the definite possibility of 1,4-addition of phenoxide ion to the acrylic ester. Also, in the presence of diphenyl ether as a solvent instead of excess phenol, phenyl acrylate was isolated in 20% yield based on consumed phenol. This ester-interchange reaction tends to support the proposal that in the analogous reaction of aluminum phenoxide and acrylonitrile the nitrilo-group displaces phenoxide ion from the aluminum complex.

EXPERIMENTAL

Reaction of acetonitrile with aluminum phenoxide. Eighteen g. (0.67 mole) of aluminum turnings was added in small portions over a period of 3 hr. to 184 g. (2 moles) of freshly distilled phenol held at 172–185° under an atmosphere of nitrogen gas. The addition of aluminum metal was carried out conveniently in glass apparatus until a temperature of 185° was noted for the molten mass, at which time it was transferred to a 1-l. stainless steel bomb. The bomb was heated to 195° with the remaining aluminum until no more phenol was lost through the vent.

The bomb was cooled to room temperature and opened. Eighty-two g. (2 moles) of freshly distilled acetonitrile was added and the bomb-head replaced. Air was purged from the bomb by means of nitrogen after which the reaction mixture was heated to 185° with constant mechanical shaking for a period of 6 hr. A maximum pressure of 115 p.s.i. was noted. Heating and shaking were continued for an additional 2 hr. at 220° and 165 p.s.i., after which the bomb was cooled to room temperature and opened. The mixture, consisting of a watery liquid and a brittle crystalline solid, was poured over 1 kg. of cracked ice containing 150 ml. of concentrated hydrochloric acid (*d*, 1.2). (Two g. of unreacted aluminum was recovered at this point.)

The organic phase was separated and steam-distilled. The distillate was shaken with sodium chloride and the oils were recovered by extraction with three 50-ml. portions of toluene. The hydrocarbon solution was washed three times with 50-ml. portions of saturated sodium chloride, separated, and distilled through a 100-cm. modified Claisen column. One hundred and thirty g. of phenol (0.57 mole) was recovered at 89° and 24 mm. after which the residue was transferred to a Claisen flask of 10 ml. capacity. Three g. (0.04 mole) of colorless liquid was recovered at 95–99° at 18 mm. which was identified as *o*-hydroxyacetophenone (oxime, m.p. 114–116° uncorr., which is in agreement with the literature).[5]

The residual tar which was involatile in steam was taken up in ether and separated from the aqueous phase. Benzene was added and the solvents distilled until a thick oil was obtained. A small amount of hot 3:1 alcohol-benzene mixture was added and crystallization took place upon standing in an ice chest. Seven g. (0.05 mole) of *p*-hydroxyacetophenone, m.p. 104–106°, was obtained.[6]

Reaction of acrylonitrile with aluminum phenoxide. In a procedure similar to that described for acetonitrile and aluminum phenoxide, 9 g. (0.37 mole) of aluminum turnings was caused to react with 282 g. (3 moles) of phenol at 170–172° under nitrogen. Since an excess of phenol was present as a solvent it was unnecessary to transfer the mixture to the bomb until all the aluminum has been dissolved. Fifty-three g. (1 mole) of freshly distilled phenol was added and the mixture was held with continual shaking at 172–180° for 9 hr. From the dark red oil 177 g. (1.2 moles) of phenol was recovered and a viscous dark brown resin remained which was undistillable.

Examination of the infrared spectrum of a resin-potassium bromide-pellet showed practically complete disappearance of the nitrile bond at 2251 cm.$^{-1}$ and the appearance of strong aromatic ketone bands at 1578, 1641, 1223, and 1169 cm.$^{-1}$

Reaction of ethyl acrylate with aluminum phenoxide. In a procedure similar to that employed for the reaction of phenol and acrylonitrile 282 g. (3 moles) of phenol, 9.0 g. (0.37 mole) of aluminum turnings and 900 g. of ethyl acrylate gave a yellow oil from which ethyl acrylate and phenol were removed by distillation. The residue consisted of rubbery red crumbs. Extraction with toluene followed by vacuum stripping of this solvent gave 9 g. of a tan fusible residue, which was recrystallized from hot water to a melting point of 85–93°. Further recrystallization from benzene gave needles of β-phenoxyproprionic acid, m.p. 93–96°,[7] identified by conversion into the semicarbazone of 4-chromanone, m.p. 223–226°. Louden and Razden[8] report a melting point of 227° for this derivative.

In a second experiment, 18 g. (0.67 mole) aluminum turnings was caused to react with 184 g. (2 moles) of phenol in 75 ml. of diphenyl ether. Two hundred g. (2 moles) of ethyl acrylate was added to the salt and held at 175–182° for 11 hr. under pressures of 40 to 60 p.s.i. Decomposition of the reaction mixture in acid followed by isolation of distillable products as described above gave 52 g. (0.35 mole) of phenyl acrylate, b.p. range, 65° at 15 mm. to 71° at 14 mm. Redistillation of this fraction at ordinary pressures gave a product of b.p. 106–168° at 712 mm., sp. gr., 0.975 20°/4°. Infrared analysis showed strong bands at 1610, 1590, 1500, 1480, 1300, 1240, 1180, 1120, 1050, 690 cm.$^{-1}$ A ferric chloride test was negative; bromine was strongly absorbed.

In addition, 24 g. of phenol was recovered to complete recovery of the diphenyl ether. A gelatinous material, presumably polyethyl acrylate and its cross-linked phenolic derivatives, was noted.

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An Attempted Synthesis of Dipyrazolo[*def*, *qrs*]flavanthrene-8,16-dione

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Fusion of pyrazolanthrone (I) with alkali produces a dye known as "pyrazolanthrone yellow," for which, at one time, structure II was proposed.[1]

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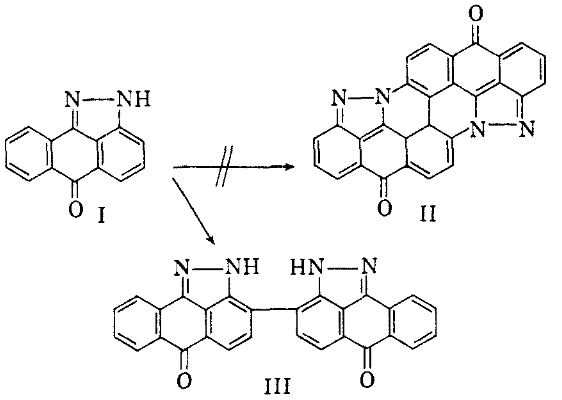
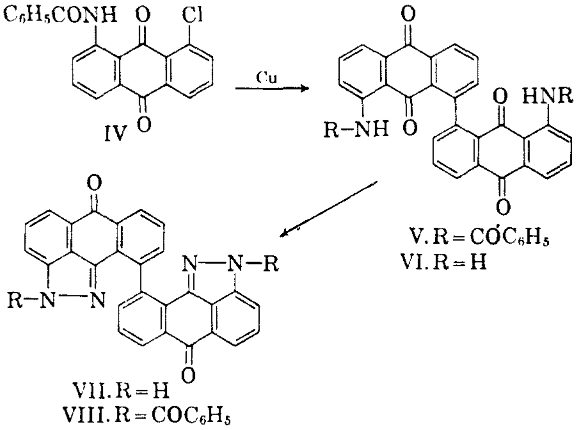
(1) F. Mayer and R. Heil, *Ber.*, **55**, 2155 (1922).

Although the dye is now recognized[2] to have structure III, no synthesis of the interesting compound dipyrazolo[*def*, *grs*]flavanthrene-8,16-dione (II) has been reported. Following is an account of an attempt to prepare II, and of its failure in the final step.



Treatment of 1 - benzamido - 8 - chloroanthraquinone (IV) with copper powder in a solvent resulted chiefly in dehalogenation, giving 1-benzamidoanthraquinone. However, when the volume of solvent was drastically reduced, a good yield of the bianthraquinonyl compound V was produced. Acid hydrolysis readily afforded the free amine (VI).



The diamine VI was tetrazotized, reduced and cyclized to produce VII in a manner analogous to the synthesis[3,4] of pyrazolanthrone from 1-aminoanthraquinone. Unfortunately, no way was found to convert either VII, or its dibenzoyl derivative (VIII) into the desired quinone II. Under acidic conditions (heating with aluminum chloride in pyridine or nitrobenzene or in an aluminum chloride–sodium chloride melt) VII was recovered unchanged. Heating VII with potassium hydroxide and methanol yielded a small amount of insoluble, alkali-sensitive pale orange dye (bright green vat solution), probably produced by bimolecular coupling in the 3,3′-positions analogous to the formation of III from I. Introduction of manganese dioxide into a caustic melt with VII afforded a product readily soluble in dilute base, which in behavior and color reactions resembles the *o*-carboxyphenylindazoles obtained[5] under similar conditions from I and III. These two undesired products were not investigated further.

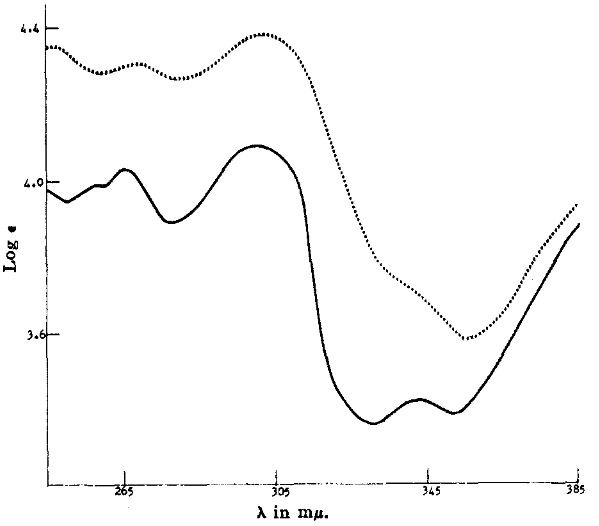


Fig. 1. Ultraviolet spectra in dimethylformamide solution of pyrazolanthrone (——) and of compound VII (- - -).

One obstacle to the facile conversion of VII into II may be noted from an examination of the ultraviolet spectrum of VII (Fig. 1). From the virtual superimposability of the curves of VII and I (with doubling of the extinction coefficient) it appears that the plane of the upper half of the molecule of VII is approximately orthogonal to that of the lower half. This barrier to coplanarity plus the need to lose four hydrogen atoms (two as hydride ions), doubtless indicate a high activation energy for the transformation of VII into II, and permit one of the possible side reactions to occur preferentially.

A curious difference in the reactivity of 1-chloro-8-nitroanthraquinone was encountered in treating it with hydrazine and with *p*-toluenesulfonamide. Reaction with hydrazine occurred with displacement of the nitro group, giving the known[3] 10-chloropyrazolanthrone, while 1-nitro-8-(*p*-toluenesulfonamido)-anthraquinone resulted from reaction with *p*-toluenesulfonamide.

EXPERIMENTAL

8,8′-Dibenzamido-1,1′-bianthraquinonyl (V). A mixture of 16.0 g. of 1-benzamido-8-chloroanthraquinone (m.p. 226.5–

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[2] A. Lüttringhaus, P. Nawiasky, and A. Krause, Ger. Patent 457,182; *Frdl.*, 16, 1371 (1931). U. S. Patent 1,817,-995.

[3] R. Möhlau, *Ber.*, 45, 2233 (1912).

[4] *B.I.O.S. Final Report No. 987*, p. 128.

[5] W. Bradley and K. W. Geddes, *J. Chem. Soc.*, 1636 (1952).

228.5°), 10 ml. of *o*-dichlorobenzene, and 16.0 g. of copper powder was stirred and heated under reflux to 150–160° and held there for 4 hr. The cooled, dark brown reaction product was transferred to a Soxhlet thimble and extracted with 700 ml. of chlorobenzene for 16 hr. Upon cooling, the chlorobenzene solution deposited 10.10 g. of V (70% yield), m.p. 345–349°. Two recrystallizations from chlorobenzene gave bright yellow plates, m.p. 347–349°.

Anal. Calcd. for $C_{42}H_{24}N_2O_6$: C, 77.45; H, 3.71; N, 4.30; O, 14.72. Found: C, 76.70; H, 3.61; N, 4.25; O, 14.60.

8,8'-Diamino-1,1'-bianthraquinonyl (VI) was obtained from the dibenzamido compound (V) by warming it with concentrated sulfuric acid at 100°. The crude product was crystallized twice from chlorobenzene, giving an 84% yield of shiny red plates, m.p. >350°.

Anal. Calcd. for $C_{28}H_{16}N_2O_4$: C, 75.66; H, 3.63; N, 6.30; O, 14.40. Found: C, 74.80; H, 3.60; N, 6.42; O, 13.90.

10,10'-Dipyrazolanthronyl (VII). A solution of 4.66 g. of the diamine (VI) in 50 ml. of concentrated sulfuric acid was converted into the tetrazo derivative by treatment with 1.70 g. of sodium nitrite. The addition of approximately 40 g. of ice caused the diazonium sulfate to precipitate, and this was filtered off and added to a solution of 11.6 g. of sodium bisulfite, 12 g. of ice, 14 ml. of 28% sodium hydroxide, and 14 ml. of water. The resulting suspension was heated to 80° and held there 45 min., during which time a further 18 ml. of 28% sodium hydroxide and 5.0 g. of sodium bisulfite were added. The initial yellow color of the solution changed to red. Then 20 g. of sodium chloride was added and the solution was cooled. The red precipitate was filtered, pressed dry, and added to 75 ml. of 99.5% sulfuric acid at 40–50°. The temperature of the solution was then raised slowly to 90–98°, where it was held for 1.5 hr. Pouring the solution onto ice gave a yellow precipitate, which after filtration, washing, and drying weighed 3.90 g. (85% yield). A sample recrystallized twice from nitrobenzene melted above 350° and had λ_{max} 268 and 300 mμ (ϵ 20,500 and 24,200).

Anal. Calcd. for $C_{28}H_{14}N_4O_2$: C, 76.70; H, 3.22; N, 12.78. Found: C, 76.20; H, 3.50; N, 12.30.

The *dibenzoyl derivative* (VIII), obtained from VII by treatment with benzoyl chloride in pyridine, crystallized from chlorobenzene in pale yellow plates, m.p. >350°.

Anal. Calcd. for $C_{42}H_{26}N_4O_4 \cdot {}^1/_4C_6H_5Cl$: C, 77.00; H, 4.02; Cl, 1.31; N, 8.28; O, 9.42. Found: C, 77.30; H, 3.49; Cl, 1.62; N, 8.42; O, 9.50.

10-Chloropyrazolanthrone. The reaction of 1-chloro-8-nitroanthraquinone (m.p. 263°) with hydrazine hydrate in pyridine yielded a purple solid which was triturated with 10% sodium hydroxide solution and filtered. Acidification of the basic filtrate gave a light yellow solid, which was crystallized from *o*-dichlorobenzene, giving a 71% yield of the known 10-chloropyrazolanthrone, m.p. 346–347° (lit. 346–347°[5]; >360°[3]), identified by comparison of melting point and infrared spectrum with those of an authentic sample.

1-Amino-8-nitroanthraquinone. 1-Chloro-8-nitroanthraquinone was treated with *p*-toluenesulfonamide, sodium acetate, and cuprous chloride in boiling amyl alcohol, giving a 95% yield of crude 1-toluenesulfonamido-8-nitroanthraquinone. A sample after crystallization from acetic acid melted at 255.0–256.5°. This tosyl derivative was hydrolyzed in 81% yield to the amine by warming it in concentrated sulfuric acid for a few minutes, and pouring the resulting solution into water. Crystallization from *o*-dichlorobenzene gave red needles, m.p. 298–299° (dec.) (lit. 294°[6] and 283–284°[7]).

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N-Substituted Imides. II. Potassium Naphthalimide as a Reagent for the Identification of Alkyl Halides[1]

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Many reagents have been suggested for the identification of alkyl halides.[4] Recent studies have included *N*-substituted phthalimides[5] and saccharins.[6] Continuing work in this laboratory concerned with *N*-substituted imides possessing physiological activity suggested that potassium naphthalimide might be a satisfactory reagent for this purpose.

The derivatives were prepared by condensing potassium naphthalimide and the appropriate alkyl halide using dimethylformamide as solvent. The reaction went smoothly for primary and secondary chlorides, bromides, and iodides but yields were low with the secondary halides. Tertiary halides did not react.

The crude products were recrystallized from various alcohols or alcohol-water mixtures. In each case a white crystalline solid with a sharp melting point was obtained. Attempts to determine saponification equivalents were unsuccessful as the imide linkage resisted all attempts at hydrolysis.

Although the melting points of the products (Table I) were close together in the higher members of the series, all were solids and could be used as derivatives. Only *N*-methyl- and *N*-ethyl naphthalimide have been previously reported.[7]

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