

carbanilate which results in an increased tendency toward ionization to the enol anion. The enolic form can then react with phenyl isocyanate to give allophanate containing a stable pseudo six-membered ring containing an intramolecular hydrogen bond.<sup>1</sup>

When the aromatic ring of the aryl isocyanate and the ethyl carbanilate both contain a methyl group (Table I, Nos. 10, 11) the rate of reaction of *o*-tolyl isocyanate with ethyl *o*-methylcarbanilate is slightly greater than the rate of reaction of *p*-tolyl isocyanate with ethyl *p*-methylcarbanilate. Two factors are taken into consideration to account for this enhanced reactivity of the *o*-methyl system; (a) effect of the methyl substituent on the aromatic ring of the isocyanate and (b) effect of the methyl substituent on the aromatic ring of the carbanilate. It was previously shown that at room temperature *p*-tolyl isocyanate reacts approximately 4 times faster than *o*-tolyl isocyanate toward alcohol or water at 25°. However, as the temperature of the reaction is increased to 100° the relative rates of reaction of the *o*- and *p*-methyl groups begin to approach each other and are differ-

ent by a factor of approximately 2. On the other hand, as shown above, an *o*-methyl group activates the carbanilate group approximately 3.5 times greater than a *p*-methyl group. Therefore, a larger rate constant should be observed for the formation of allophanate from *o*-tolyl isocyanate with ethyl *o*-methylcarbanilate than from *p*-tolyl isocyanate with ethyl *p*-methylcarbanilate.

The results of the rate measurements for the *N*-methylmorpholine catalyzed reaction of phenyl isocyanate with ethyl carbanilate show that the amine does not have any appreciable catalytic effect on allophanate formation (Table I, Nos. 2 and 4). The spectral data show that carbanilate concentration decreases with time at the same rate as the uncatalyzed reaction (Fig. 3). As the reaction approaches equilibrium a large exotherm occurs followed by solidification of the solution to a mixture of triphenylisocyanurate and ethyl carbanilate. Thus the disappearance of the carbanilate NH absorption band with time indicates that ethyl  $\alpha,\gamma$ -diphenylallophanate is being formed and is an intermediate reaction product in the formation of triphenylisocyanurate from phenyl isocyanate and ethyl carbanilate.

*Acknowledgment.* The writer wishes to thank Dr. Karl Frensdorff for his aid in deriving the rate equation used in this paper.

WILMINGTON, DEL.

(7) (a) J. Burkus and C. F. Eckert, presented before the Division of Paints and Plastics at the 132nd National Meeting of the American Chemical Society, New York, New York, September 1957. (b) K. C. Smeltz, E. J. Goldberg, I. C. Kogon, W. C. Woodland, Reaction of Water with Isocyanate, submitted for publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

## A New Synthesis of 9-Phenanthrol; Absorption Spectra of the Quinhydrone-Type Molecular Compound between 9-Phenanthrol and Phenanthrenequinone

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A new synthesis of 9-phenanthrol from phenanthrene is described in which the novel step is a quantitative pinacol rearrangement of *cis*- or *trans*-9,10-dihydro-9,10-phenanthrenediol. The infrared spectra of 9-phenanthrol shows it to be completely enolized in both the solid state and in solution. Infrared and ultraviolet absorption spectra, combustion analysis, and chromatographic separation support the conclusion that 9-phenanthrol forms a quinhydrone-type molecular compound with phenanthrenequinone in a 1:1 molar ratio.

*9-Phenanthrol.* 9-Phenanthrol (III), first prepared by Lachowitz<sup>1</sup> via 9,10-phenanthrenequinone (I) and 10,10-dichloro-9,10-dihydro-9-phenanthrone, has been of interest because of its conversion in high yields to 9-phenanthrylamine and *N*-alkyl-9-phenanthrylamines (Bucherer reaction) which are structurally related, in at least one important respect, to morphine.<sup>2</sup> III also has marked analgesic properties<sup>3a</sup> and fungi toxicity.<sup>3b</sup>

Improvements in Lachowitz' procedure,<sup>4,5</sup> or alternatively, reduction of I with hydriodic acid and phosphorus,<sup>6,7a</sup> with hydrazine in absolute ethanol<sup>8</sup>

(1) B. Lachowitz, *J. prakt. Chem.*, **28**, 172 (1883); *Ber.*, **17**, 1161 (1883).

(2) L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Am. Chem. Soc.*, **58**, 2163 (1936).

(3) (a) N. B. Eddy, *J. Pharmacol. Exptl. Therap.*, **48**, 183 (1933); **51**, 75 (1934). (b) S. Rich and J. G. Horsfall, *Proc. Natl. Acad. Sci. U. S. A.*, **40**, 139 (1954); *Chem. Abstr.*, **48**, 8831 (1954).

(4) J. Schmitt and H. Lumpp, *Ber.*, **41**, 4215 (1908).

(5) S. Goldschmidt and M. A. Bredig, *Ann.*, **445**, 135 (1925).

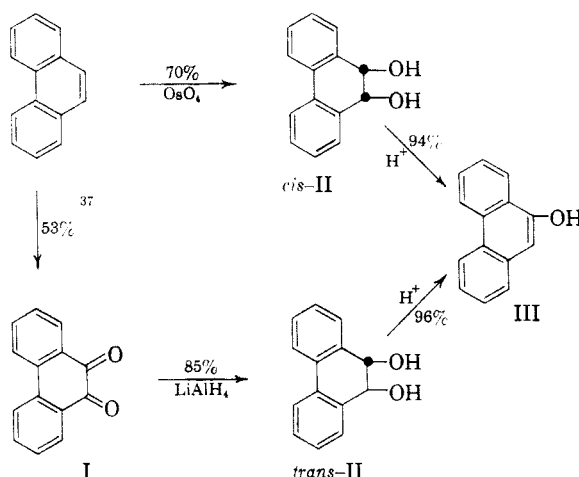
(6) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **63**, 770 (1893).

(7) (a) E. Fourneau and J. Matti, *Bull. soc. chim.*, **7**, 615 (1940). (b) E. Fourneau and J. Matti, *Bull. soc. chim.*, **9**, 633 (1942).

or with hydrogen in the presence of nickel<sup>9</sup> left much to be desired<sup>2</sup> from the viewpoint of yield and procedure.<sup>10</sup> Thereafter three substantially new and direct routes to III were reported: (i) Potassium hydroxide fusion of potassium 9-phenanthrenesulfonate<sup>11</sup> gave III in unreported yields.<sup>16</sup> (ii) Fieser's three-step synthesis from phenanthrene *via* 9-bromo-10-methoxy-9,10-dihydrophenanthrene gave III in 28–30% yields.<sup>2</sup> By this same route, however, Hunsberger, Ketcham, and Gutowsky<sup>17</sup> obtained a 12% yield.<sup>18</sup> In both cases, the yields are based on phenanthrene consumed. (iii) Finally, Schultz, Schultz, and Cochran<sup>19</sup> reported a 5% yield of III in the reaction of fluorenone with two equivalents of diazomethane.<sup>20</sup>

In a previous paper,<sup>22</sup> *cis*- and *trans*-9,10-dihydro-9,10-phenanthrenediols (*cis*- and *trans*-II) were shown to be configurationally related by conversion to the same acid-catalyzed rearrangement product,

III.<sup>23</sup> In this paper we wish to report that on the basis of yields and simplicity of procedure, the pinacol rearrangement of *cis*- and *trans*-II diols according to the following scheme seems to be the best available to date for the laboratory preparation of III.



(8) S. Dutt and N. K. Sen [*J. Chem. Soc.*, **123**, 3420 (1923)] reported quantitative yields of III from a sealed tube reaction (200°, 6 hr.) between I and hydrazine hydrate in absolute ethanol. However, S. Goldschmidt, A. Vogt, and M. A. Bredig [*Ann.*, **445**, 126 (1925)] showed that under almost identical conditions (sealed tube, 180°, 6 hr.), the product was exclusively tetrabenz(a,c,h,j)phenazine, and not III. With milder conditions (12-hr. reflux), the Dutt and Sen procedure gave only phenanthrenehydroquinone.

(9) J. von Braun and O. Bayer, *Ber.*, **58**, 2667 (1925).

(10) Worthy of note are the multistep or incidental preparations of III from 9-phenanthrylmagnesium bromide [W. E. Bachmann, *J. Am. Chem. Soc.*, **56**, 1363 (1934)]; from diphenic anhydride [N. Chatterjee, *J. Indian Chem. Soc.*, **12**, 410 (1935); *Chem. Abstr.* **30**, 454 (1936)]; from ethyl biphenyl-2-acetate [R. Sherwood, W. F. Short, and J. Woodcock, *J. Chem. Soc.*, 322, (1936); A. Schönberg and F. L. Warren, *Chem. & Ind. (London)*, **1939**, 199, and Chatterjee (*vide supra*)]; from 9-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene [C. D. Gutsche and W. S. Johnson, *J. Am. Chem. Soc.*, **68**, 2239 (1946)]; from phenanthrene [J. W. Cook and R. Schoental, *J. Chem. Soc.*, **47**, (1950)]; and from 9-phenoxyphenanthrene [R. L. Huang, *J. Chem. Soc.*, 3295, (1955)].

(11) Prepared in 6%,<sup>12</sup> 7–14.5%,<sup>13</sup> 13%,<sup>14</sup> and 24–30%<sup>15</sup> yields by the sulfonation of phenanthrene.

(12) A. Werner and E. Frey, *Ann.* **321**, 270 (1902).

(13) H. Sandquist, *Ann.*, **392**, 76 (1912).

(14) L. F. Fieser, *J. Am. Chem. Soc.*, **51**, 2460 (1929).

(15) Sister M. G. Solomon and D. J. Hennessy, *J. Org. Chem.*, **22**, 1649 (1957).

(16) A. Werner and E. Frey, *Ann.*, **321**, 299 (1902).

(17) I. M. Hunsberger, R. Ketcham, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **74**, 4839 (1952).

(18) R. P. Linstead, R. R. Whitstone, and P. Levine, *J. Am. Chem. Soc.*, **64**, 2014 (1942) also found that very poor yields were obtained by the Fieser, Jacobsen, and Price procedure unless the sodium or potassium acetate was omitted from the reaction mixture.

(19) R. F. Schultz, E. O. Schultz, and J. C. Cochran, *J. Am. Chem. Soc.*, **62**, 2902 (1940).

(20) Other products isolated and identified and their yields, were: 30% 9-methoxyphenanthrene,<sup>21</sup> 1.5% di-9-phenanthryl ether, and 30% unchanged fluorenone.

(21) Using this procedure, Hunsberger, Ketcham, and Gutowsky<sup>17</sup> obtained a 36% yield of 9-methoxyphenanthrene.

(22) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn, and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957).

Thus, *cis*-II diol, prepared by an osmium tetroxide hydroxylation of phenanthrene,<sup>22,24</sup> or sodium-amalgam reduction of diphenaldehyde (20%),<sup>22</sup> and *trans*-II diol, obtained by the reduction of I with lithium aluminum hydride<sup>25</sup> or sodium borohydride (70%),<sup>26</sup> can be quantitatively rearranged to III in over-all yields of 66% and 43%, respectively, from phenanthrene. The infrared spectra of III showed a hydroxyl band at 2.76  $\mu$  (CCl<sub>4</sub>) and at 3.10  $\mu$  (Nujol).<sup>27,28</sup> The absence of carbonyl absorption in both the solid state and in solution indicates III to be completely enolized.<sup>17,29</sup>

**9-Phenanthrol:Phenanthrenequinone.** When wet or in solution, but more slowly in the solid state, III is

(23) Named 9,10-dihydro-9-phenanthrone in ref. 22 by analogy to the other phenanthrones reported therein.

(24) R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99(1942).

(25) J. Booth, E. Boyland, and E. E. Turner, *J. Chem. Soc.*, 1188, 2808 (1950).

(26) Sodium trimethoxyborohydride reduction gave a negligible amount of *trans*-II diol and a small amount of phenanthrenehydroquinone isolated as the corresponding quinhydrone. See Experimental section.

(27) Hunsberger, Ketcham, and Gutowsky<sup>17</sup> report a hydroxyl band at 2.77  $\mu$  (CCl<sub>4</sub>) and 3.06  $\mu$  (Nujol).

(28) Infrared spectra by Mr. Joseph Tesar.

(29) Although III is tautomeric with its keto form, 9,10-dihydro-9-phenanthrone, it exhibits no ketone reactions under normal conditions.<sup>30,31a</sup> Cf. the transannular tautomerism of 9-anthrol (89%)  $\rightleftharpoons$  anthrone (11%) in methanol [K. H. Meyer, *Ann.*, **379**, 37 (1911)]; although both forms can be isolated and the substance reacts in either form depending on conditions, the keto form is the more stable. In acetic acid, the equilibrium concentration of anthrone is 98.7%.<sup>31b</sup>

(30) F. R. Japp and A. Findlay, *J. Chem. Soc.*, **71**, 1115 (1897). See ref. 33 for reported exceptions.

(31) (a) S. Coffey and J. Van Alphen in E. H. Rodd's *Chemistry of Carbon Compounds*, Vol. III<sup>b</sup>, Elsevier Publishing Co., D. Van Nostrand Co., Inc., New York, 1956, p. 1436. (b) *Ibid.*, p. 1383.

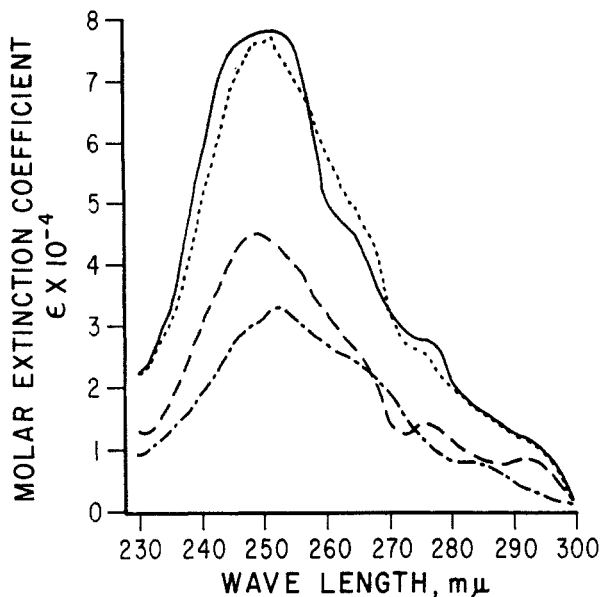
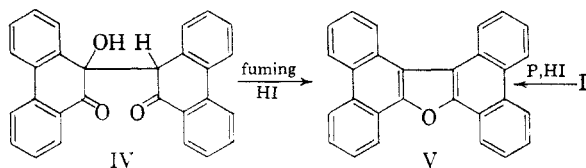


Fig. 1. Ultraviolet spectra of: 9-phenanthrol (III) - - - -; phenanthrenequinone (I) - - - -; 9-phenanthrol:phenanthrenequinone molecular compound (VII) —; Molecular compound calculated by addition of component spectra . . . .

oxidized by air to a dark red, crystalline solid,  $C_{28}H_{18}O_3$ , m.p., 156–157°. The  $C_{28}H_{18}O_3$  compound can also be obtained by simply mixing equimolecular proportions of I and III.<sup>8,30</sup> On reaction,  $C_{28}H_{18}O_3$  gave I and 9-phenanthryl acetate with acetic anhydride,<sup>30</sup> I with chromic acid,<sup>31a</sup> and diphenanthro(9,10-*b*,9',10'-*d*)furane (V) with fuming hydriodic acid<sup>6,30,32</sup> or hydriodic acid with red phosphorus.<sup>8</sup> V could also be obtained by a similar reduction of I with hydriodic acid.<sup>6,30</sup> On the basis of these reactions, Japp and Findlay<sup>30</sup> suggested IV, an aldol condensation product of III (acting in the keto form) and I,<sup>33</sup> both as the structure of  $C_{28}H_{18}O_3$  and as the intermediate in the reduction of I to V.

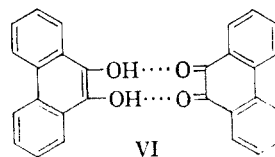


Alternatively, it has been suggested that  $C_{28}H_{18}O_3$  is an impure quinhydrone-type molecular compound between I and phenanthrenehydroquinone (oxidation product of III)<sup>31a</sup> of probable structure VI, analogous to that proposed between I and 10-amino-9-phenanthrol.<sup>34</sup>

(32) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, 57, 663 (1890).

(33) This was one of the two instances noted by these authors<sup>30</sup> in which III behaved as a ketone. The second example was the reaction of III with phenylhydrazine at 200° with the elimination of water and ammonia to form an indole derivative. In both cases, they noted that under the vigorous conditions employed, these reactions proved little of the structure of  $C_{28}H_{18}O_3$ .

(34) G. M. Jaffe and A. R. Day, *J. Org. Chem.*, 8, 43 (1943).



Using Japp and Findlay's procedure,<sup>30</sup> we have prepared the  $C_{28}H_{18}O_3$  compound from I and III. Combustion analyses showed a 1:1 molar ratio. Its infrared spectrum ( $CS_2$ ) is virtually a superimposition of the absorption spectra of the pure components I and III (Table I). The ultraviolet absorption spectra (ethanol) of the  $C_{28}H_{18}O_3$  compound, the pure components I and III, and the calculated curve by adding the molar extinction coefficients of I and III are shown in Fig. 1. The spectrum of the  $C_{28}H_{18}O_3$  compound nearly equals the sum of the

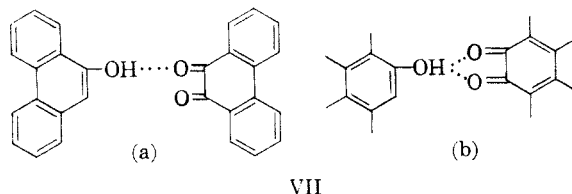
TABLE I

COMPARISON OF INFRARED ABSORPTION BANDS<sup>a</sup> AND INTENSITIES<sup>b</sup> OF PHENANTHRENEQUINONE (I), 9-PHENANTHROL (III), AND MOLECULAR COMPOUND (VII) COMPOSED OF I AND III IN 1:1 MOLE RATIO

Wave Length, Microns		
Phenanthrenequinone (I)	9-Phenanthrol (III)	Molecular compound (VII)
	2.79 m (OH)	2.81 w (OH)
3.28 <sup>e</sup>	3.26 w	3.26 w
5.93 s (C=O)		5.93 s (C=O)
	6.12 m	6.13 w
7.52 w	7.58 m	7.58 w
7.80 s		7.81 s
8.17 m		8.17 <sup>c</sup>
	8.26 s	8.26 m
	8.57 w	8.60 vw
	8.73 m	8.74 w
8.94 w		8.95 w
	9.02 m	9.03 w
	9.34 s	9.35 m
	9.64 m	9.65 w
9.88 w		9.88 w
10.42 vw		10.42 vw
	10.54 w	10.55 vw
	10.65 w	10.65 vw
10.85 m		10.85 m
	11.67 w <sup>d</sup>	11.66 vw <sup>d</sup>
	12.09 s	12.10 m
	13.10 s	13.10 <sup>c</sup>
13.17 s		13.17 s

<sup>a</sup> Concn. in  $CS_2$ : I and III, 0.02M; VII, 0.005M; the solubility of VII seems to depend on the rate of dissociation into its compounds I and III with increasing dilution. <sup>b</sup> Band intensities are reported according to the suggestion of H. M. Randall, N. Fuson, R. G. Fowler, and J. R. Dangle, *Infrared Determination of Organic Structures*, D. Van Nostrand Co., Inc., New York, 1949, p. 20: strong (s) = bands of the same order of intensity as the strongest band in the entire spectrum; moderate (m) = bands of  $1/3$  to  $2/3$  as intense as the strongest band; weak (w) = bands  $1/4$  to  $1/2$  as intense; very weak (vw) = bands of less than  $1/4$  intensity. Thus for pure components I and III, band intensities are directly comparable. For less soluble VII, the actual concentration of its components I and III is considerably less, and band absorption intensities appearing in VII should be weaker in some cases than identical bands in the spectra of the pure components. <sup>c</sup> Shoulder. <sup>d</sup> Broad band. <sup>e</sup> Inflection.

components. Finally, we have separated the components of the  $C_{23}H_{18}O_3$  compound by chromatography on an alumina column. Thus the analytical and absorption data support our belief that the  $C_{23}H_{18}O_3$  compound is neither IV nor VI but is an intermolecularly, hydrogen-bonded molecular compound of probable structure VIIa, or VIIb (bifurcated hydrogen bond), which is completely dissociated into its components in very dilute solution.



### EXPERIMENTAL

All melting points are uncorrected. The infrared spectra were determined with a Model 21 Perkin-Elmer recording spectrometer with NaCl optics. The ultraviolet spectra were observed in a Beckmann quartz spectrophotometer Model DU using 1 cm. quartz cells. The reported  $\epsilon$  values are for concentrations ranging from 0.00500 g./l. to 0.00250 g./l. in absolute ethanol. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

*cis-9,10-Dihydro-9,10-phenanthrenediol (cis-II)*. Purified phenanthrene, m.p. 98–98.5°<sup>35</sup> (0.705 g., 3.96 mmoles), was added to a solution of 1.010 g. (3.97 mmoles) of osmium tetroxide in 15 ml. of thiophene-free benzene. The orange solution turned yellow on further addition of 1 ml. of pyridine. On standing 5 days at room temperature, the dark brown crystals of the adduct were filtered off and the filtrate evaporated to dryness. The combined solid residues were dissolved in 50 ml. methylene chloride to which was added a solution of 10 g. mannitol and 1 g. potassium hydroxide in 100 ml. water. The mixture was mechanically shaken until the methylene chloride layer was colorless. If solid material (crude diol) appeared, it was filtered off, and the methylene chloride layer of the filtrate was separated and evaporated to dryness to yield the larger portion of crude diol. The combined pale green residues were recrystallized once from toluene (charcoal) to yield 0.588 g. (2.77 mmole, 70%) of fine, white silky needles, m.p. 179–180°; lit. m.p. 177–178°.<sup>24</sup>

*trans-9,10-Dihydro-9,10-phenanthrenediol (trans-II)* as white, fine silky needles from cyclohexane, m.p. 185–187°<sup>22,25</sup> was obtained in 85% yield<sup>36</sup> from the lithium aluminum hydride reduction of I, and in 70% yield using sodium borohydride according to the following procedure: Dried I,<sup>37</sup> 0.520 g. (2.50 mmoles), was extracted for 12 hr. in a Soxhlet extractor with 150 ml. of carefully dried anhydrous ether containing 0.150 g. (4.00 mmoles) of sodium borohydride, after which the complex was decomposed by adding 20–30 ml. of *N* sulfuric acid in portions to the cooled solution. The

(35) Bachmann's [*J. Am. Chem. Soc.*, 57, 557 (1935)] modified procedure [C. A. Dornfeld, J. E. Callan, and G. H. Coleman, *Org. Syntheses*, 28, 19 (1948)] followed by Solomon and Hennessy's<sup>15</sup> chromatographic technique was used to purify 90–95% phenanthrene (Gesellschaft f. Teerverwertung m. b. H. Duisburg-Meiderich, Germany).

(36) This was our average yield of *trans*-II diol for three runs. At variance with our results, R. F. Nyström and W. G. Brown [*J. Am. Chem. Soc.*, 70, 3738 (1948)] report a 98% yield of phenanthrenehydroquinone in a similar reduction.

(37) R. Wendland and J. La Fonde, *Org. Syntheses*, 34, 76 (1954); L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd ed., D. C. Heath and Co., Boston, 1956, p. 757.

flask was carefully swirled to avoid a possible vigorous reaction of the unreacted hydride. The ether layer was separated and the aqueous layer extracted with an additional 50 ml. of ether. The combined ether extracts were washed with *N* sodium hydroxide solution and any insoluble material removed by filtration. The ether solution then was evaporated to dryness. The crude diol (0.420 g.) on recrystallization from benzene and then from cyclohexane gave 0.370 g. (70%) of the *trans*-II diol, m.p. 184–185°.

*Reduction of I with sodium trimethoxyborohydride*. I (0.52 g., 2.5 mmoles) was extracted for 12 hr. in a Soxhlet with 200 ml. of anhydrous ether containing 0.64 g. (5.0 mmoles) of sodium trimethoxyborohydride. The color of the resulting solution was bluish green. The complex was decomposed by the same acid treatment described in the sodium borohydride reduction. Treatment of the combined ethereal extracts with 30–40 ml. of *N* NaOH, precipitated a considerable amount of dark brown material. This was filtered, washed with water, and thrice recrystallized from benzene to yield dark purple-brown flakes, m.p. 169–171°, of phenanthrenequinhydrone (VI),<sup>26</sup> lit. m.p. 167°<sup>7b</sup>; 165–169°.<sup>38</sup>

*Anal.* Calcd. for  $C_{23}H_{19}O_4$ : C, 80.37; H, 4.34; Mol. wt., 418. Found: C, 80.52; H, 4.59; Mol. wt., 203 (Rast camphor).<sup>39</sup>

Unreacted I and negligible amounts of *trans*-II diol were recovered from the ether layer. It is of experimental value to note the color changes of the ethereal solution of I with different reductants. With lithium aluminum hydride and sodium borohydride, the solution turned from yellow to colorless, while with sodium trimethoxyborohydride, the color change was from yellow to bluish green.

*9-Phenanthrol (III)*. Conc. sulfuric acid (0.05 ml.) was added to a hot (100–110°) solution of *cis*- or *trans*-II diol, (0.500 g., 2.47 mmoles) in 5 ml. glacial acetic acid. The color of the solution changed from yellow to pink and gradually to orange. After about 10 min. heating the solution was rapidly cooled to room temperature by the addition of small pieces of ice during which time the crude III simultaneously precipitated. The white solid was filtered off and air dried to yield approximately 0.5 g. of crude III. The crude material turned pink immediately after separation from the acetic-sulfuric acid solution and darkened further on air drying on the filter paper. One recrystallization from methanol gave 0.450 g. (2.32 mmoles, 94% yield) from the *cis*-II diol and 0.460 g. (2.37 mmoles, 96% yield) from *trans*-II diol of cream colored III, m.p. 149–150°, lit. m.p. 149–152.1°.<sup>17</sup> The color of the methanolic solution remained yellow in air and III in methanol was far less susceptible to air oxidation than in the original acetic-sulfuric acid solution in which the rearrangement was carried out. III can be stored under nitrogen at 0° for at least several months before it darkens. A spectral sample of III, m.p. 156–157°, was prepared by vacuum sublimation of the recrystallized product at 135–140° and 1–3 mm.

*Anal.* Calcd. for  $C_{14}H_{10}O$ : C, 86.57; H, 5.19. Found: C, 86.55; H, 5.21.

*Molecular compound between I and III (VII)*. Equimolar amounts of I and III were dissolved in excess, warm anhydrous benzene. The cooled solution was permitted to evaporate slowly to dryness in air. The brown-to-red colored residue (m.p. range, 120–130°) was twice recrystallized from

(38) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).

(39) This is confirmation of the molecular compound nature of VI. The Rast camphor f.p. was 163°. At this temperature, VI must thermally dissociate into its component parts I (mol. wt., 208) and phenanthrenehydroquinone (mol. wt., 210). Each component will depress the f.p. independently of the other, and the f.p. depression is additive. However, since the f.p. depression is proportional to the molecular weight, the experimentally determined molecular weight (203) should be an average of the molecular weights of both components (209).

benzene to yield the red molecular compound VII, m.p. 156–157°, lit. m.p.: 156–157°<sup>30,31a</sup>, 158°.<sup>8</sup>

*Anal.* Calcd. for C<sub>28</sub>H<sub>16</sub>O<sub>2</sub>: C, 83.56; H, 4.51; Mol. wt., 402. Found: C, 83.78; H, 4.71; Mol. wt., 202 (Rast camphor).<sup>30,40</sup>

A mixed m.p. of VI and VII was depressed to 130–145°. A benzene solution of VII was passed over aluminum oxide (Woelm, acid, activity grade 1). III fluoresces under ultraviolet light and the slow separation of VII into its com-

(40) Rast camphor, f.p., 159°; Mol. wts. of I and II are 194 and 208, respectively; average, 201.

ponents can be followed as III is eluted with large volumes of benzene. I remains adsorbed on the column.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

## Oxidation of Phenols by Periodate<sup>1</sup>

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Polyhydric phenols and their monomethyl ethers have been oxidized by periodic acid. The extent of the reaction is determined by the orientation of the hydroxyl groups in the ring. Those with vicinal hydroxyls consume three moles of periodate very quickly and a fourth mole more slowly. The extent and rate of oxidation is very nearly the same for all compounds studied. The phenols with meta oriented hydroxyls react more slowly; the extent of the reaction depends upon the number of hydroxyl groups in the molecule. Hydroquinone quickly consumes one mole of oxidant; methylation of one of the hydroxyl groups increases the extent of the reaction.

While there are many reports in the literature concerning the use of periodic acid and its salts as reagents for degrading 1,2-glycols and related substances, very little work has been done on the action of these oxidants on phenols. In 1935, Clutterbuck and Reuter<sup>2</sup> reported the successful oxidation of a 1,2-diketone containing the resorcinol structure but restricted their attention to changes in the aliphatic portion of the molecule. In 1946, Pennington and Ritter<sup>3</sup> published the preliminary results of an investigation of the action of periodic acid on certain phenols of interest in lignin research as well as on lignin sulfonic acids. They reported that the appearance of yellow to red colorations accompanied the oxidation of all phenols studied except resorcinol and phloroglucinol. Windrath<sup>4</sup> has utilized such colorations in the development of a color and precipitation test for polyhydric phenols.

Quite recently, three different investigators have attacked this problem in much greater detail. Adler<sup>5</sup> and his coworkers have carefully studied the action of sodium periodate on guaiacol and many compounds representing lignin models. Initial studies on simple molecules showed that compounds

containing the guaiacyl structure liberated about 0.9 mole of methanol in the oxidation, and this was shown to be very general for this type of structure if oxidation took place. In addition, *cis-cis*-muconic acid was identified among the oxidation products of catechol itself. They have not, as yet, reported any findings on either oxidation with periodic acid or oxidations of resorcinol and hydroquinone structures. Stumpf and Rumpf<sup>6</sup> have also examined the action of sodium periodate on guaiacyl-containing structures as well as on catechol and resorcinol. They report that all three dihydric phenols consume periodate quickly. Ishikawa and Nakajima<sup>7</sup> have studied the action of periodic acid on lignin; their studies have included some work on phenols.

Another type of periodate oxidation involves the oxidation of an active hydrogen on a carbon between two carbonyl groups; the resulting substance can then be cleaved as in a normal periodate oxidation. There are numerous examples of this.<sup>8–10</sup> Recently, Wolfrom and Bobbitt<sup>11</sup> have shown that 1,3-cyclopentanedione and 1,3-cyclohexanedione

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