extracts were washed twice with 70-ml portions of saturated Na_2CO_3 (aqueous) and dried ($MgSO_4$), and the solvent was removed, leaving a colorless oil, bp 58–59° (0.1 mm) [lit.[14] bp 108° (2.5 mm)] which gave one spot on a thin layer chromatogram, and whose ir and NMR spectra were as expected.

General Procedure for Triphenylphosphine Dibromide Cleavage of Lactones. To 52.4 g (0.2 mol) of triphenylphosphine in 200 ml of dry, freshly distilled acetonitrile under N_2 was added dropwise 32 g (0.2 mol) of bromine. The mixture was stirred at 0° throughout the addition, and the stirring was continued for 30 min thereafter. The lactone (22.8 g, 0.2 mol) in acetonitrile was then added dropwise, and the mixture was stirred under reflux for 10 hr, during which time it changed color to dark brown. After cooling, 20 ml of anhydrous methanol was added and the stirring was continued for a further 30 min. Removal of the solvent left a dark, viscous residue, which was dissolved in ether–benzene. This solution was washed several times with water and then dried ($MgSO_4$). The solvents were removed, and the dark residue thus produced was passed through a 14 × 2 in. dry alumina column, benzene being used as eluent. Examination of the column under uv light allowed identification of the fluorescent $Ph_3P{=}O$ band. The faster moving bromomethyl ester band appeared lower down, and methylene chloride extraction of the bottom section of the column gave a relatively pure sample of the expected ester, which was then distilled. A thin layer chromatogram showed one spot. Anal. Calcd for $Br(CH_2)_5COOCH_3$: C, 40.19; H, 6.22. Found: C, 39.91; H, 6.02. Ir 1730 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ 1.8 [m, 6, $-(CH_2-)_3$], 2.3 (t, 2, $-CH_2COOCH_3$), 3.4 (t, 2, $-CH_2Br$), 3.7 (s, 3, ester CH_3). This is consistent with literature reports [Sadtler NMR spectrum no. 4566M and ir spectrum no. 32825 for $Br(CH_2)_4COOEt$].

Registry No.—Triphenylphosphine dibromide, 1034-39-5.

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Reaction of Phenanthrenequinone with Ammonium Acetate

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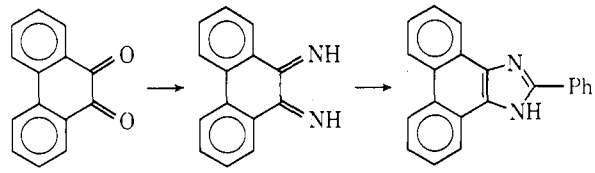
One of the synthetic methods available for the preparation of 2-aryl-1*H*-phenanthro[9,10-*d*]imidazoles is the condensation of phenanthrenequinones with an aromatic aldehyde in the presence of excess ammonium acetate in glacial acetic acid. This reaction has been suggested to proceed via diimine **1**, which condenses with the aldehyde forming a labile adduct that yields imidazole **2** after a facile proton shift and ring closure. From the condensation of phenanthrenequinone and ammonium acetate, Day et al.[2,3] isolated a base-soluble compound which was considered to be the intermediate **1**; it was indicated that this product was converted to **2** by reaction with benzaldehyde in base.

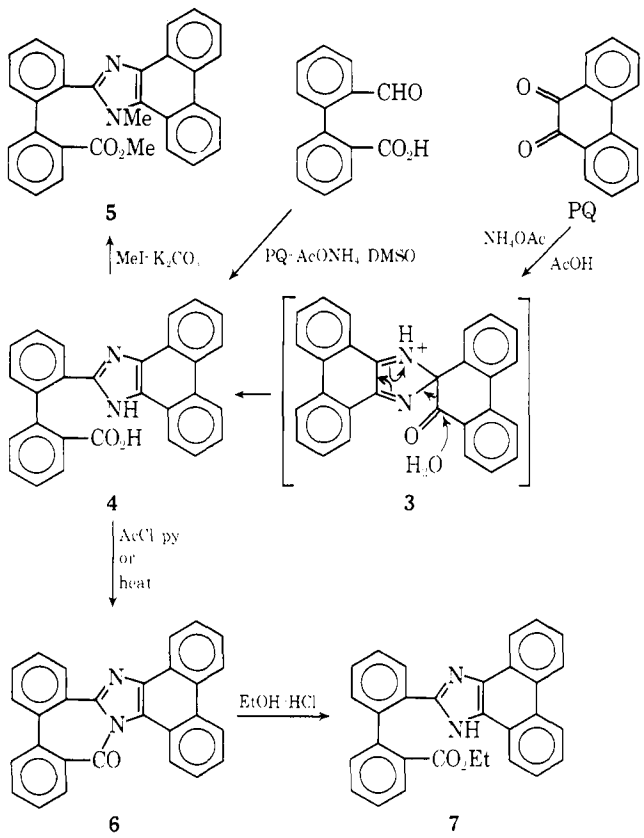


1 **2**

In a reexamination of this reaction, we found that condensation of the quinone, ammonium acetate, and benzaldehyde indeed leads to the imidazole **2**. We also obtained a crystalline product, apparently the same as that described by Day et al., from the reaction of the quinone with ammonium acetate. This substance, however, did not furnish **2** on treatment with benzaldehyde.

The quinone–ammonium acetate product was base soluble; acidification caused the compound to reprecipitate unchanged (under these conditions, hydrolysis of **1** would be expected). The uv, ir, NMR, and high-resolution mass spectra together with the chemical transformations shown in Scheme I leave little doubt that the compound is correctly formulated as 2′-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-2-biphenylcarboxylic acid (**4**). Acid **4** could be dimethylated with methyl iodide in alkaline DMSO solution or in refluxing acetone and potassium carbonate to yield the *N*-methyl methyl ester **5**. Vacuum sublimation of **4** or reaction with acetyl chloride gave the dehydration product **6**. On refluxing in ethanolic hydrochloric acid, **6** was converted to the ester **7**. Structure **4** was further substantiated by independent synthesis. Condensation reactions aimed at the formation of aromatic phenanthroimidazoles (cf. **2**) showed much improved yields when the quinone, aromatic aldehyde, and ammonium acetate were allowed to react in DMSO instead of the glacial acetic acid employed pre-

Scheme I



viously. No reaction between the quinone and ammonium acetate was observed in this solvent, however; essentially quantitative conversion to 4 was observed when diphenaldehydic acid was added to the reaction mixture. We interpret this result not only as support for our proposed structure **4**, but also as an indication for an acid-catalyzed mechanism of formation.

It appears likely that spiro intermediate **3**, which is first formed, undergoes an acid-catalyzed stereoelectronically favored realignment involving the cleavage of the C_9–C_{10} bond and leading to the formation of **4**.

Experimental Section

All melting points were uncorrected. Unless otherwise stated, NMR, uv, and ir spectra were obtained in DMSO-d_6, absolute ethanol solutions, and Nujol mulls, respectively. Molecular formulae were arrived at by computer analysis of the high-resolution mass spectra. NMR positions are reported in τ units relative to Me_4Si standard.

2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazole (2). Phenanthrenequinone (4.0 g, 0.02 mol), benzaldehyde (2.0 g, 0.02 mol), and ammonium acetate (15.0 g, 0.2 mol) were mixed with thorough stirring in DMSO (50 ml). The mixture was heated to 95° with continued stirring for 0.5 hr. The solution was cooled and diluted with water (250 ml), and the precipitate was filtered. Recrystallization of the solid from 2-butanone yielded 5.0 g of product, mp 318–320°; picrate mp 292–294° (lit.[2] mp 314, 289–290°, respectively); uv λ_{max} 362 nm (ϵ 12,500), 348 (13,500), 326 (23,000), 312 (22,000), 260 (56,000).

2′-(1*H*-Phenanthro[9,10-*d*]imidazol-2-yl)-2-biphenylcarboxylic Acid (4). Phenanthrenequinone (10.0 g, 0.045 mol) and ammonium acetate (75 g, 1.0 mol) were refluxed in glacial acetic acid (150 ml) for 1 hr. The solution was cooled and the crystalline precipitate was filtered and dried. Purification was effected by crystallization once from acetic acid and twice from cellosolve, giving 8.0 g of crystalline material, mp 320–322° (lit.[2] mp 290–292°; the crystalline compound obtained from acetic acid had mp 286–285°). Purification of material from other runs was accomplished by dissolving the crude compound in alcoholic potassium hydroxide solutions.

Anal. Calcd for $C_{28}N_{18}N_2O_2 \cdot H_2O$: C, 77.75; H, 4.66; N, 6.47. Found: C, 77.95; H, 4.98; N, 6.47.

The molecular water of crystallization could not be liberated by drying at 140° for 2.5 days at 6 mmHg pressure: picrate mp 307–309°; ir 3300–2800 (COO–H–N), 1660–1570 cm^{-1} (COO^- and NH, NH_2^+); hydrochloride 1670 cm^{-1} (CO); NMR 3.80 (s, D_2O exchanged), 1.10 (s, D_2O exchanged), 1.10–3.18 ppm (complex m, 16 H); uv 358 nm (ϵ 5,500), 340 (5,500), 306 (17,500), 286 (18,000), 258 (61,000).

The compound was also prepared by the following method. Phenanthrenequinone (1.0 g, 0.005 mol), diphenaldehydic acid[5] (1.10 g, 0.005 mol), and ammonium acetate (10 g, 0.13 mol) were heated in DMSO (25 ml) for 1 hr at 100°. The solution was allowed to cool and diluted with water to a final volume of 100 ml. After acidification of the solution with dilute hydrochloric acid, the precipitated compound was purified as above.

10H-Dibenzo[*f,h*]phenanthro[9,10-*b*]imidazo[1,2-*a*]azepin-10-one (6). Compound 4 (2 g, 0.005 mol) was dissolved in pyridine (25 ml) and the solution was cooled in an ice bath. Acetyl chloride (1.5 ml) was added and the solution was allowed to warm to ambient temperature. The reaction was allowed to proceed with stirring for an additional 2 hr and was diluted with water to 60 ml. The solid precipitate was collected and crystallized from 2-butanone, yielding 1.5 g of compound: mp 260–261°; ir 1710 cm^{-1} (CO); NMR 1.10–3.16 ppm (complex m); uv 360 nm (ϵ 11,250), 345 (12,2), 300 (35,000); MS *m/e* 396 ($C_{28}H_{16}N_2O$), 367 ($C_{27}H_{15}N_2$), 183 ($C_{11}H_7N_2O$), 163 ($C_{13}H_7$).

Anal. Calcd for $C_{28}H_{16}N_2O$: C, 84.83; H, 4.07; N, 7.07. Found: C, 84.38; H, 4.23; N, 7.25.

Ethyl 2′-(1*H*-Phenanthro[9,10-*d*]imidazo-2-yl)-2-biphenylcarboxylate (7). Compound 6 (0.5 g) was refluxed in a solution of ethanol (40 ml) and concentrated hydrochloric acid (10 ml) for 3 hr. The solution was cooled, diluted with water to 100 ml; and neutralized with Na_2CO_3. The product (0.25 g) was crystallized from ethanol: mp 185°; ir 1690 cm^{-1} (CO); NMR 1.17–3.0 (complex m, 16 H), 5.80 (q, J = 7 Hz, 2 H), 8.99 ppm (t, J = 7 Hz, 3 H); MS *m/e* 442 ($C_{30}H_{22}N_2O_2$), 396 (P – C_2H_5OH), 368 (P – $CO_2C_2H_5$), 184 ($C_{11}H_8N_2O$), 183 ($C_{11}H_7N_2O$); uv 358 nm (ϵ 6,000), 340 (7,000), 300 (17,000), 258 (56,700).

Methyl 2′-(1-Methyl-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-2-biphenylcarboxylate (5). Compound 4 (1 g) was refluxed with methyl iodide (2 ml) and potassium carbonate (1 g) in 50 ml of acetone and 2.5 ml of water for 20 hr, diluted with water to twice the original volume, and extracted with chloroform (3 × 50 ml). The organic extract was dried, evaporated to almost dryness, and crystallized from 1-butanol: mp 190–192°; ir 1705 cm^{-1} (CO); NMR 0.74–3.34 (complex m, 16 H), 6.05 (s, 3 H), 6.28 ppm (s, 3 H); uv 354 nm (ϵ 4500), 338 (4500), 306 (13,500), 284 (18,500), 254 (63,000); MS *m/e* 442 ($C_{30}H_{22}N_2O_2$), 383 (P – CO_2CH_3), 368 (P – CH_3, CO_2CH_3), 183 ($C_{11}H_7N_2O$).

Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.43; H, 5.01; N, 6.33. Found: C, 80.98; H, 4.82; N, 6.41.

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Registry No.—**2**, 6931-31-3; **2** picrate, 54774-64-0; **4**, 54774-65-1; **4** picrate, 54774-66-2; **5**, 54774-67-3; **6**, 32005-25-7; **7**, 54774-68-4; ammonium acetate, 631-61-8; phenanthrenequinone 84-11-7.

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Acid-Catalyzed Epoxide Cleavage of 3,4-Epoxytricyclo[4.2.2.0^{2,5}]deca-7-ene[1]

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With a hope of providing a synthetic entry for new carbon-skeleton construction and further additional data for understanding the transannular reactions of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives **1** and **2** (1:1 adducts of cyclooctatetraene with maleic anhydride and methyl maleate) with electrophiles,[2-4] we have investigated the reactions of **1** and **2** with *m*-chloroperbenzoic acid and the acid-catalyzed cleavage of the resulting epoxide derivatives.[5]

Reaction of **1** with *m*-chloroperbenzoic acid gave a monoepoxide product **3**.[6] Similar reaction of **2** gave **4**[6] together with a trace amount of unknown compound **5**. The NMR spectrum of **5** exhibits signals at δ 1.93 (4 H, m), 2.68 (4 H, m), 3.02 (4 H, s), 3.18 (4 H, m), 3.60 (12 H, s), and 6.50 (4 H, t) suggesting the presence of two cyclohexene moieties, and also the syn or anti dimer of **4** (Chart I).

Treatment of the epoxide **4** with hydrogen chloride in methanol at 0° gave compound **6** in an almost quantitative yield. The yields of **6** under various acidic conditions are summarized in Table I.

Similar treatment of **3** with the acid under various conditions gave a complex mixture, which we were unsuccessful in further purifying.

The NMR spectrum of **6** exhibits a methine proton at δ 4.75 (dd) adjacent to a lactone moiety, a sharp singlet at δ 4.06 (1 H) adjacent to a hydroxyl group, and one methoxyl group at δ 3.68 (3 H, s), but lack of olefinic protons. The