Tetrahedron, 1967. Vol. 23, pp. 2911 to 2926. Pergamon Press Ltd. Printed in Northern Ireland

STRUCTURAL ELUCIDATION OF THE PENTACYCLIC CINNOLINE OBTAINED BY THE REACTION OF 1,4-NAPHTHOQUINONE WITH HYDRAZINE

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(*Received in USA* 18 *July* 1966; *accepted for publication* 15 *November* 1966)

Abstract—The highly insoluble, black compound obtained by treatment of 1,4-naphthoquinone with hydrazine has been shown to be identical with the material which Pummerer had obtained in the reaction of dinaphthoquinone (Ia) with hydrazine and which he had tentatively formulated as Ib. The structure has now been shown to be the pentacyclic cinnoline IIb on the basis of elemental and spectral analyses, derivative formation and its behavior on reduction and oxidative degradation.

INTRODUCTION

ALTHOUGH many reactions of quinones with ketone reagents have been reported,[2] remarkably few reactions of quinones with hydrazine are recorded in the literature. *p*-Benzoquinone gives a resinous product with hydrazine hydrochloride,[3] while 2,2′-dinaphthoquinone (Ia) is reported to form a hydrazone with hydrazine hydrate[4] (see below). Curiously, the reaction of hydrazine with 1,4-naphthoquinone has not been reported. The probable reason for this is the unusual nature of the product, the structure determination and properties of which are the subject of this paper.

STRUCTURE PROOF

When an ethanolic solution of naphthoquinone is treated with hydrazine hydrate, a large amount of dark solid deposits during the course of several days. Crystallization of the solid from pyridine gives a copper-colored material, which turns black on trituration with ethanol or acetone or on heating above 100°. The black material, which will be referred to as the "hydrazone", upon crystallization from pyridine again gives the copper-colored material. The empirical formula of the black compound, $C_{20}H_{10}N_2O_3$, indicates at once that two molecules of naphthoquinone per molecule of hydrazine are incorporated into the "hydrazone". Furthermore, its physical properties are just those described for the hydrazone of 2,2′-dinaphthoquinone (Ia) to which Pummerer *et al.*[4] have tentatively assigned structure Ib.[5] It should be noted that this structure requires two hydrogen atoms more than our analysis indicates to be present.

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[1] National Aeronautics and Space Administration Postdoctoral Fellow, 1964–1965.

[2] For general surveys see: *Chemistry of Carbon Compounds* (Edited by E. H. Rodd) Vol. IIIB; Chaps 11, 20 and 21. Elsevier, New York (1956); and L. F. Fieser and M. Fieser, *Advanced Organic Chemistry* Chap. 26. Reinhold, New York (1961).

[3] N. Schapiro, *Ber. Dtsch. Chem. Ges.* **62**, 2135 (1929).

[4] R. Pummerer, A. Pfaff, G. Riegelbauer and E. Rosenhauer, *Ber. Dtsch. Chem. Ges.* **72**, 1623 (1939).

[5] The structure resulting from condensation at the other possible carbonyl group was deemed unlikely since it would be expected to lose a molecule of water to form an azine.

The reported[4] analytical data also seem to indicate less hydrogen. Pummerer's synthesis was repeated and the identity of this product and the "hydrazone" established by IR spectral comparison. Acetylation under several conditions gives a greenish golden-yellow mono-acetyl derivative, $C_{22}H_{12}N_2O_4$, from which the "hydrazone" can be regenerated by hydrolysis; treatment of the "hydrazone" with dimethyl sulfate and base gives a black monomethyl derivative, $C_{21}H_{12}N_2O_3$.

A number of structural features are indicated by the IR spectra of these compounds. A Nujol mull[6] of the pyridine-free "hydrazone" has medium to strong bands at 3·13, 5·96, 6·09, 6·16, 6·29, 6·40 and 6·56 μ. The first two bands are attributed to OH or NH and quinone absorption, respectively; the others are reminiscent of vinylogous amide absorption bands[7] superimposed on aromatic bands. The spectrum of the methylated "hydrazone" lacks the NH or OH absorption, and has bands at 5·97, 6·08, 6·20, 6·30, 6·49 and 6·59 μ, similar in position and complexity to those of the "hydrazone". The acetylated "hydrazone" shows phenolic acetate absorption at 5·69 and 8·28 μ, bands due to a quinone and possibly a double bond at 5·96 and 6·01 μ, and aromatic bands at 6·25 and 6·31 μ, the 6 μ region being much less complex than in the case of the "hydrazone".[8] The profound difference in the 6 μ region of the spectra of the derivatives indicates the possibility of tautomerism in the "hydrazone", perhaps of the pyridazone type where N-methylation, but O-acylation generally prevail.[9] The similarity of the IR spectra, as well as the colors, of the "hydrazone" and its Me derivative leads to the conclusion that no change other than replacement of hydrogen by Me occurs during the derivatization. This is confirmed by the great similarity of the UV spectra of the two compounds (Experimental). Since an alkoxy determination on the Me derivative gave only about 5% of the calculated value for a MeO group, the Me group must be attached to a nitrogen atom, and therefore a hydrogen atom must be attached to this nitrogen in the parent compound. X-ray crystallographic studies and density measurements on the Me derivative gave a mol. wt. of 341, in accord with a C-21 compound.

Several structures of the "hydrazone" which could accommodate these data may now be considered. The presence of the 2,2'-binaphthyl skeleton with oxygen atoms located at three of the original four positions of its progenitor is implied by its formation from Ia and since the compound contains only ten hydrogen atoms, of which at least one is attached to a nitrogen atom, it must contain five or more rings. The simplest structures which fit these requirements are IIb–VI. The spectra of the acetylated and the methylated "hydrazone" in Nujol or hexachlorobutadiene do not show even a broad band that can be attributed to NH or OH absorption. Therefore, structures V and VI, whose monosubstituted derivatives would contain one of these groups, are less likely than IIb–IV.

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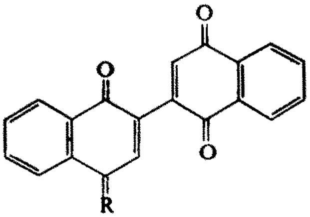
[6] Nearly all the compounds were much too insoluble in solvents suitable for spectral analysis. Unless otherwise stated, band positions refer to solid state spectra determined as Nujol mulls.

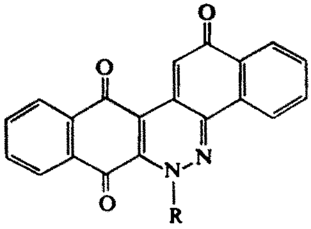
[7] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *J. Am. Chem. Soc.* **71**, 3337 (1949); E. S. Hand, Ph.D. Dissertation, Radcliffe College, 1961.

[8] General references for IR spectral data: L. J. Bellamy, *The Infrared Spectra of Complex Molecules.* Wiley, New York (1954); and R. N. Jones and C. Sandorfy, *The Application of Infrared and Raman Spectrometry to the Elucidation of Molecular Structure* in *Technique of Organic Chemistry* (Edited by A. Weissberger) Vol. IX. Interscience, New York (1956).

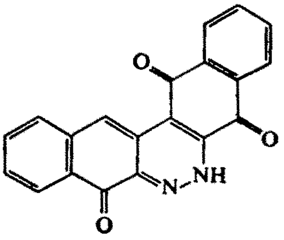
[9] See for example, J. R. Keneford, J. S. Morley, J. C. E. Simpson and P. H. Wright, *J. Chem. Soc.* 1104 (1950) and J. M. Hearn, R. A. Morton and J. C. E. Simpson, *Ibid.* 3318 (1951).



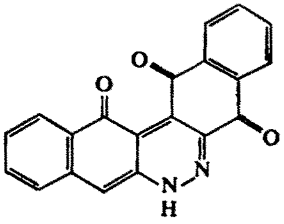
I a, R = O
b, R = NNH_2



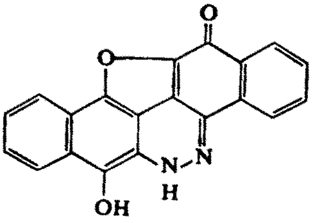
II a, R = Me
b, R = H



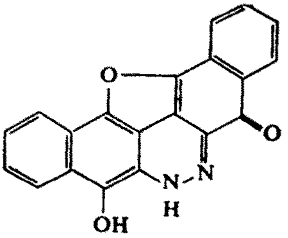
III



IV



V



VI

Structures IIb–IV are supported by the NMR spectrum of the acetylated "hydrazone" in concentrated sulfuric acid:[10] if the sharp singlet that is observed at high field (τ 7·30 ppm, relative to external TMS in CCl_4),[11] is attributed to the three acetyl protons, then there are approximately nine protons in the aromatic region and one of these is a sharp *singlet* (τ 1·09 ppm). The only other absorption observed is the very strong sulfuric acid peak. If deuterated sulfuric acid is used as solvent, the singlet in the aromatic region is absent and the ratio of acetyl to aromatic hydrogens is three to eight. Upon dilution of this solution with non-deuterated sulfuric acid, the singlet reappears. The spectrum is most directly interpretable[12] in terms of the conjugate acids of IIb, III or IV. Each of these contains an aromatic proton which should give

[10] The solubility characteristics of the compound dictated this choice of solvent.

[11] An attempt to use the usual aqueous solution standard, sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), failed since the peak presumed to be due to DSS was quickly displaced by two new singlets of different intensities.

[12] Although cleavage of the furan ring in V or VI could give rise to a proton which would appear as a singlet such a ring opening seems improbable in view of the fact that the "hydrazone" is obtained again when the H_2SO_4 soln of the acetylated "hydrazone" is diluted with water.

rise to a singlet and which is expected to exchange with deuterium.[13] The NMR spectrum of the methylated "hydrazone" in concentrated sulfuric acid displays a singlet due to the Me protons (τ 4·74 ppm) as well as peaks in the aromatic region which have very nearly the same appearance as those of the acetate and are again due to nine protons. The unlikely event of C-methylation, in which case only eight aromatic protons would be observed, is thus ruled out.

The absence of the furan ring (and the presence of the quinone) in the "hydrazone" is demonstrated as follows. Hydrogenation experiments indicate that the reduction product is very readily oxidized to starting material by air. This behaviour is frequently found with quinones. However, when the acetylated "hydrazone" is hydrogenated under acetylating conditions, a dihydrotriacetate, $C_{26}H_{18}N_2O_6$, can be isolated. The same compound is obtained more readily by reducing the "hydrazone" with sodium borohydride in pyridine and treating the resultant mixture directly with acetic anhydride. The IR spectrum shows conclusively that all three acetyl groups are attached to oxygen: the strong bands at 5·67 (sh), 5·70, 8·22 and 8·32 μ indicate phenolic acetate groups, and the weak bands at 6·27 and 6·32 (sh) μ, aromatic rings; bands attributable to NH or amide groups are absent. Basic hydrolysis in the presence of air regenerates the "hydrazone". The formation of a dihydrotriacetate which lacks amide absorption in its IR spectrum and from which the "hydrazone" can be regenerated excludes structures V and VI from further consideration.

The nature of the skeleton was ascertained by oxidative degradation. Treatment of the "hydrazone" with alkaline permanganate leads to the formation of at least four products: the trivial one, phthalic acid; a small amount of orange solid which was not identified; a canary yellow carboxylic acid, $C_{19}H_{10}N_2O_5$; and a nearly colorless carboxylic acid, $C_{18}H_{10}N_2O_4$. The last compound proved to be most directly useful in the structure determination of the "hydrazone" and its structure elucidation will now be presented. Treatment of the C-18 compound with ethanol–sulfuric acid yields a very pale yellow ethyl ester, $C_{20}H_{14}N_2O_4$; and reaction with acetic anhydride–pyridine gives a deep yellow dehydration product, $C_{18}H_8N_2O_3$. The latter, which can also be formed by pyrolysis of either the acid or the ethyl ester, readily reverts to the acid upon hydrolysis. The IR spectrum of the acid exhibits bands at 3·05, 3·78, 3·98, 5·87 (sh), 5·90 and 5·98 μ, and that of the ester at 3·12, 5·89 and 5·98 μ. The last band also persists in the dehydration product (see below) and is assigned to a quinone. Since the ester contains only four oxygen atoms, already accounted for by the ester and quinone functions, the band at 3·12 μ can then be assigned to an NH function. The NMR spectrum of the ester shows only the typical ethyl ester and presumed NH

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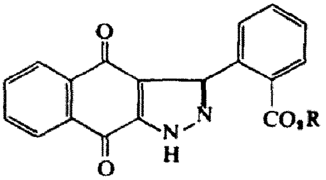
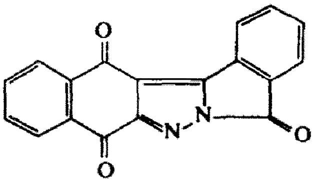
[13] This exchange is analogous to that observed with phenols. In liquid DBr the exchange of the *ortho* and *para* hydrogens of phenol at room temperature is complete in less than 10 min: A. I. Shatenshtein, A. V. Vedeneev and P. P. Alikhanov, *J. Gen. Chem. U.S.S.R.* English Transl. **28**, 2666 (1958). We have found that the exchange in conc H_2SO_4 is also very rapid: the NMR spectra obtained immediately after dissolution of phenol in H_2SO_4 and D_2SO_4 differ considerably. The strongest peaks in the former are an AB system (Δδ 0·75 ppm, J ~ 9 c/s), while in the latter a sharp singlet dominates. Since phenol is readily sulfonated, particularly in the *para* position [see, for example, J. Obermiller, *Ber. Dtsch. Chem. Ges.* **40**, 3623 (1907)], these features are ascribed to the *ortho* and *meta* protons of *para*-sulfonated phenol and the *meta* protons of *ortho*-deuterated, *para*-sulfonated phenol, respectively. It may be mentioned that the spectra continue to change during the course of several days. The dominant features observed after 8 days indicate that *ortho, para*-disulfonated phenol is formed.

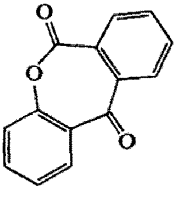
absorptions and bands in the aromatic region. On the basis of these data, structures VIIa and b, which will be shown to be correct, are now advanced for the acid and its ester. Two structures, VIII and IX, can be envisaged for the dehydration product. The lactam structure, VIII, is preferred since the IR spectrum of the compound has bands at 5·58 (strong), 5·70 (weak) and 5·95 (strong) μ,[14] whereas the lactone (in IX) is expected to absorb near 5·78 μ, the lactone absorption of the model compound *o*-salicyloylbenzoic acid-ε-lactone (X).[17]



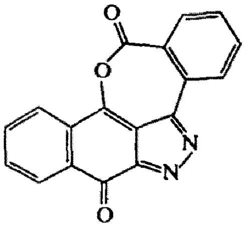
VII a, R = H
b, R = Et



VIII



X



IX

For purposes of spectral comparisons, the model compound, 1H-benz[f]indazole-4,9-dione (XI), was prepared.[18] The NH stretching vibration is found at 3·07 μ and the quinone band at 5·98 μ. UV data are collected in Table 1. The similarity of the spectra of XI[19] and VII confirms the presence of the pyrazolonaphthoquinone system in the latter.

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[14] The reason for the apparent bifurcation of the band attributable to the lactam function (in VIII) is not known, but it seems possible that Fermi resonance is involved. The presence of the weak band near 11·4 μ would be consistent with this interpretation.[15] In any event, the lactam, fused to another 5-membered ring and substituted with strongly electron withdrawing groups, is expected to absorb at a shorter wavelength than unsubstituted lactams. No close model for the effect of the fused ring is available, but from the work on penicillin it is known that fusion of another ring with a lactam causes the absorption to shift to lower wavelength.[16] To demonstrate the effect of an electron withdrawing substituent, the carbonyl absorption of N-nitrosophthalimidine at 5·72 μ (Nujol) may be compared with that of N-methylphthalimidine at 5·98 μ.

[15] For a number of other carbonyl compounds showing this behavior and a discussion of the phenomenon, see R. N. Jones, C. L. Angell, T. Ito and R. J. D. Smith, *Canad. J. Chem.* **37**, 2007 (1959).

[16] H. W. Thompson, R. R. Brattain, H. M. Randall and R. S. Rasmussen, *Infrared Spectroscopic Studies on the Structure of Penicillin* in H. T. Clarke, J. R. Johnson and R. Robinson, *The Chemistry of Penicillin* Chap. 13. Princeton Univ. Press, N.J. (1949).

[17] The ketone absorption of this compound is at 6·0 μ. Models indicate that only one CO group at a time can be oriented in the plane of either benzene ring.

[18] L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.* **53**, 4080 (1931).

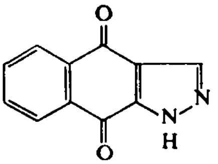
[19] The appearance of the spectrum recorded by C. J. P. Spruit, *Rec. Trav. Chim.* **68**, 325 (1949) for this compound is nearly the same, but the extinction coefficients that he reports are approximately twice as large.

TABLE 1. UV DATA OF NAPHTHOPYRAZOLES IN 95% ETHANOL

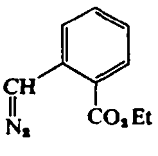
VIIa	λ_{max} 243 (4·58),[a]	~263 sh (4·31),	326 (3·73)
VIIb	243 (4·60),	~263 sh (4·33),	327 (3·76)
XI[b]	243 (4·60),	264 (4·16),	319 (3·59)

[a] Wavelength in mμ, log ε in parentheses. [b] Twice recrystallized from acetic acid and dried at 100°/0·03 mm; colorless, m.p. 350°.

The synthesis of the ester (VIIb) itself was accomplished as follows. Diazo compounds are known to add to the double bond(s) of quinones and the initially formed adduct readily becomes oxidized. Thus, XI is formed from naphthoquinone and diazomethane, followed by air oxidation.[18] The diazo-compound XII required for the formation of VIIb from naphthoquinone was obtained by treating N-nitrosophthalimidine with sodium ethoxide[20] and its reaction with naphthoquinone proceeded smoothly to give the ester VIIb directly. Approximately one equivalent of 1,4-naphthalenediol was also obtained, i.e. the expected addition product was oxidized *in situ* by unreacted naphthoquinone.[21]

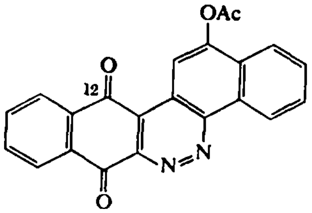


XI

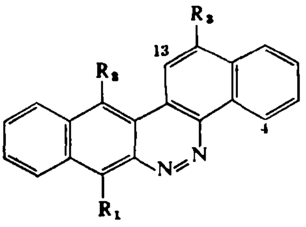


XII

Certainty of the structure of the C-18 oxidation product now permits a choice to be made among structures IIb, III and IV for the "hydrazone". Since in the oxidation product a phenyl group, and *not* a benzoyl group, is attached to the pyrazole ring, the precursor cannot be III or IV. Structure IIb is now assigned to the "hydrazone"; the acetyl and N-methyl derivatives must then have structures XIII and IIa respectively;[22] and the dihydrotriacetate has structure XIVa.



XIII



XIV

a, $R_1 = R_2 = R_3 = OAc$
b, $R_1 = R_2 = OAc$
$R_3 = H$
c, $R_1 = R_3 = OAc$
$R_2 = H$
d, $R_2 = R_3 = OAc$
$R_1 = H$

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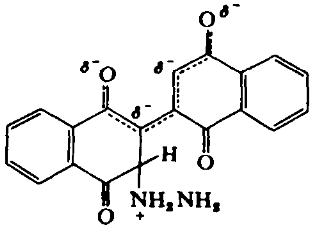
[20] A. Oppé, *Ber. Dtsch. Chem. Ges.* 46, 1095 (1913).

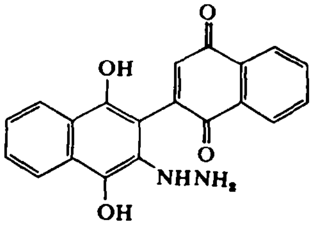
[21] Fieser and Peters, *loc. cit.*, had observed the same phenomenon in the reaction of diazoacetic ester with naphthoquinone.

[22] The alternative structure of the acetyl derivative in which the acetate group is located at C_{12} is improbable in view of its spectral properties.

Structure IIb is also the most reasonable one for the hydrazone on mechanistic grounds. Its production from dinaphthoquinone (Ia) would be expected to proceed by attack of hydrazine at C-3, which is probably the most electrophilic position in the molecule due to the resonance stabilization of the resulting intermediate XV. Prototropic shifts could then produce XVI which, upon ring closure and oxidation (by a quinone or air), could yield IIb. Dinaphthoquinone (Ia) is a likely precursor in the production of the "hydrazone" from 1,4-naphthoquinone since the latter is readily oxidatively dimerized in the presence of bases.



XV

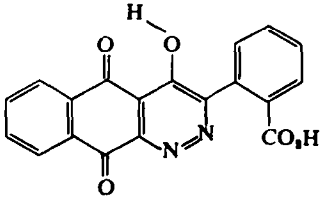


XVI

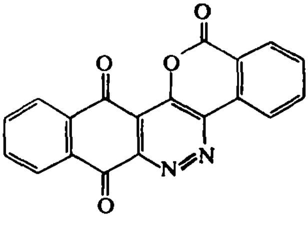
RELATED REACTIONS

The assignment of structure IIb to the "hydrazone" is consistent with the nature of other products of its oxidation and reduction.

The other product, obtained together with VIIa in the alkaline permanganate oxidation, is a yellow C-19 acid, which yields a dehydration product, $C_{19}H_8N_2O_4$, upon attempted Fischer esterification or attempted acetylation with acetic anhydride–pyridine. The IR spectrum of the acid displays typical carboxyl absorption bands at 3·1–4·0 and 5·92 μ, as well as a band at 5·99 μ, which is again assigned to a quinone. The NMR spectrum of the acid in alkaline water (or heavy water) shows only a complex multiplet in the aromatic region. The dehydro-compound has bands in its IR spectrum at 5·71 and 5·97 μ. These data considered together with the structure of the precursor (IIb) lead to the formulations XVII and XVIII for the structures of the C-19 acid and its dehydration product.[23]



XVII



XVIII

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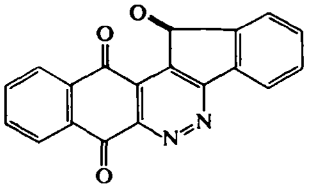
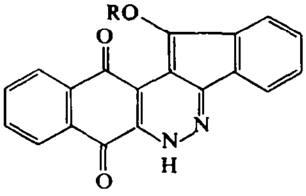
[23] The formation of a dehydration product under the esterifying conditions is readily explicable when it is recognized that XVIII is an aza analogue of the benzocoumarin system. Like many other coumarins, 3,4-benzocoumarin, for example, is so stable that its hydrolysis product can not be isolated.[24] The greater stability of the hydroxy acid XVII compared to the acid derived from benzocoumarin may be due to intramolecular hydrogen bonding by the hydroxyl and perhaps also the carboxylic acid groups. The absence of a discrete band in the IR spectrum of XVII that could be assigned to the phenolic hydroxyl group can also be attributed to intramolecular hydrogen bonding, the absorption presumably coinciding with that of the carboxylic acid.

[24] Von C. Graebe and P. Schestakow, *Liebigs Ann.* **284**, 306 (1894).

Nitric acid oxidation of IIb gives an orange solid which was not submitted for elemental analysis because its color progressively darkens upon repeated manipulation. However, structure XIX can be assigned to this substance on the basis of the following evidence. Its IR spectrum, which exhibits strong absorption at 5·80 and 5·95 μ, is consonant with the presence of a 5-membered aromatic ketone[25] and a quinone moiety. Treatment of XIX with hydrazine in an attempt to prepare the azine gives a black crystalline material, which reverts to XIX upon attempted recrystallization but which can be acetylated. The elemental analysis of the acetate, $C_{21}H_{12}N_2O_4$, and its IR spectrum [NH bands at 3·05 and 6·48, vinyl acetate bands at 5·69 and 8·30, and quinone bands at 6·00 and 6·04 (sh) μ], support structure XXb for this material. Thus, the hydrazine simply reduces[26] XIX to XXa. Oxidation of XIX with alkaline permanganate gives small amounts of phthalic acid, the C-18 acid (VIIa), its dehydration product (VIII), and the C-19 acid (XVII). The major product of the oxidation is an unstable material which gives both phthalic anhydride and VIII on sublimation and is transformed into the C-18 acid (VIIa) upon attempted crystallization.


XIX


a, R = H
b, R = Ac

XX

The nitric acid oxidation of IIb to XIX is supposed to proceed *via* the *o*-quinone XXI, followed by ring contraction[27] to XXII and subsequent oxidation.[28] Compound XIX may also be an intermediate in the permanganate oxidation of IIb, and the other oxidation products can be accounted for by the following reasonable reaction sequence. Hydroxylation of the appropriate double bond in XIX can give XXIII which is expected to undergo base-induced cleavages. Attack at (a) leads, *via* a reverse Claisen condensation of the vinylogous β-diketone and loss of water, to XVII. Alternatively, a reverse Aldol condensation, initiated by proton removal from either OH group, followed by tautomerization can give XXIV which can undergo cleavages or trans-annular condensations. A condensation leading to the pyrazole[30] ring (of XXV) is indicated by the arrows in XXIV. The C-18 acid (VIIa) can arise from XXV by loss of water, oxidation of the α-diketone to a dicarboxylic acid, decarboxylation and

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[25] The 5-membered ring ketone absorption may be compared with that of fluorenone at 5·83 μ.

[26] For a review of hydrazine reductions see: A. Furst, R. C. Berlo and S. Hooton, *Chem. Revs.* **65**, 51 (1965).

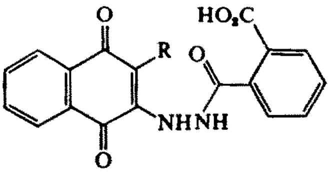
[27] Examples of benzilic acid rearrangements of *o*-quinones under acidic conditions are known: T. Zincke and F. Küster, *Ber. Dtsch. Chem. Ges.* **21**, 2719 (1888); T. Zincke and C. Gerland, *Ibid.* **21**, 2379 (1888).

[28] It may be noted that naphthoquinone itself can be oxidized with nitric acid to 1,3-indanedione under the proper conditions.[29]

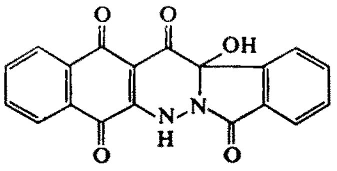
[29] J. Schmidt, *Ber. Dtsch. Chem. Ges.* **33**, 543 (1900); see also the oxidative ring contraction of an azaphenanthrene reported by G. M. Badger and R. Pettit, *J. Chem. Soc.* 1874 (1952).

[30] Precedents for forming C—C bonds under mild conditions at amide carbonyl groups are reported by G. P. Rice, *J. Am. Chem. Soc.* **45**, 222 (1923) and L. J. Dolby and D. L. Booth, *Ibid.* **88**, 1049 (1966).

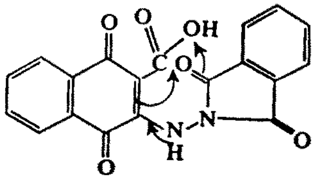
tautomerization.[31] Since the lactam VIII was also isolated from the oxidation reaction and since the acid VIIa is not converted to VIII under the work-up conditions, the lactam ring may be formed prior to the pyrazole. The intermediacy of XXIV or one of its tautomers can also be invoked for this reaction.[32]



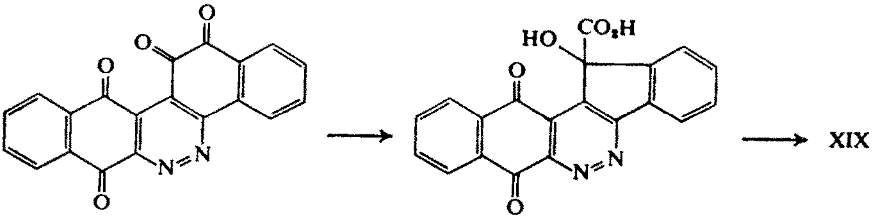
i, R = CO_2H
ii, R = H



iii

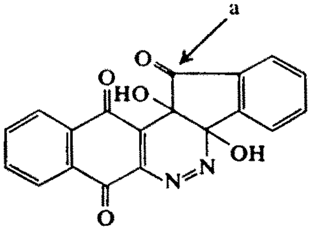


iv

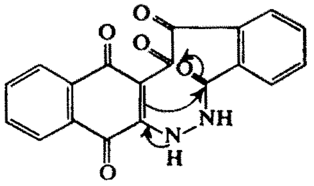


XXI

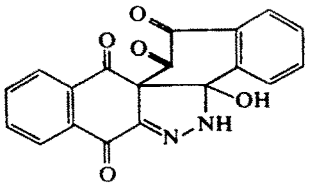
XXII



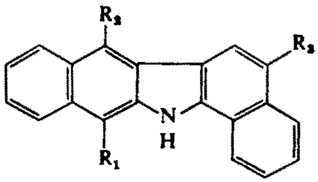
XXIII



XXIV



XXV



XXVI

a, $R_1 = R_2 = OAc$
$R_3 = H$
b, $R_1 = R_3 = OAc$
$R_2 = H$
c, $R_2 = R_3 = OAc$
$R_1 = H$

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[31] The various steps could of course take place in a different order. If, for example, cleavage of the α-diketone in XXIV is the first step, i would be formed. Either this or its decarboxylation product ii is expected to have the characteristics observed for the unstable major product of the oxidation of XIX.

[32] For example, XXIV could condense to form iii, oxidation of which would produce iv. Ring closure of the latter, before or after decarboxylation, would give VIII.

Reduction of the "hydrazone" (IIb) with alkaline sodium hydrosulfite followed by acetylation yields the triacetate XIVa and a diacetate (XIVc or d) which lacks one of the nuclear oxygen atoms of IIb. The assignment of structure XIVc or d follows from a remarkable similarity of the UV spectrum of the diacetate to that of the triacetate (XIVa)[33] and from the NMR spectrum which exhibits two low-field singlets[34] at τ 0·66 and 1·06 ppm, attributable to the isolated proton R_1 or R_2 and the one at C_{13}. The low-field absorption of both hydrogens is consistent with their location with respect to the neighbouring rings.[35] There is also a very low-field multiplet (τ 0·16 ppm), which is assigned to the proton at C_4.

When the "hydrazone" (IIb) is reduced with zinc and acid followed by acetylation, there are obtained two isomeric diacetates (XXVI) which lack both a nuclear oxygen and one of the nitrogen atoms of IIb. The great similarity of the UV spectra[33] of these two diacetates indicates that they are closely related structurally. The ring contraction to a carbazole (see structure XXVI) is consistent with the formulation of the starting material IIb as a tautomer of a cinnoline, since cinnolines upon reduction frequently lose a nitrogen atom (to give indoles).[36] The resemblance of the UV spectra of the known dibenzocarbazoles having [*a*] ring junctures[37] to those of the diacetates supports the structures XXVI. Of the three structures XXVI, (a) can probably be excluded, because oxidation of the crude reduction product with acidic ferric chloride caused only minor alterations in its IR spectrum. A marked change would be expected if a hydroquinone, oxidizable to a quinone, had been present in appreciable quantity. It is not known which of the two isomers has structure (b). With regard to the loss of nuclear oxygen atoms in these reactions, it should be noted that this phenomenon has been observed occasionally during the reduction of quinones.[38]

PHYSICAL PROPERTIES

The black appearance and great insolubility prompted an investigation of several physical properties of the "hydrazone" (IIb) and its N-methyl derivative (IIa).

Both IIa and IIb exhibit unresolved EPR signals indicating about 10^{20} spins/mole (line width 5·6 gauss). The g-values are solvent sensitive and range from 2·0030 for both in hexamethylphosphoramide to 2·0039 and 2·0040 for IIa and IIb respectively in pyridine. In the case of the N-methyl derivative, the signal disappears upon reduction with sodium borohydride and reappears upon air oxidation. Although the source of these signals has not been established, it seems likely that they are caused by a small amount of semiquinone impurity.

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[33] [a] Tables of the UV maxima of the acetates XIVa, XIVc or d, and the two isomers of XXVI are available from one of the authors (T. C.) upon request. [b] Acetoxy groups appear to cause only minor changes in the UV spectra of the parent hydrocarbons: H. Brockmann and G. Budde, *Ber. Dtsch. Chem. Ges.* **86**, 432 (1953); C. Daglish, *J. Am. Chem. Soc.* **72**, 4859 (1950).

[34] Since structure XIVb has no protons which would exhibit unsplit peaks, it is excluded from consideration.

[35] For the extent of deshielding of various aromatic protons see for example; J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance* p. 248. McGraw-Hill New York (1959).

[36] C. M. Atkinson and J. C. E. Simpson, *J. Chem. Soc.* 1649 (1947); P. W. Neber, G. Knöller, K. Herbst and A. Trissler, *Liebigs Ann.* **471**, 113 (1929).

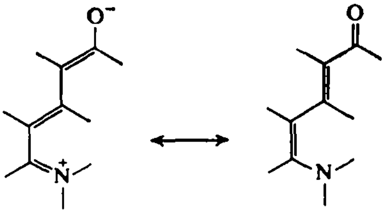
[37] N. P. Buu-Hoï, P. Jacquignon and F. Périn, *Bull. Soc. Chim. Fr.* 109 (1962).

[38] L. F. Fieser and A. R. Bader, *J. Am. Chem. Soc.* **73**, 681 (1951); K. Fries and P. Ochwart *Ber. Dtsch. Chem. Ges.* **56**, 1291 (1923); C. Liebermann, *Ibid.* **21**, 1172 (1888).

The N-methyl compound behaves as an electrical insulator. The resistivity of individual crystals is 1 × 10^{10} ohm-cm at room temperature and increases by a factor of 10 upon compaction under 4 kbar pressure.

X-ray crystallographic data on the N-methyl derivative, which forms larger single crystals than the "hydrazone", reveal the following cell dimensions: $a = 14{\cdot}65$ Å; $b = 8{\cdot}15$ Å; $c = 25{\cdot}56$ Å; The crystals are orthorhombic. There are eight molecules in the unit cell and the space group is Pbca. The measured density is 1·485; the calculated density is 1·480.

The compounds show extensive absorption in the visible and UV regions of the spectrum (Table 2, Expt'l). They may be compared to the merocyanines which are highly colored substances containing an odd number of carbon atoms between a carbonyl oxygen and a nitrogen atom and linked by conjugated double bonds.[39] The absorption of such materials is attributed to transitions involving the betaine-like hybrids,[40] such as shown below in a part structure of IIa or b. The solvatochromism of merocyanines[40c] was also observed with compound IIa (Table 2, Expt'l).



EXPERIMENTAL

IR spectra, taken as Nujol mulls with a Beckman IR 8 instrument, were calibrated with the 6·24 μ band of polystyrene; UV spectra, measured in 95% EtOH with a Carey model 14 spectrophotometer, were reproducible to ±1 mμ; NMR spectra were determined with a Varian A60 instrument; m.ps are uncorrected; microanalyses were carried out by the Scandinavian Microanalytical Laboratory, Box 25, Herlev, Denmark.

The "hydrazone" IIb (benzo[g]naphtho[1.2-c]cinnoline-7,12,14(6H)-trione)

(i) Pure naphthoquinone (30 g, 0·19 mole) was dissolved in EtOH (ca. 600 ml) at 65°, hydrazine hydrate (10 ml, 0·2 mole) added in portions and the mixture maintained at 60–65° for 3·5 days. The solid was filtered off and triturated with EtOH (4 × 100 ml). When the dark material (20 g) was recrystallized from 200 ml of pyridine and triturated 4 times with acetone, 4·2 g of the black compound IIb was obtained. A yield of 11·7%, comparable to the overall yield based on naphthoquinone of the following preparation (12%), was calculated on the assumption that air is the oxidizing agent; if naphthoquinone is the oxidizing agent, the yield is 23%.

(ii) The procedure of Pummerer *et al.*,[4] starting with 2,2′-dinaphthoquinone[4] (Ia) gave, after crystallization of the product, a 25% yield. The material partially decomposes ~300°, and seems to disintegrate ~340°. When the copper-colored solid, obtained by crystallization from pyridine, was either thoroughly washed with acetone or EtOH or sublimed at 260°/0·03 mm, it became black. The IR spectra (see text) of these last materials were the same, but differed from the pyridine-crystallized material which had bands at 3·6–4·6 (very broad, weak), 5–5·6 (very broad, weak), 5·97, 6·0 (sh), 6·3 μ. (Found: C, 73·59; H, 3·01; N, 8·94. $C_{20}H_{10}N_2O_3$ requires: C, 73·62; H, 3·09; N, 8·58%.)

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[39] F. H. Hamer, *The Cyanine Dyes and Related Compounds*, Interscience, Wiley, New York (1964).

[40] See, for example [a] W. Jenny, *Helv. Chim. Acta* **34**, 539 (1951); [b] A. E. Pohland, M. C. McMaster, R. C. Badger, N. H. Cromwell, *J. Am. Chem. Soc.* **87**, 2510 (1965); [c] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman and S. G. Dent, Jr. *Ibid.* **73**, 5332 (1951).

In EtOH the compound does not obey Beer's Law; however, in the presence of dilute acid (ca. 0·01N H_2SO_4 in 95% EtOH) Beer's law is obeyed. The ethanolic solution is yellow-brown. For UV and vis. data, see Table 2. The compound dissolves in conc H_2SO_4 to give a deep red soln from which it can be recovered by pouring the soln into ice-water. The compound is slightly soluble in dil 50% ethanolic KOH with deep blue coloration. While it is quite stable toward dilute base, the "hydrazone" is decomposed by very strong base. The compound is nearly insoluble in most organic solvents, except pyridine.

TABLE 2. SPECTRAL DATA OF THE "HYDRAZONE" AND ITS DERIVATIVES[a]

IIb[b]	IIa[c]	XIII[c]	IIa[d]
237 (4·63)	239 (4·33)	233 (4·64)	422 (4·18)
266[e] (4·41)	252[e] (4·29)	~255[e] (4·42)	440 (4·11)
313 (4·45)	313[e] (4·25)	304 (4·50)	576 (3·37)
333[e] (4·37)	324 (4·26)	408 (3·80)	423 (4·18)
	337[e] (4·22)	~570 (2·62)	443 (4·13)
417 (4·12)	400[e] (4·00)		570 (3·40)
437 (4·13)	420 (4·19)		426 (4·15)
~475[e] (3·72)	442 (4·17)		447 (4·15)
~565[e] (3·24)	548 (3·41)		557 (3·43)

[a] Max are in mμ; log ε values in parentheses. [b] In 95% EtOH which was 0·01N in H_2SO_4. Since not all of the 11·2 mg dissolved in 500 ml of solvent, the extinction coefficients are too low. [c] In 95% EtOH. [d] The first three were taken in pyridine, the middle three in 90% pyridine–10% water and the last three in 40% pyridine–60% water. [e] Shoulder.

The "hydrazone"-acetate XIII (*14-acetoxybenzo*[g]*naphtho*[1.2-c]*cinnoline-7,12-dione*)

A mixture of IIb (120 mg), pyridine (8 ml) and Ac_2O (2 ml) was swirled for 10 min and then filtered. The solid was rinsed with AcOH and acetone (105 mg, 78%). An analytical sample, which was golden-yellow, dec ~290°, was crystallized from large volumes of chlorobenzene followed by trituration with EtOH. The compound can be crystallized more easily from AcOH or pyridine. UV and vis. data are shown in Table 2. τ (D_2SO_4) singlet, 7·30; multiplet centered about 1·75; multiplet, 0·80 ppm (area ratio 3:7:1). (Found: C, 72·00; H, 3·36; N, 7·78. $C_{22}H_{12}N_2O_4$ requires: C, 71·74; H, 3·28; N, 7·61%.)

No further reaction could be achieved by treating IIb or XIII with Ac_2O–pyridine at the b.p. for 2 hr. After heating IIb at reflux in AcCl for 16 hr, only XIII (93%) was obtained.

The methyl-"hydrazone" IIa (*6-methylbenzo*[g]*naphtho*[1.2-c]*cinnoline-7,12,14-trione*)

A stirred mixture of IIb (200 mg), 1M KOH (10 ml), and MeOH (30 ml) was heated to 50°, and Me_2SO_4 was then added dropwise. Whenever the blue supernatant became brownish, a small portion of aqueous 20% KOH was added to keep the soln basic. After a total of 3·5 ml of Me_2SO_4 had been added, the basic supernatant was no longer blue. The mixture was boiled for 10 min and the product filtered off, and rinsed with water and EtOH. The solid (180 mg, 86%) crystallizes as black glistening needles from anisole to which it imparts a deep green color. On a Kofler block, utilizing polarized light, needles appear at ca. 260° and the compound liquifies near 265° (depends on rate of heating). UV and vis. data are shown in Table 2. τ (H_2SO_4) singlet, 4·74; multiplet centered about 1·60; singlet, 1·00; multiplet 0·68 ppm (area ratio 3:7:1:1). (Found: C, 74·21; H, 3·66; N, 8·39; OCH_3, 0·49. $C_{21}H_{12}N_2O_3$ requires: C, 74·11; H, 3·55; N, 8·23; OCH_3, 9·1% [if it were methylated on oxygen].)

Oxidation of IIb

(i) *Potassium permanganate.* A stirred mixture of IIb (4·0 g, 12 mmole) and 0·5M KOH (200 ml) was heated nearly to the b.p. and $KMnO_4$ (10 g, 63 mmole) was added in portions. After 20 min the mixture was cooled, filtered, and the solids (A) rinsed with a little water. The combined washings and filtrate were cooled in ice and brought to pH 4–5 with conc HCl. The ppt, predominantly compound XVII (0·70 g) was filtered off and washed with water. The filtrate and washings were further acidified to pH 1–2; the ppt, predominantly compound VIIa (0·52 g) was filtered off and rinsed with water. The filtrate was extracted with ether (3 × 100 ml) and the dried (Na_2SO_4) ether extract stripped of solvent to give a residue (0·59 g) which was predominantly phthalic acid. From the solids (A) was obtained an orange material (0·32 g) which could not be properly purified and was not identified.

Crude compound XVII, *3(2'-carboxyphenyl)4-hydroxybenzo*[g]*cinnoline-5,10-dione*, was purified by crystallization from AcOH (charcoal). It crystallizes very slowly as a canary yellow powder which does not melt or darken below 330°. λ_{max} 245, 296, 405 mμ (log ε 4·27, 4·32, 3·58); λ_{max} (in ethanolic dil KOH) 240, 268 (sh), 308, 443 mμ (approx. log ε 4·48, 4·07, 4·14, 3·87);[41] τ (dil KOHaq) complex multiplet near 2·5 ppm. The compound tenaciously retains AcOH as shown by analysis of a sample dried for 6 hr at 100°/0·05 mm. (Found: C, 63·61; H, 3·26. $C_{19}H_{10}N_2O_5 \cdot 0{\cdot}5\ CH_3CO_2H$ requires: C, 63·83; H, 3·21%). When the sample was dried for 30 hr at 100°/0·025 mm the AcOH was removed. (Found: C, 65·61; H, 3·13; N, 8·01. $C_{19}H_{10}N_2O_5$ requires: C, 65·90; H, 2·91; N, 8·09%.)

The dehydration product XVIII, *3(2'-carboxyphenyl)4-hydroxybenzo*[g]*cinnoline-5,10-dione-δ-lactone*, was obtained when the orange solution of XVII (120 mg) in boiling pyridine (15 ml) was treated dropwise with Ac_2O (1·5 ml), or when XVII was treated with abs EtOH and a little conc H_2SO_4 at reflux overnight. The bright yellow fine glistening needles (90 mg, 80%) separated at once. An analytical sample was crystallized from large volumes of DMF. The compound does not melt or darken below 325°. λ_{max} 225 (sh), 243, 295, 408 mμ (log ε, 4·25, 4·17, 4·16, 3·44). (Found: C, 69·09; H, 2·59; N, 8·83. $C_{19}H_8N_2O_4$ requires: C, 69·50; H, 2·46; N, 8·54%.)

After an attempt to crystallize the crude compound VIIa from AcOH failed, the material was treated with pyridine (4 ml) and Ac_2O (6 ml) on the steam bath for 10 min. The mixture was cooled, some precipitated XVIII was removed by filtration, and the solvents were evaporated under reduced press. The residue was treated with AcOEt and filtered to give crude lactam VIII (200 mg). The filtrate contained phthalic anhydride mixed with VIII. Pure lactam, *isoindolo*[1,2-b]*benz*[f]*indazole-5,8,13-trione* (VIII), a yellow powder, m.p. 315° dec (sealed cap.), was obtained by sublimation at 240°/0·05 mm. (Found: C, 72·26; H, 2·84; N, 9·34. $C_{18}H_8N_2O_3$ requires: C, 72·00; H, 2·68; N, 9·33%.)

In order to effect complete soln for a quantitative UV spectrum it was necessary to heat the mixture for several hr. The spectrum then was the same as that of the acid VIIa or the ester VIIb.

(ii) *Nitric acid.* Compound IIb (0·5 g) was added to 70% HNO_3 (25 ml) which was stirred magnetically and immersed in an oil bath heated to 120°. The clear red fuming soln was stirred for 30 min, partially cooled, and poured onto water and ice (ca. 100 ml). The precipitated orange solid XIX, 13H-*benz*[g]*indeno*[1,2-c]*cinnoline-7,12,13-trione*, was filtered after 15 min and rinsed with water and acetone. The product (0·35 g) was much darker after crystallization from AcOH or anisole. It darkens when heated and begins to sublime at ca. 300°; by 335° colorless needles and a yellow solid have sublimed and the residue has changed to glistening needles which turn black by 350°. Attempts to purify the solid by sublimation at 260°/0·05 mm also failed. Extraction of the HNO_3aq filtrate with AcOEt gave a solid from which phthalic anhydride was isolated by sublimation.

Reduction of XIX *with hydrazine*

When a soln of crude XIX (130 mg) in pyridine (15 ml) was treated with hydrazine hydrate (0·75 ml) and the soln was then left to stand for 3 hr, concentrated on the hot-plate to 3 ml, cooled and filtered, there were obtained 110 mg of glistening black long needles (XXa), *13-hydroxy*-6H-*benz*[g]*indeno*[1.2-c]*cinnoline-7,12-dione*, m.p. 320° dec (colorless and orange materials sublime), λ_{max} 3·05, 6·00, 6·19, 6·27, 6·30, 6·48 μ.

Treatment of XIX under nitrogen with hydrazine hydrate in diglyme at reflux for 6·5 hr also gave only XXa. The solid was triturated with 5% Na_2CO_3 (10 ml) at 70°, filtered, rinsed with water and EtOH and then dissolved in boiling pyridine. While 35 ml of the latter was required to effect soln, no solid separated again until the soln had been concentrated to 4 ml. The red-brown solid then had the IR spectrum of XIX.

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[41] The UV data are rather similar to those of 1-hydroxyanthraquinone reported by R. H. Peters and H. H. Sumner, *J. Chem. Soc.* 2101 (1953) and J. C. P. Spruit, *Rec. Trav. Chim.* **68**, 325 (1949). The two sets of reported data differ somewhat.

Acetylation of the reduction product XXa

The reaction of hydrazine with XIX (250 mg) was repeated. After the soln had been concentrated, Ac_2O (3·5 ml) was added and the soln was boiled down to a very small volume. The fine purple-greyish needles of 13-*acetoxy*-6H-*benz*[g]*indeno*[1.2-c]*cinnoline*-7,12-*dione* (XXb) (200 mg, 70%) were recrystallized from very little pyridine and had m.p. ca. 300° (dec). λ_{max} 240, ~300 (sh), ~320 (sh), 337, 425–455, ~485 (sh) mμ (log ε 4·34, 4·11, 4·22, 4·27, 3·48–3·49, 3·33). The compound can be sublimed at 260°/0·4 mm. (Found: C, 70·86; H, 3·54; N, 8·00. $C_{21}H_{12}N_2O_4$ requires: C, 70·78, H, 3·39, N, 7·86%.)

Oxidation of XIX *with potassium permanganate*

To stirred, hot, aqueous 0·5M KOH (25 ml) crude XIX (700 mg, 2·25 mmole) was added, followed by $KMnO_4$. At once a deep green color developed. The mixture was maintained at 80° while more $KMnO_4$ (1·1 g, 7 mmole total) was added until a purple tinge seemed to remain superimposed on the green color. After 15 min excess oxidizing agents were destroyed with EtOH. The hot mixture was filtered and the solid extracted once with 15 ml of hot water. The combined filtrate and washings were treated with conc HCl (pH ca. 1). The yellowish ppt, which soon coagulated, was filtered to give a solid (A) and filtrate (A). The solid (A) was washed with water (10 ml) and acetone (ca. 20 ml). The combined washings, from which a solid had separated, gave on heating to boiling a clear, red soln which on cooling deposited greyish needles (30 mg) of VIII. The red filtrate lost its color overnight and deposited 50 mg of VIIa. This was dissolved in 10 ml of EtOH, treated with an equal volume of water, and boiled down to ca. 12 ml. On cooling and scratching, VIIa, 3(2′-*carboxyphenyl*) 1H-*benz*[f]*indazole*-4,9-*dione*, separated as a tan solid. On rapid heating to 280°, it changes to a glistening yellow solid (VIII) which then sublimes. (Found: C, 67·66; H, 3·16; N, 8·70. $C_{18}H_{10}N_2O_4$ requires: C, 67·93; H, 3·02; N, 8·38%.)

The air-dried solid (A) had λ_{max} 2·75–4, 5·8 (sh), 5·97, 6·18 6·28 μ. On heating, the yellow powder changed to a glistening yellow-greenish solid at ca. 250° and at ca. 300° phthalic anhydride and VIII sublimed. Attempts to crystallize the material from either AcOH–water or EtOH–water gave VIIa. Conversion of solid (A) to pure VIIa was best accomplished by dissolving (A) (170 mg) in hot aqueous 0·5M KOH, precipitating with conc HCl, heating the solid with EtOH (40 ml), filtering, diluting the filtrate with water, concentrating to a small volume, cooling and filtering the tan solid (VIIa, 120 mg).

The filtrate A on standing overnight deposited a brilliant yellow solid, which was filtered and rinsed with water and acetone. The material (50 mg) was a mixture of compound (A) and XVII as shown by spectral comparisons. After dissolution in base, reprecipitation with acid and brief boiling, the material had the spectrum of a mixture of XVII and VIIa. Phthalic acid (40 mg) was isolated from the filtrate.

Esterification of VIIa

A mixture of VIIa (120 mg), abs EtOH (15 ml), benzene (15 ml) and a little conc H_2SO_4 was boiled down to ca. 5 ml during 1 hr; another portion of EtOH and benzene was added, the soln was concentrated again and crystallization induced by cooling and scratching. The glistening very pale yellow needles of VIIb, after recrystallization from abs EtOH, had m.p. 210·5–211·5°. Upon admixture with a sample of VIIb, prepared independently (see below), the m.p. was 210–211·5°. (Found: C, 69·38; H, 4·09; N, 8·23. $C_{20}H_{14}N_2O_4$ requires: C, 69·36; H, 4·07; N, 8·09%.)

An NMR spectrum in hexadeuteriodimethylsulfoxide—determined with excellent results by use of a microtube (NMR Specialties Co., New Kensington, Pa., USA)—had peaks at τ complex multiplet centered about 2·1; quartet, 5·88; triplet, 8·88 ppm (area ratio 8:2:3). A broad peak near 4·3 (3 protons) was attributed to the NH of VIIb and the water absorbed by the solvent. A solvent blank showed absorption of residual protons at 7·40 and a water peak at 6·65 and the latter was absent in the spectrum of VIIb. The shifts are relative to external TMS = 0.

Synthesis of 3(2′-*carbethoxyphenyl*)-1H-*benz*[f]*indazole*-4,9-*dione* (VIIb)

N-nitrosophthalimidine, (XXVII), prepared by Oppé's[30] excellent method and recrystallized from 95% EtOH, had m.p. 157–160°. By adapting Oppé's[30] method of preparing *o*-carbomethoxyphenyldiazomethane, starting with 1·1 g (6·8 mmole) of XXVII, and using 25 ml of 0·5M EtONa in abs

EtOH, a soln of the Et ester XII was obtained and added at once to an ethereal soln of 1,4-naphthoquinone (1·1 g, 7 mmole). After 1 hr the soln was gently warmed to evaporate the ether and finally heated more vigorously to concentrate the soln to ca. 15 ml. On cooling and scratching, compound VIIb (450 mg) was obtained. The concentrated mother liquor deposited a second crop overnight. It was diluted with EtOH and filtered at once to give 300 mg. Recrystallization from abs EtOH afforded 550 mg of fine buff needles, m.p. 210–211·5°. A second crop had m.p. 205–208°. From the mother liquor of the reaction was obtained 1,4-naphthalenediol (350 mg). After acetylation of the material remaining in the mother liquor, there was obtained additional VIIb (60 mg, 34% total), 1,4-naphthalenediol diacetate (50 mg, total yield of naphthalenediol 35%), and ethyl 2-carbethoxymethylbenzoate, identified as the acid, m.p. 78–80° (reported[42] m.p. 84·5°).

o-*Salicyloylbenzoic acid-ε-lactone* (X)

The acid precursor of the lactone was prepared according to Ullmann and Schmidt.[43] The lactone, readily obtained from impure acid by the method of Baker *et al.*,[44] after crystallization from CCl_4 had m.p. 177·5–179·5° (reported[44] m.p. 179–180°). Base hydrolysis of the lactone gave the acid which after crystallization from either water or small amounts of methanol had m.p. ~120° (sinters ~80°) (reported[44] m.p. 169–171°; reported[43] m.p. 171–172°; reported[45] m.p. 170–171°). IR spectra of Chf solns of the acid (m.p. ~120°) and a sample of the higher melting acid kindly provided by Prof. Baker and Dr. Ollis were the same. Furthermore, on seeding a Chf soln of the acid (m.p. ~120°) with the higher melting acid, the higher melting form was obtained.

Reductions of "hydrazone" IIb

(i) *Hydrogen.* Although IIb suspended in EtOH in the presence of Pd–C consumed ca. one equiv. of hydrogen, only starting material was reisolated. Hydrogenation of the acetate XIII under acetylating conditions proved successful: a soln of XIII (140 mg, 0·38 mmole) in Ac_2O (15 ml), AcOH (35 ml) and conc H_2SO_4 (6 drops) was stirred with H in the presence of 5% Pd–C (ca. 20 mg). The reaction was stopped after 3 hr when a total of 13·4 ml H (1·4 equiv) had been consumed, a solid had separated and the supernatant had become wine-red. The filtered solids were treated with hot pyridine (40 ml) containing Ac_2O (1 ml) and the catalyst was removed by filtration. The filtrate, after concentration to ca. 6 ml, deposited bright yellow needles (70 mg, 40%) of 7,12,14-*triacetoxy-benzo*[g]*naphtho*[1.2-c]*cinnoline* (XIVa), which were recrystallized from pyridine containing a little Ac_2O and had m.p. ca. 285° (dec, began to darken about 270°).[38a] (Found: C, 68·88; H, 4·08; N, 6·20. $C_{26}H_{18}N_2O_6$ requires: C, 68·72; H, 3·99; N, 6·16%.)

From other experiments in which only one equiv. of H was consumed, it appears that the hydrogenation product is soluble in the reaction medium, that it is readily reoxidized in the presence of air, and that acetylation of the reduced material proceeds only slowly in the presence of H_2SO_4 to give the insoluble XIVa. Hydrolysis with aqueous ethanolic base (air oxidation) regenerated IIb.

(ii) *Sodium borohydride.* When $NaBH_4$ (350 mg) was added to the brown soln of IIb (350 mg, 1·07 mmole) in pyridine (30 ml), a deep green soln containing some solid was obtained. The mixture was swirled for a few min and then cautiously treated with Ac_2O (10 ml total). Heat was evolved, the mixture foamed and some solids separated. After 20 min, ice and water were added to a volume of 110 ml. The insoluble light brown solid was rapidly filtered and treated at once with pyridine (10 ml) and Ac_2O (1·5 ml). The mixture was heated to boiling and then cooled to give 240 mg (49%) of XIVa as yellow needles.

(iii) *Sodium hydrosulfite.* To a stirred vigorously boiling mixture of IIb (0·50 g), EtOH (15ml) and 0·5M KOH (20 ml) in an Erlenmeyer flask were added alternately sodium hydrosulfite (6·0 g total) and 1M KOH (35 ml total) during 15 min. The mixture was boiled for an additional 5 min (the pH dropped to 5–6), cooled slightly, and filtered; the brown-red solid was rinsed with water and a little EtOH and was then treated at once with 6 ml each of pyridine and of Ac_2O. The soln was boiled down to 8 ml, cooled and scratched to accelerate the slow crystallization. After 1 hr, the greenish solid (XIVc or d), *diacetoxy-benzo*[g]*naphtho*[1.2-c]*cinnoline*, was filtered and rinsed with

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[42] W. A. Noyes and J. A. Coss, *J. Am. Chem. Soc.* **42**, 1280 (1920).

[43] F. Ullmann and W. Schmidt, *Ber. Dtsch. Chem. Ges.* **52**, 2098 (1919).

[44] W. Baker, D. Clark, W. D. Ollis and T. S. Zealley, *J. Chem. Soc.* 1452 (1952).

[45] A. Sieglitz, *Ber. Dtsch. Chem. Ges.* **57**, 316 (1924).

pyridine and ether (to give filtrate A). The solid (240 mg), after recrystallization from pyridine containing Ac_2O (charcoal), was yellow; it darkens above 220° and decomposes rapidly at 239°; λ_{max} 5·68 μ.[33a] (Found: C, 72·51; H, 4·05; N, 7·23. $C_{24}H_{16}N_2O_4$ requires: C, 72·72; H, 4·07; N, 7·07%). Some XIVa was also obtained from the filtrate A.

(iv) *Zinc.* A stirred mixture of IIb (1·0 g) and AcOH (50 ml) was heated to boiling, and Zn dust (3·0 g) was added in portions, followed by conc HCl (1·5 ml). The mixture, which soon became yellow, was stirred at the b.p. for 45 min, conc HCl (1·5 ml) added and stirring continued for 90 min. The supernatant liquid and suspended solid were decanted from excess Zn (which had coagulated) into 3 volumes of water; the brown ppt was filtered, rinsed with water and air-dried to give 800 mg. The material failed to oxidize when heated with $FeCl_3$ in AcOH containing a little water and HCl. An attempt to hydrogenate 400 mg of the reduction product in AcOH and in the presence of 5% Pt–C failed. The recovered material was treated with Ac_2O–pyridine at the b.p. for 5 min; the dark soln was cooled, poured into water and the solid filtered. After the solid had been extracted with boiling benzene (2 × 8 ml), there was obtained 200 mg of yellow solid A. Evaporation of the benzene gave a residue which was slurried with ca. 8 ml of AcOEt. The insoluble material (40 mg), *diacetoxy*[a,h]*dibenzocarbazole* (XXVI b or c), was recrystallized 3 times from AcOEt (2–3 ml); m.p. 278–279° and λ_{max} 2·95, 5·68, 5·74, 7·71, 11·68 and 11·97 μ. (Found: C, 75·24; H, 4·57; N, 3·72. $C_{24}H_{17}NO_4$ requires: C, 75·19; H, 4·47; 3·65%.)

The AcOEt contained another material that could not be purified. The solid A was boiled with 30 ml of AcOEt; the insoluble part was dissolved in 50 ml of boiling AcOH and the soln concentrated to ca. 15 ml, although the fine yellow powder, the other isomer XXVIb or c, had already begun to separate. The product was filtered and the process repeated once with AcOH and once with AcOEt. The pale yellow powder did not melt below 350° and had λ_{max} 2·95, 5·68, 5·72, 7·65 and only very weak absorption between 11·5 and 12 μ.[33a] (Found: C, 74·82; H, 4·41; N, 3·86. $C_{24}H_{17}NO_4$ requires: C, 75·19; H, 4·47; N, 3·65%.)

In an earlier experiment in which a different work-up was used a ca. 35% yield of the lower melting isomer was isolated. No search for the other isomer had been attempted.

Acknowledgments—We wish to thank Mrs. Diet Tigchelaar and Dr. Tadakazu Tsuji for performing preliminary experiments, Dr. William Landgraf of Varian Associates for obtaining and interpreting the EPR spectra. Dr. F. J. Darnell of the Central Research Department of E. I. du Pont de Nemours and Co. for the electrical resistivity measurements, and Mrs. Helen Berman of the Crystallography Laboratory, University of Pittsburgh, for the crystallographic data.