layers occurred and the chloroacetaldehyde hydrate layer obtained was used in the preparation of 2-methylthiazole, b.p. 65–67° (80 mm.), lit. b.p. 129–130° (760 mm.),⁵ 49% yield.

(9) T. Roubleff, *ibid.*, **259**, 253 (1890).

(10) L. Arapides, *ibid.*, **249**, 7 (1888); A. Hantzsch, *ibid.*, **250**, 257 (1889).

(11) H. Erlenmeyer and P. Schmidt, *Helv. Chim. Acta*, **29**, 1957 (1946).

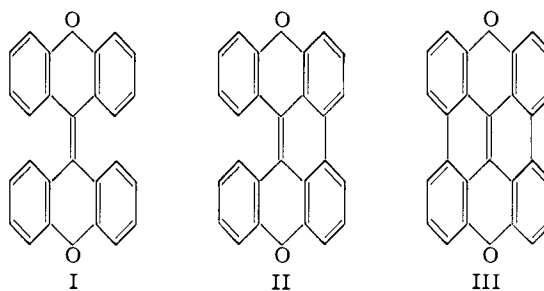
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The Absorption Spectra of $\Delta^{10,10'}$ -Bianthrone, Helianthrone and Mesonaphthobianthrone in Concentrated Sulfuric Acid

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It is commonly known that $\Delta^{10,10'}$ -bianthrone (I), and mesonaphthobianthrone (III) give deep red colored solutions in concentrated sulfuric acid while helianthrone (II) gives a deep blue-green solution.



Eckert and Tomaschek¹ reported the absorption spectra of III in concentrated sulfuric acid from 458–615 μ . Meyer, Bondy and Eckert² published the absorption spectra of I, II and III in concentrated sulfuric acid from 515–683 μ . All curves, except that of I, agreed qualitatively with this research.

Experimental

$\Delta^{10,10'}$ -Bianthrone was made by a modification of the method of Schonberg and Ismail³ in which anthrone was

(1) A. Eckert and R. Tomaschek, *Monatsh.*, **39**, 839 (1918).

(2) H. Meyer, R. Bondy and A. Eckert, *ibid.*, **33**, 1447 (1912).

(3) A. Schonberg and A. F. A. Ismail, *J. Chem. Soc.*, 307 (1944); M. B. Goren, Doctoral Dissertation, Harvard University, 1949.

(5) H. Erlenmeyer, *et al.*, *Helv. Chim. Acta*, **31**, 1142 (1948).

(6) J. R. Catch, *et al.*, *J. Chem. Soc.*, 272 (1948); J. F. Norris, *J. Ind. Eng. Chem.*, **11**, 817 (1919).

(7) J. U. Nef, *Ann.*, **335**, 247 (1904).

(8) K. Hubacher, *ibid.*, **259**, 228 (1890).

oxidized to bianthrone and the latter, after isomerization in base, oxidized to the desired compound. The $\Delta^{10,10'}$ -bianthrone was analyzed; calcd.: C, 87.5; H, 4.20. Found: C, 87.5; H, 4.17.

The helianthrone was prepared by the method of Scholl and Mansfeld⁴ starting with α,α' -bianthraquinonyl. Efforts to prepare pure α,α' -bianthraquinonyl by the method of Scholl⁵ were unsuccessful because a black powder was obtained from which it was not possible to separate the pure product by recrystallization from nitrobenzene or by continuous extraction with xylene. The α,α' -bianthraquinonyl was therefore prepared by the method of Ullmann and Minajeff⁶ in a 75% yield (on recrystallization from nitrobenzene) from α -chloroanthraquinone.⁷

The procedure of Scholl and Mansfeld⁴ was modified slightly by placing the mixture of helianthrone and copper dust in dilute nitric acid for 30 minutes to effect removal of the copper dust. Crystallization from xylene gave an equal mixture of yellow needles and red nuggets. These two forms melted with no decomposition at 294–297° compared to 296° reported by Sauvage⁸ and had identical absorption spectra. A crude yield of about 80% was obtained which was reduced to 60% on recrystallization from xylene. The purified material was analyzed; calcd.: C, 88.0; H, 3.69. Found: C, 87.7; H, 3.7.

Pure mesonaphthobianthrone was easily prepared by the exposure of a solution of $\Delta^{10,10'}$ -bianthrone in xylene to strong sunlight for 3 days.² The crude product was purified by recrystallization from nitrobenzene.

Absorption Spectra.—All absorption spectra were determined with a Beckman DU spectrophotometer using calibrated cells of path length 1.000 ± 0.001 cm. All measurements were made at room temperature.

Results

In Fig. 1 the absorption spectra of $\Delta^{10,10'}$ -bianthrone, helianthrone and mesonaphthobianthrone in concentrated sulfuric acid are given.

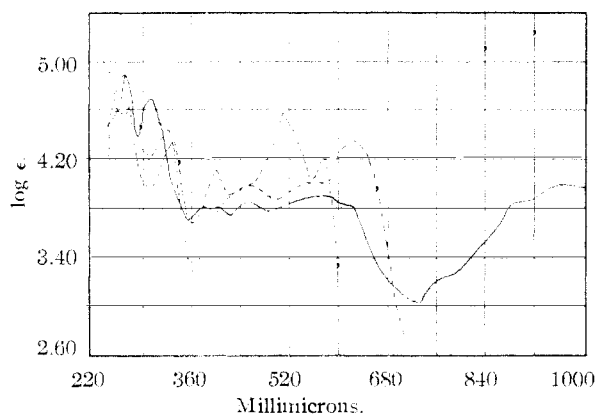


Fig. 1.—The absorption spectra of $\Delta^{10,10'}$ -bianthrone, —; helianthrone, ---; and mesonaphthobianthrone in concentrated sulfuric acid, — · —.

Since the extinction coefficient changes with time, the absorption spectra were standardized for time as follows: the solutions were made up in dim light and the measurements were started 30 minutes after mixing with all measurements finished 80 minutes after mixing.

$\Delta^{10,10'}$ -Bianthrone was reisolated from a sulfuric acid solution 80 minutes after mixing and analyzed by comparison of the absorption spectrum of the reisolated substance with the absorption spectrum

(4) R. Scholl and J. Mansfeld, *Ber.*, **43**, 1734 (1910).

(5) R. Scholl, *ibid.*, **40**, 1691 (1907).

(6) F. Ullmann and V. Minajeff, *ibid.*, **45**, 687 (1912).

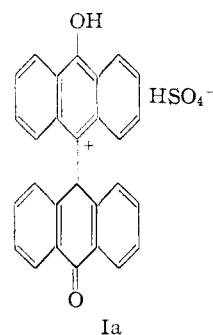
(7) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 128.

(8) G. Sauvage, *Ann. chim.*, **12**, 844 (1947).

of known $\Delta^{10,10'}$ -bianthrone. No differences were noted in these spectra.

Discussion

The changes in color which occur on solution of these compounds in sulfuric acid, we believe, may be attributed to the formation of oxonium salts which are in resonance with structures that may be classed as triarylcarbonium ions and are analogs of the well known halochromic salts. Thus, the coordination of a proton on a carbonyl oxygen of $\Delta^{10,10'}$ -bianthrone would give a hybrid consisting of fifteen charge-distributing polar structures among which Ia may be considered analogous to the halochromic salts. It is possible, of course, that the system may be doubly protonated. A cryoscopic examination of the system in pure sulfuric acid was made, but the data were inconclusive and not interpretable.



Coördination of other electrophilic agents might be expected to give rise to similar color phenomena. Indeed, stannic chloride in xylene and in nitrobenzene coordinates with I and II to afford colored complexes, although apparently not with III. The colors, however, are not as vivid as those produced by concentrated sulfuric acid.

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Synthesis and Properties of 1,2,5,6-Tetraphenylhexa-1,5-diene-3-yne

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In an investigation on aryl substituted vinyl-acetylenes, we carried out the condensation of acetyldimagnesium bromide with desoxybenzoin. The product, 1,2,5,6-tetraphenylhexa-1,5-diene-3-yne (I), behaved like other derivatives of divinyl-acetylene¹; the compound adds two molecules of maleic anhydride to yield the hydronaphthalene derivative (II) (or an isomer of it (IIa) produced by rearrangement of the double bonds). The hydrocarbon adds three molecules of bromine in the titration with 0.1 *N* potassium bromide-potassium bromate solution. However, bromination of (I), using carbon tetrachloride as a solvent gave a tetrabromide (probably produced by dehydro-

(1) E. Dane, H. Höss, A. W. Bindseil and J. Schmitt, *Ann.*, **532**, 39 (1937); E. Dane, O. Höss, K. Eder, J. Schmitt and O. Schön, *ibid.*, **536**, 183 (1938); L. W. Butz and co-workers, *J. Org. Chem.*, **5**, 379 (1940); *THIS JOURNAL*, **63**, 3348, 3344 (1941); **64**, 1311 (1942).