water (2.0 g, 69%): mp >320°; nmr (TFA) δ 8.22 and 8.63 (AB quartet, 2, J = 9 Hz), 10.92 (s, 1), 10.97 (s, 1); mass spectrum m/e 186 (M^+).

Anal. Calcd for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.09. Found: C, 58.06; H, 3.44; N, 30.00.

9-Mercaptoimidazo[4,5-*f*]quinazoline. Phosphorus pentasulfide (2.4 g) was dissolved in pyridine (36 ml) with heating, 0.6 g (3 mmol) of imidazo[4,5-*f*]quinazolin-9-one was added, and the mixture was heated at reflux for 17 hr. The volume was reduced to 12 ml by removal of the solvent *in vacuo*, and the solution was poured into boiling water (500 ml). The yellow crystals that were deposited were recrystallized from aqueous dimethyl sulfoxide (0.5 g, 78%): mp >320°; nmr (TFA) δ 8.15 and 8.56 (AB quartet, 2, J = 9 Hz), 10.63 (s, 1), 10.91 (s, 1); mass spectrum m/e 202 (M^+).

Anal. Calcd for $C_9H_6N_4S$: C, 53.45; H, 2.99; N, 27.70; S, 15.85. Found: C, 53.69; H, 3.00; N, 27.47; S, 15.91.

9-Aminoimidazo[4,5-*f*]quinazoline (2). A. *Via* 9-Hydrazinoimidazo[4,5-*f*]quinazoline. A solution of 9-mercaptoimidazo[4,5-*f*]quinazoline (1 g, 5 mmol) in hydrazine hydrate (6 ml) and methyl cellosolve (4 ml) was heated at 100° for 2 hr. The reaction mixture was poured into ethanol (20 ml) and upon cooling, tan crystals of 9-hydrazinoimidazo[4,5-*f*]quinazoline were obtained (1 g, 100%): mp 225° dec; mass spectrum m/e 200 (M^+). The hydrazino derivative was dissolved in hot methyl cellosolve (300 ml), and the solution was refluxed for 2 hr with addition of 2-ml portions of Raney nickel suspension every 20 min. The catalyst was removed by filtration, and the volume was reduced to 40 ml. Upon cooling, tan crystals of **2** were obtained (0.336 g, 37%). Recrystallization from ethanol yielded an analytical sample: mp >320°; nmr [$(CD_3)_2SO$] δ 7.73 and 8.25 (AB quartet, 2, J = 9 Hz), 8.72 (s, 1), 8.82 (s, 1); $\lambda_{max}^{95\%\ EtOH}$ 238 nm (ε 19,000), 251 (17,300), 258 (18,000), 278 (sh), 312 (5900), 324 (9300), 335 (sh), 339 (8500); $\lambda_{max}^{0.1\ N\ HCl}$ (95% EtOH) 229 (11,000), 237 (10,800), 270 (20,500), 290 (sh), 324 (8600), 335 (sh); $\lambda_{max}^{0.1\ N\ NaOH}$ (95% EtOH) 269 (27,700), 296 (4900), 333 (7600), 346 (sh); mass spectrum m/e 185 (M^+).

Anal. Calcd for $C_9H_7N_5$: C, 58.37; H, 3.81; N, 37.82. Found: C, 58.20; H, 3.91; N, 37.53.

B. *From* 9-Mercaptoimidazo[4,5-*f*]quinazoline. A sealed tube containing the mercapto compound (0.5 g, 2.5 mmol) and ammonia-saturated butanol (20 ml) was heated at 220° for 24 hr. The crystals were filtered and dissolved in water (10 ml) by the addition of formic acid. Upon adjusting to pH 8 with ammonia, *prox*-benzoadenine was obtained as colorless crystals (0.38 g, 67%), identical with material synthesized in part A (ir, tlc).

pK_a Determinations. In 66% dimethylformamide (34% water) the following pK_a values were observed: *lin*-benzoadenine (**1**), 5.6, 11.7; *prox*-benzoadenine (**2**), 5.2, 11.4; *dist*-benzoadenine (**3**), 4.9, 12.25.

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Registry No.—**2,** 53449-43-7; **3,** 53449-44-8; **4,** 53449-15-3; **5,** 53449-45-9; **6,** 16064-14-5; **7,** 53449-46-0; **8,** 53449-47-1; **9,** 16064-11-2; **10,** 53449-48-2; imidazo[4,5-*h*]quinazolin-6-one, 53449-49-3; 6-mercaptoimidazo[4,5-*h*]quinazoline, 53449-50-6; 6-amino-5-nitro-4-quinazolone, 53449-51-7; imidazo[4,5-*f*]quinazolin-9-one, 53449-52-8; 9-mercaptoimidazo[4,5-*f*]quinazoline, 53449-53-9; 9-hydrazinoimidazo[4,5-*f*]quinazoline, 53500-17-7.

References and Notes

(1) N. J. Leonard, A. G. Morrice, and M. A. Sprecker, *J. Org. Chem.*, preceding paper.
(2) The prefix *lin* refers to the linear relationships of the three rings in compound **1**; *prox* for proximal and *dist* for distal refer to the spatial relationship of the amino group in compounds **2** and **3**, respectively, with respect to the imidazole ring. The term "benzo" presents no ambiguity for only when the ring is central does it contain no nitrogens and is accordingly "benzo."
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(9) For uv spectra not recorded, consult the Ph.D. dissertation of A. G. Morrice, University of Illinois, 1974.

Cyclization of 1-Acetylanthraquinone[1]

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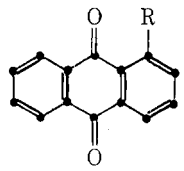
1-Acetylanthraquinone (**1b**) cyclizes under alkaline conditions to give 1-methoxy-2,6-aceanthrylenedione (**2b**). The mechanism of the reaction is discussed.

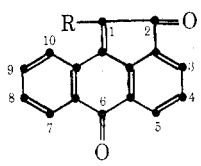
Anthraquinone (**1a**) is, of course, the parent substance of an extensive family of polycyclic quinones,[2] but one of the simplest possible members of the family, 2,6-aceanthrylenedione (**2a**), has never been prepared. This is simply a cyclic vinylog of anthraquinone and, as such, might be capable of reversible reduction to the dihydro or "vat" form (**3**), corresponding to anthrahydroquinone (**4**).

We have attempted the synthesis of **2a** by cyclodehydration of 1-acetylanthraquinone (**1b**), but this reaction does not succeed under a variety of acidic and basic conditions that were tried. The cyanoacetyl derivative (**1c**) might be expected to cyclize more easily, but we were unable to prepare this compound in working quantities. Bromination of **1b** to **1d** proceeded smoothly, but replacement of Br by CN did not.

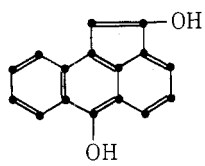
We then found that **1b** is readily cyclized in dimethyl sulfoxide containing "Triton B." The product is not, indeed, **2a,** but (as shown by analysis and molecular weight determination) a methoxy derivative of it, and since oxidation of this product gives a mixture of 1-anthraquinonecarboxylic acid (**1e**) and the glyoxylic ester (**1f**), it is evidently the 1-methoxy derivative (**2b**). Two other structures (**5b** and **6b**) can be written for a methoxyaceanthrylenedione capable of oxidation to **1e,** but neither system is a plausible cyclization product of **1b,** and neither would be capable of oxidation to **1f.** In addition, we have synthesized isomer **5b**



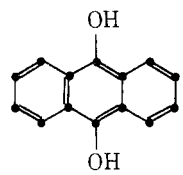
1a, R = H
b, R = $COCH_3$
c, R = $COCH_2CN$
d, R = $COCH_2Br$
e, R = COOH
f, R = $COCOOCH_3$
g, R = $COCHBr_2$



2a, R = H
b, R = CH_3O
c, R = OH



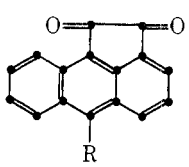
3



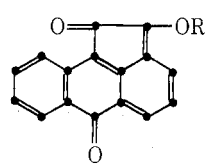
4

and found it to be different from **2b.** The synthesis is based upon our finding that 1,2-aceanthrylenedione **5a**[3] brominates cleanly in the 6-position to give **5c** (as shown by oxidation to **1e**), which readily gives **5b** by methanolysis. (Piperidine gives **5d.**)

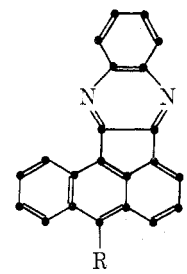
The 1,2-dione structures of **5a–d** are confirmed by their rapid condensation with *o*-phenylenediamine, eliminating two molecules of water to give quinoxalines **7a–d,** respectively; these are convenient derivatives for characterization purposes. The 2,6-dione (**2b**) does not react in this way.



5a, R = H
b, R = CH_3O
c, R = Br
d, R = $(CH_2)_5N$



6a, R = H
b, R = CH_3



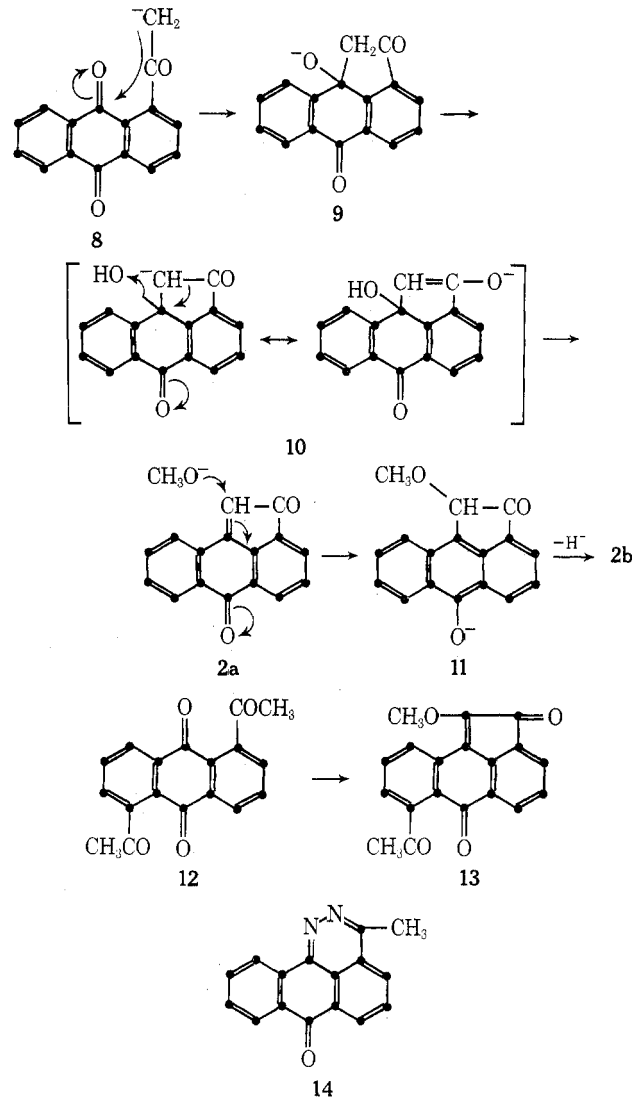
7a, R = H
b, R = CH_3O
c, R = Br
d, R = $(CH_2)_5N$

In our view, the most plausible explanation for the formation of **2b** from **1b** is that the expected product (**2a**) does form but is not stable under the reaction conditions; instead it undergoes nucleophilic methoxylation. The first step of the reaction is evidently loss of a proton from **1b** to form the anion (**8**), followed by cyclization to anion **9.** Proton transfer then gives the resonance stabilized **10,** which can eliminate hydroxyl to form the fully conjugated **2a.** Methoxide attack at the 1-position then gives **11,** converted to **2b** by hydride elimination under the influence of atmospheric oxygen.

Under similar conditions, 1,5-diacetylanthraquinone (**12**) cyclizes once, giving **13.**

Liebermann and Kardos reported in 1914[4] that boiling KOH attacked **5a** to give a hydroxyl derivative, formulated as **2c** or its tautomer (**6a**), which formed a dark red methyl ether of mp 233°. These properties correspond to those of **2b,** but an attempt to repeat these experiments gave equivocal results, unfortunately, so that it has not been possible to make a direct comparison.

1-Acetylanthraquinone (**1b**), which reacts with hydrazine to give the dibenzocinnolone (**14**), behaves normally on alkaline hydrosulfite reduction, *i.e.,* it gives a deep red solu-



8 9 10 2a 11 12 13 14

tion of the dihydro form, readily reoxidized to **1b** by air. Reduction of **2b** under these conditions is not reversible, but causes degradation of the system.

Experimental Section

Melting points are corrected.

1-(Bromoacetyl)anthraquinone (1d). A solution of 11.0 g (0.043 mol) of 1-acetylanthraquinone (**1b**)[5] in 150 ml of acetic acid was stirred on the steam bath during the addition over a 1-hr period of a solution of 7.8 g (2.5 ml, 0.049 mol) of bromine in 10 ml acetic acid. The reaction mixture was heated 15 min longer and then cooled and filtered to yield 11.1–12.6 g (79–89%) of buff colored solid, mp 188° dec. Additional product was obtainable from the filtrate by dilution. Crystallization from toluene (26 ml/g) gave an 84% recovery of white needles, dec 192°.

Anal. Calcd for $C_{16}H_9O_3Br$: C, 58.4; H, 2.7; Br, 24.3. Found: C, 58.6; H, 2.7: Br, 24.1.

1-(Dibromoacetyl)anthraquinone (1g), prepared in the same way but with two equivalents of bromine, crystallized as a white solid from toluene, dec 189–191°, depressed on admixture with **1d.**

Anal. Calcd for $C_{16}H_8O_3Br_2$: C, 47.1; H, 2.0. Found: C, 46.9; H, 2.0.

1-Methoxy-2,6-aceanthrylenedione (2b). To a solution of 5.0 g (0.020 mol) of 1-acetylanthraquinone (**1b**) in 200 ml of dimethyl sulfoxide was added 23 ml of "Triton B" solution (35% benzyltrimethylammonium hydroxide in methanol), causing the color to change from pale yellow-green to purple. For 2 hr, a gentle stream of air was passed through the solution, which turned greenish. The product separated upon the addition of 35 ml of acetic acid followed by 50 ml of methanol. Chilling, filtration, and washing with methanol gave 2.1–2.6 g (40–50%) of brick red solid, mp 233–6° dec. (The attempt to isolate further material from the mother li-

quor was unsuccessful.) Crystallization from pyridine or acetic acid did not affect the mp.

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.9; H, 3.8; mol wt, 262. Found: C, 77.9; H, 3.8; mol wt (mass spectrum), 262.

Under similar conditions 1,5-diacetylanthraquinone (**12**)[5] gave 7-acetyl-1-methoxy-2,6-aceanthrylenedione (**13**), crystallizing from acetic acid as a brick red solid, dec 246–253°.

Anal. Calcd for $C_{19}H_{12}O_4$: C, 75.0; H, 3.9; mol wt, 304. Found: C, 74.9; H, 4.0; mol wt (mass spectrum), 304.

Oxidative Degradation of 2b. To a solution of 1.0 g of **2b** in 20 ml of hot acetic acid was added a solution of 1.0 g of CrO_3 in about 5 ml of 50% acetic acid. The resulting mixture was heated 10–15 min on the steam bath, cooled, diluted, and filtered to give a mixture of solids that was digested with sodium bicarbonate solution. The soluble fraction consisted of 0.16 g of pale yellow 1-anthraquinonecarboxylic acid (**1e**), which crystallized from 2-nitrobutane as an off-white solid of mp 289–293° dec, unchanged on admixture with an authentic specimen. Identification was confirmed by ir comparison. The insoluble fraction was insoluble in NaOH as well and consisted of 0.53 g of very pale yellow methyl 1-anthraquinoneglyoxylate (**1f**), mp 234–240°. Crystallization from acetic acid raised the mp to 238–243°. It showed three distinct carbonyl bands at 1680, 1712, and 1755 cm^{-1}.

Anal. Calcd from $C_{17}H_{10}O_5$: C, 69.4; H, 3.4; O, 27.2; mol wt, 294. Found: C, 69.5; H, 3.4; O, 27.4; mol wt (mass spectrum), 294.

1,2-Aceanthrylenedione (**5a**) was prepared from oxalyl chloride and anthracene by the procedure of Liebermann and Zsuffa.[3] It condensed rapidly with *o*-phenylenediamine in refluxing pyridine to give the orange quinoxaline (**7a**), which could be crystallized from chlorobenzene or pyridine, mp 245–247°.

Anal. Calcd for $C_{22}H_{12}N_2$: C, 86.8; H, 4.0; N, 9.2. Found: C, 87.1; H, 3.7; N, 9.2.

6-Bromo-1,2-aceanthrylenedione (5c). A solution of 10.4 g (0.045 mol) of 1,2-aceanthrylenedione (**5a**) in 25 ml of nitrobenzene, heated in an oil bath to 140–145°, was stirred with an efficient stirrer while a solution of 2.50 ml (7.80 g, 0.049 mol) of bromine in 10 ml of nitrobenzene was added dropwise during a period of approximately 1.5 hr. The thick mixture was heated and stirred 15 min longer, cooled, and diluted with alcohol to facilitate the filtration, which gave, after washing with a little alcohol and drying, 11.0–11.9 g (80–85%) of tan product, dec *ca.* 252–256°. Crystallization from *o*-dichlorobenzene (1.1 ml/g) gave an 85% recovery, dec 264–267°. Yellow analytical specimens, dec *ca.* 260–264°, were obtained by crystallization from pyridine, acetic anhydride, or methoxyethanol.

Anal. Calcd for $C_{16}H_7O_2Br$: C, 61.8; H, 2.3; Br, 25.7. Found: C, 62.1; H, 2.2; Br, 25.4.

Oxidation with CrO_3 in refluxing acetic acid gave a good yield of 1-anthraquinonecarboxylic acid (**1e**), identified by melting point, mixture melting point, and ir comparison. *o*-Phenylenediamine condensed rapidly with **5c** in boiling pyridine to give a quantitative yield of the quinoxaline (**7c**), which crystallized from chlorobenzene or nitromethane as a bright yellow solid, mp 289–290°.

Anal. Calcd for $C_{22}H_{11}BrN_2$: C, 69.0; H, 2.9; Br, 20.9; N, 7.3. Found: C, 69.0; H, 3.0; Br, 20.6; N, 7.3.

6-Methoxy-1,2-aceanthrylenedione (5b). A solution of sodium methoxide was prepared from 1.0 g of 57% sodium hydride by washing with petroleum ether and dissolving in 50 ml of methanol. To this was added 1.00 g (3.2 mmol) of **5c**, followed by 15–20 min stirring at reflux, cooling, dilution, and filtration to give 0.70 g (83%) of orange product, dec from 190°. Crystallization from acetic acid or toluene raised the dec temperature to about 230°.

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.9; H, 3.8; mol wt, 262. Found: C, 77.8; H, 3.8; mol wt (mass spectrum), 262.

Condensation with *o*-phenylenediamine was effected by 15-min heating in pyridine solution on the steam bath, giving the orange quinoxaline (**7b**), mp 227–229° dec. Crystallization from acetic acid or toluene raised the melting point to 229–230° dec.

Anal. Calcd for $C_{23}H_{14}N_2O$: C, 82.7; H, 4.2; N, 8.4. Found: C, 82.9; H, 4.1; N, 8.3.

6-Piperidino-1,2-aceanthrylenedione (5d). A mixture of 1.5 g (4.8 mmol) of **5c** and 1.2 ml (1.0 g, 12 mmol) of piperidine in 50 ml of ethanol was stirred at reflux for 4 hr, chilled, and filtered, yielding 1.4 g (93%) of purple-brown product, mp 196–201° dec. Crystallization from acetic acid or isobutyl alcohol raised the melting point to 202–205°.

Anal. Calcd for $C_{21}H_{17}NO_2$: C, 80.0; H, 5.4; N, 4.5. Found: C, 79.8; H, 5.2; N, 4.2.

Quinoxaline (**7d**) was prepared from **5d** by refluxing for 0.5 hr with a slight excess of *o*-phenylenediamine in pyridine solution, followed by cooling, dilution, and filtration. The product was obtained in quantitative yield, mp 211–217°. Crystallization from methylcyclohexane containing a little toluene gave an orange solid, mp 217–220°.

Anal. Calcd for $C_{27}H_{21}N_3$: C, 83.7; H, 5.4; N, 10.9. Found: C, 83.4; H, 5.2; N, 11.1.

3-Methyldibenzo[*de,h*]cinnolone-7 (14) was prepared from **1b** and hydrazine hydrate by refluxing for 1 hr in ethanol and crystallized from methoxyethanol: mp 260–261°.

Anal. Calcd for $C_{16}H_{10}N_2O$: C, 78.0; H, 4.1; N, 11.4. Found: C, 78.4; H, 4.0; N, 11.5.

Acknowledgment. The authors are grateful to K. Valentin for nmr and mass spectra, and to J. Kobliska and his staff for microanalyses.

Registry No.—**1b,** 53336-60-0; **1d,** 53336-61-1; **1e,** 602-69-7; **1f,** 53336-62-2; **1g,** 53336-63-3; **2b,** 53336-64-4; **5a,** 6373-11-1; **5b,** 53336-65-5; **5c,** 53336-66-6; **5d,** 53336-67-7; **7a,** 203-22-5; **7b,** 53403-85-3; **7c,** 53336-68-8; **7d,** 53336-69-9; **12,** 53336-70-2; **13,** 53336-71-3; **14,** 53336-72-4; *o*-phenylenediamine, 95-54-5; piperidine, 110-89-4; hydrazine hydrate, 10217-52-4.

References and Notes

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