Tetrahedron, 1964, Vol. 20, pp. 803 to 821. Pergamon Press Ltd. Printed in Northern Ireland

QUINONE STUDIES—I

EVIDENCE FOR A NEW TYPE OF SUBSTITUTION REACTION OF PHENANTHRENE-9,10-QUINONE DERIVATIVES[1]

M. V. BHATT
Department of Organic Chemistry, Indian Institute of Science,
Bangalore, India

(*Received* 29 *November* 1963)

Abstract—The *para* orientation by the carbonyl groups in the bromination of phenanthrenequinone derivatives has been explained on the basis of an excited state resulting from thermal excitation of the quinone and/or from a $n \rightarrow \pi^*$ transition of the nonbonding electrons of the oxygen atoms. A general preparative method for the syntheses of 3-bromophenanthrenequinone derivatives has been developed. The structure of 2-nitro-6-bromophenanthrenequinone has been established by degradation. Synthesis of 2-nitro-6-bromofluorenone is described. Direct bromination of phenanthrenequinone to 2-bromo and 2,7-dibromo derivatives has also been described.

ELECTROPHILIC substitutions in phenanthrenequinone (I) follow a simple pattern. The diphenyl framework and the dicarbonyl bridge acting differently direct the substituents to the 2,7 and 4 or 5 positions. However, deactivation to electrophilic attack due to the carbonyl groups is quite pronounced. For example I can be heated to 100° in concentrated sulphuric acid without sulphonation.[2] Similarly refluxing I with bromine in acetic acid for 12 hours does not result in bromination.[3] In marked contrast to this behaviour was the reaction of I with bromine reported by Schmidt and Eitel.[4] These authors found that in dry nitrobenzene solution, I reacts with bromine at 110° to form 3-bromophenanthrenequinone (II) and with excess of bromine to form a dibromo derivative. The structure of the dibromo derivative was later shown to be 3,6-dibromophenanthrenequinone (III) by Courtot and Kronstein.[5] An enquiry into the scope and mechanism of this reaction forms the subject of the present investigation.

The influence of experimental conditions and structural modifications on the reaction are described in the present paper. Tables 1 and 2. It has now been recognized that two sets of experimental conditions can be distinguished. The reaction takes place at about 110° in nitrobenzene solution during 5–10 hr or at 140 ± 5° 3 hr. The same type of reaction also takes place with great facility when I is excited inacetic acid during by light and catalysed by peroxides. A 75 watt tungsten lamp, activates I, in nitrobenzene solution in a Pyrex vessel. Ordinarily the reaction is complete in 2 hr, without external heating, although the actual temperature of the reaction mixture was 60 ± 10°. Later during the investigation, conditions could be realized where the reaction was complete in 15 min. The crude products in all these

---

[1] Partly abstracted from the Ph.D. thesis.

[2] C. Graebe, *Liebig's Ann.* **167**, 143 (1873).

[3] cf. experimental portion.

[4] J. Schmidt and M. Eitel, *J. Prakt. Chem.* **134**, 167 (1932).

[5] Ch. Courtot and J. Kronstein, *Chim. industrie.* **45** (Special Number), 72 (1941); *Chem. Abstr.* **37**, 2729 (1943).

experiments were crystalline and melted a few degrees below the m.p. of the pure products. We have not been able to detect or isolate any 2-bromo (IV) or 2,7-dibromophenanthrene quinone (V) or any other bromo derivatives. It is apparent that the experimental conditions and the structure of the products are inconsistent with electrophilicsubstitution mechanism. Moreover, we have succeeded in brominating I directly under strongly acidic conditions and in the presence of a silver salt[6] to either IV or V.

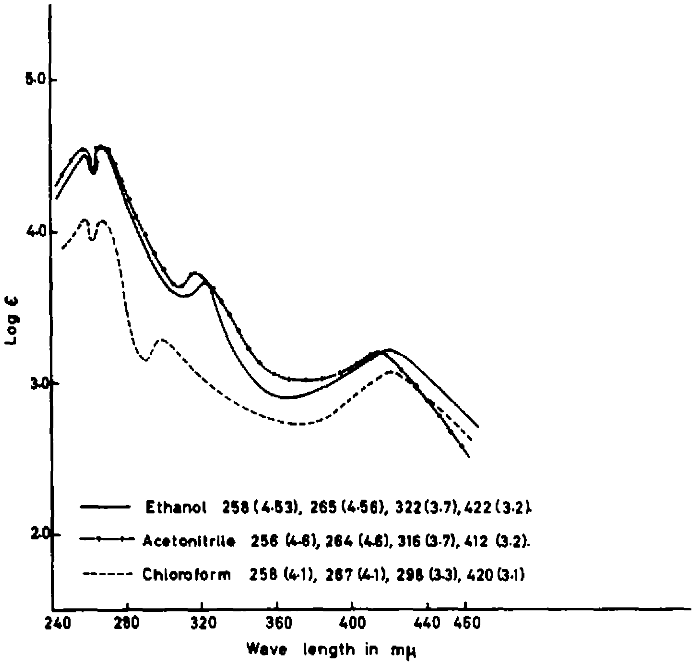


FIG. 1. Spectrum of Phenanthrenequinone

Our attention was next turned to studying the influence of solvents on the reaction. To our surprise we observed that the reaction did not proceed in boiling carbon tetrachloride solution in the presence of light and peroxides. The starting quinone (I) was also recovered, when treated with N-bromosuccinimide in boiling benzene. These experiments argue against an ordinary free-radical aromatic substitution reaction.

An understanding of the absence of reaction in carbon tetrachloride has become possible. It was observed that a 1 : 1 molecular complex of bromine with I is formed in carbon tetrachloride.

This complex is perhaps of the Mulliken type[7] involving charge transfer (VIa or VIb) (cf. Fig. 2b). The 2p electrons in nonbonding orbitals of oxygens are tied up with bromine,[8] resulting in lack of reactivity of the quinone moiety. The IR spectrum of the complex supports this view (Fig. 2b).

---

[6] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.* 573 (1950).

[7] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 600 (1950); **74**, 811 (1952); O. Bastiansen and E. W. Lund, *Ann. Reviews of Physical Chemistry* **10**, 40 (1959).

[8] A similar complex was prepared under different conditions by J. Schmidt and E. Junghans, *Ber. Dtsch. Chem. Ges.* **37**, 3556 (1904).

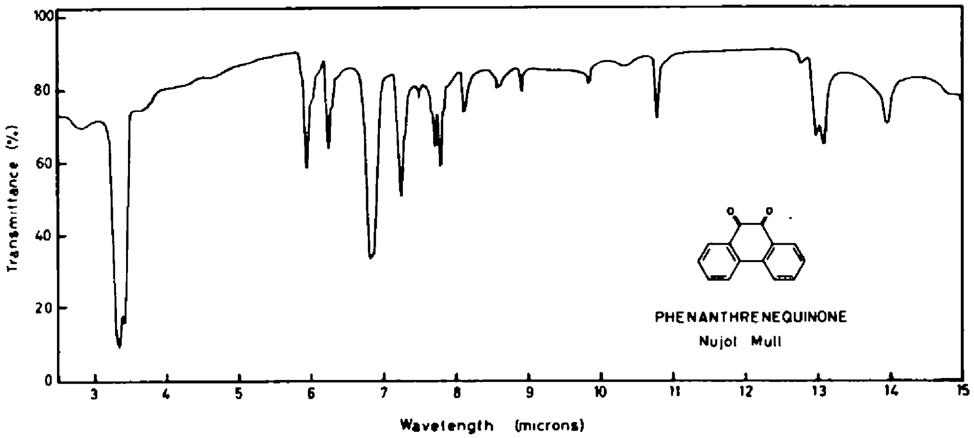
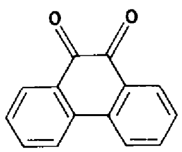
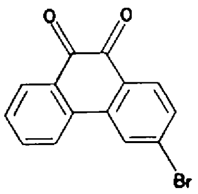


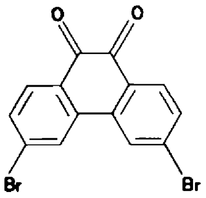
FIG. 2a



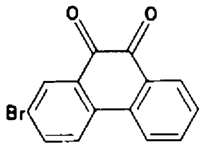
I



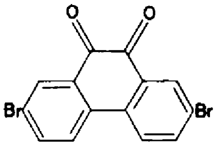
II



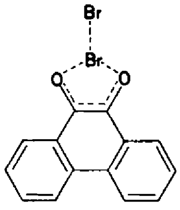
III



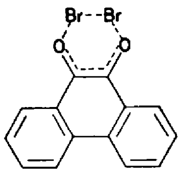
IV



V



VIa



VIb

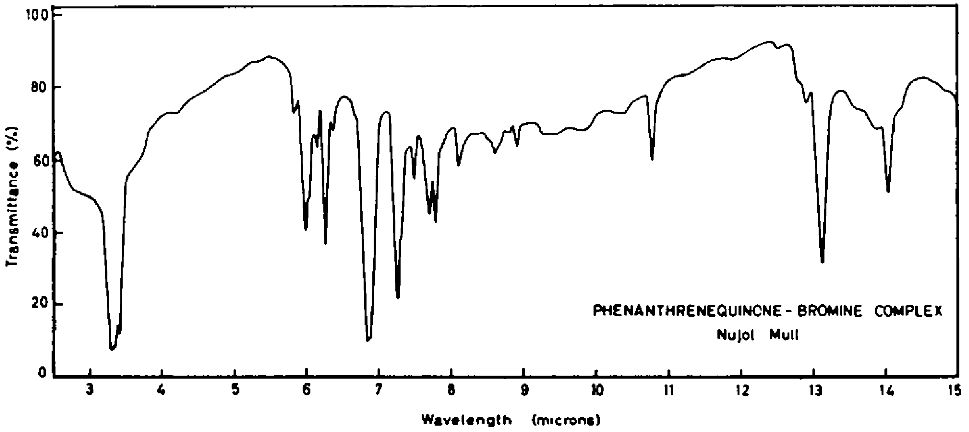
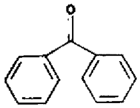
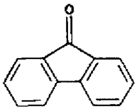
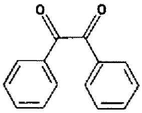
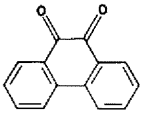
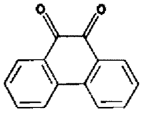
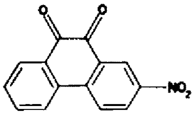
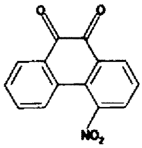
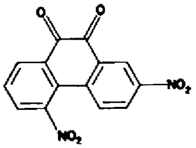
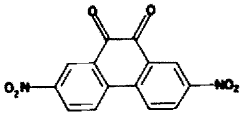


FIG. 2b

Table 1

No.	Compound	Quantity in g of compound (0·01 mole)	Reaction time in hr.	Details
1		1·8	24	Starting material was recovered
2		1·8	3	Product: 2-bromofluorenone, 2·35 g., 90%, m.p. 134–140°. Recrystallization from alcohol yielded yellow crystals, m.p. 142–143°
3		2·1	5	Starting material was recovered
4		2·1	1½	15 ml of nitrobenzene was used. 3,6-Dibromophenanthrenequinone, 3·1 g, 83%, m.p. 259–276° was formed. Recrystallized from nitrobenzene as orange needles
5		2·1	1	0·6 ml bromine (0·01 *M*) was used. 3-Bromophenanthrenequinone, 2·5 g, 86%, m.p. 286°, was obtained. Recrystallized from glacial acetic acid as orange needles, m.p. 268°
6		2·5	2	2-Nitro-6-bromophenanthrenequinone, 2·8 g, 80%, m.p. 311–312°, was obtained. Recrystallization from nitrobenzene, m.p. 318–318·5°
7		2·5	12	Starting material was recovered[11]
8		3·0	8	Starting material was recovered[11]
		3·0	8	Starting material was recovered[11]

Conditions: Solvent: nitrobenzene 10 ml. Bromine: 1·1 ml, 0·02 mole. Catalyst: benzoyl peroxide 100 mg; irradiated with 75 watt tungsten lamp; temperature inside the reaction vessel: 60 ± 10°.

Presumably the complex is stable in non-polar solvents like carbon tetrachloride but breaks down into components in nitrobenzene.[9] These results provide evidence for the important role which the non-bonding electrons of the oxygen atoms play in the bromination reaction.

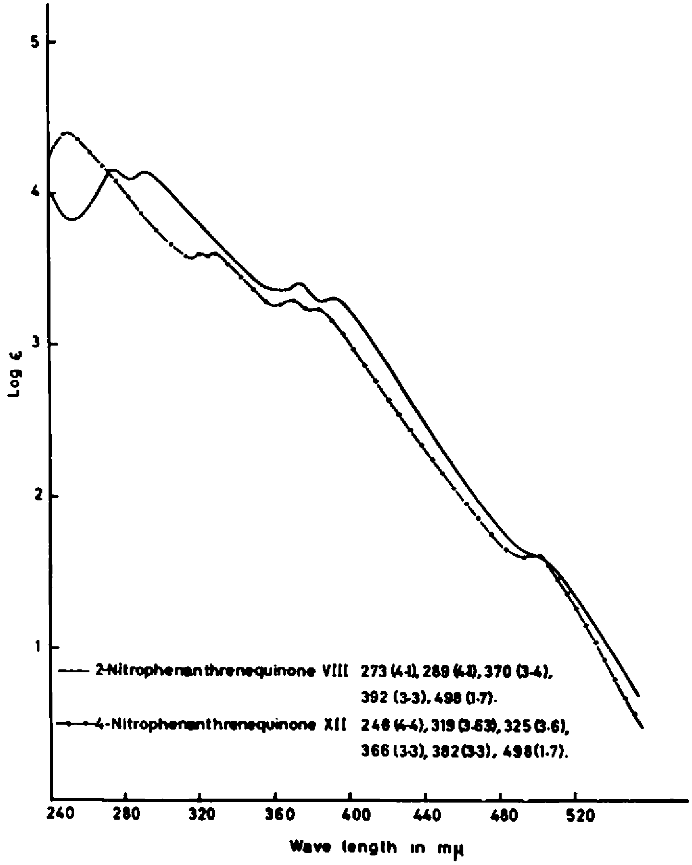


FIG. 3

This view was further strengthened by a study of the effect of structural changes on the reaction. The data obtained with eight carbonyl compounds is summarized in Table 1. A few conclusions may be drawn.

1. Nonquinonoid carbonyl compounds do not undergo the reaction under the conditions studied. Visible light apparently does not excite these compounds. Benzophenone and benzil do not react whereas fluorenone yields 2-bromofluorenone (VII) by substitution in the *meta* position. It was found that bromine reacts with fluorenone even in the dark without peroxides. Plausibly VII is formed by electrophilic substitution.

2. Nitro group deactivates the ring for further substitution. 2-Nitrophenanthrenequinone (VIII) even with excess of bromine gives only 6-bromo derivative (IX) whereas 2,7- (X) and 2,5-dinitrophenanthrenequinone (XI) do not react at all. Ordinarily a nitro group facilitates free radical aromatic substitution.[10]

[9] Because of experimental difficulties, we could not establish this point.

[10] cf. D. R. Augood and G. H. Williams, *Chem. Revs.* **57**, 123 (1957).

The observed behaviour is indicative of a mechanism different from common free-radical aromatic substitution. The absence of reaction with 4-nitrophenanthrenequinone (XII) in contrast to its isomer (VIII) is striking[11] and perhaps provides further support to the mechanism described below. The electronic influence of a nitro group on the unsubstituted ring in VIII and XII may be expected to be small and to a first approximation be assumed to be equal in magnitude. The 6-position being far removed from both 4 and 2 positions, direct steric effect does not exist. The effect of 2 and 4 nitro groups differs markedly in one particular i.e. the distortion of the phenanthrenequinone framework by molecular overcrowding (Figs. 4, 5). It is not possible to accommodate a nitro group in the plane of the aromatic rings. In the competition between the nitro group to remain in the plane of the phenyl group and the two phenyl groups to remain in the same plane, a conformation which is a compromise between the two extremes may result, in which the phenyl groups may get distorted to some extent from a single plane. Westheimer's calculations[12] on the diphenyl, indicate that this is the most likely possibility.

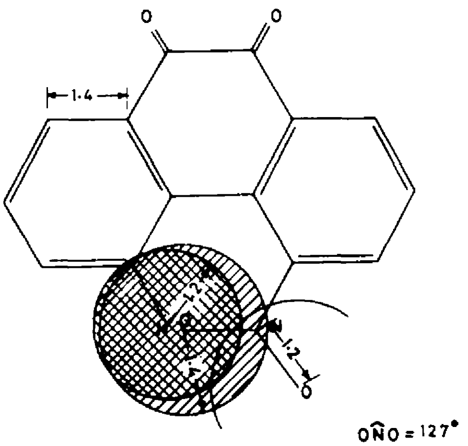


FIG. 4. 4-Nitrophenanthrenequinone

These considerations derive support from a comparison of the reduction potentials of the two quinones (VIII and XII).[13] They differ by 0·012 V, which amounts to a free energy difference of 550 cals. (by application of the relationship $E = -\Delta F/nFy$ where E = reduction potential, ΔF = free energy difference, n = number of equivalents involved in reduction, and Fy = Faraday constant).

	Normal reduction potential in volts at 25° in alcohol
VIII	0·540
XII	0·528

---

[11] We have succeeded in brominating XII to 4-nitro-6-bromophenanthrenequinone under drastic non-photochemical conditions. Report of this work is under preparation.

[12] F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.* **14**, 733 (1946); F. H. Westheimer, *Ibid.* **15**, 252 (1947); cf. F. H. Westheimer in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 523. New York (1956).

[13] L. F. Fieser, *J. Amer. Chem. Soc.* **51**, 3101 (1929).

Presumably this value represents the enthalpy difference, due to the destabilization of the hydroquinone (XIII) with respect to the quinone (XII). In XIII, the 9,10 double bond is less amenable to distortion than the corresponding single bond in the quinone. The steric requirement for aromaticity imposes a more exacting demand for planarity of the phenanthrene framework. Consequently, XIII with a nitro group in the 4-position is destabilized. It may therefore be argued that the excited state analogous to XIV, XV and XVI, involved in the bromination of XII has relatively higher energy compared to similar entity derived from VIII.

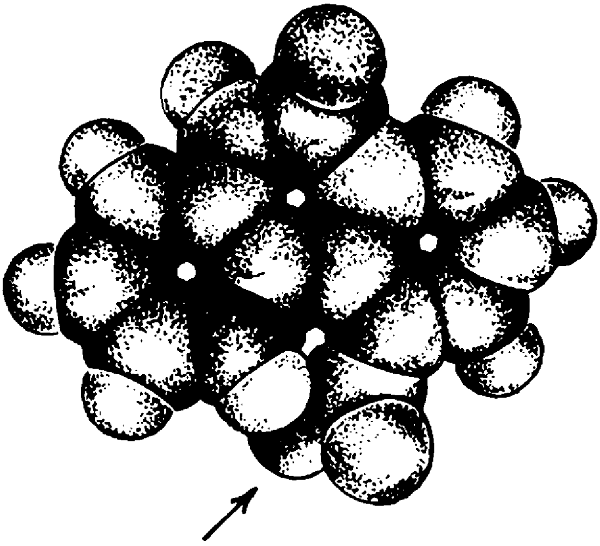


Fig. 5. Model of 4-nitrophenanthrenequinone.

Mechanism of the reaction

The necessity to account for the function of visible light and also of peroxides, requires to suppose that the reaction takes place between an excited state of the

Chart 1

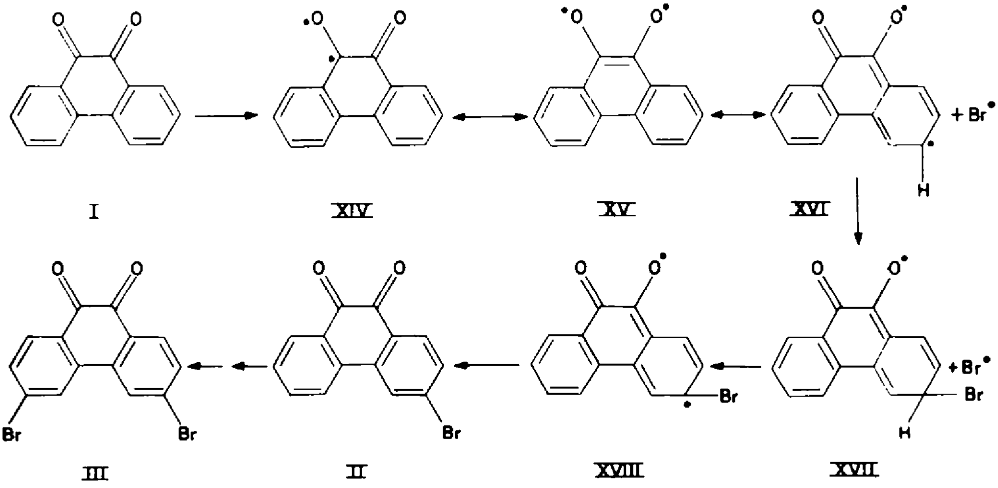
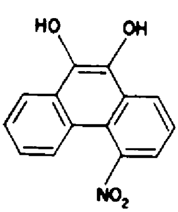
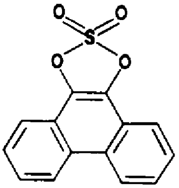


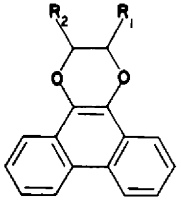
Chart 2



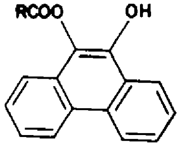
XIII



XIX



XX



XXI

quinone and bromine atoms. Accordingly a mechanism is now advanced. The excited state may be attained both by heat and light. An important question that arises is, whether it is possible to define the structure of the excited state and to isolate the absorption band responsible for it and learn about the nature of the transition. In fact the present experiments make this possible. The electronic spectrum of I has four bands in the 220 to 700 mμ region (Fig. 1), viz. at 256, 265, 322 and 422 mμ in alcohol.[14] The Pyrex vessel in which the reaction was conducted does not transmit light below 300 mμ.[15] Moreover as nitrobenzene has an absorption band[16] at 330 mμ it would filter this wavelength effectively. The visible radiation which reaches I under the experimental conditions is absorbed only at 422 mμ (alcohol). This absorption band shows a hypsochromic shift on changing the solvent from chloroform to acetonitrile (Fig. 1; chloroform 420 mμ, ethyl alcohol 422 mμ, acetonitrile 412 mμ). This type of shift of the maxima depending on the solvent polarity indicates that it involves a n → π* transition.[17,18] The nonbonding electrons of the oxygen atoms, which are in the plane of the aromatic ring in the ground state get promoted into the antibonding π* orbital of the carbonyl group, into the plane perpendicular to the aromatic ring, i.e. in the plane of the π cloud of the aromatic ring. In this position the electron is capable of getting stabilized by delocalization resulting in a resonance stabilized diradical, described by three of its canonical forms (XIV, XV and XVI). The unpaired electron density at 3 and 6 positions makes them sites of reactivity. Contrary to the normal electrophilic substitution pattern, the carbonyl groups, therefore, behave as *o*-, *p*-directing groups in this reaction.[19]

---

[14] P. K. Seshan, *Proc. Indian Acad. Sci.* A3, 172 (1936).

This author reports the following maxima for the vapour of I taken at 140–240°. The spectrum is very different from spectrum of I in solvents (Fig. 1).

Vapour	244	258	305	377 mμ
Solution (alcohol)	256	264	326	427 mμ

The great dissimilarity may be due to the vapour of I, existing principally or to a large extent as diradical (XV). A detailed study of the spectra of phenanthrenequinone derivatives is in progress in this laboratory with G. Srinivasan.

[15] A. H. Taylor and L. L. Holladay, *Trans. Illum. Eng. Soc.* **26**, 711 (1931), cited in C. Ellis and A. A. Wells: *The Chemical Action of Ultraviolet Rays* p. 181. Reinhold, New York (1941).

[16] K. L. Wolf and W. Herold, *Z. physik. Chem.* **B13**, 201 (1931).

[17] M. Kasha, *Dis. Farad. Soc.* **9**, 14 (1950).

[18] J. W. Sidman, *Chem. Revs.* **58**, 689 (1958).

[19] It is conceivable that this substitution pattern is not restricted to quinones, or even to ketones. In the case of *ortho* quinones discussed in the present paper, these excited states are easily accessible under mild conditions because they have greater resonance stabilization than the parent quinone. With aryl ketones or with the nitro compounds the diradicals may require higher energy radiation for their formation.

The absence of reaction with the ring having a nitro group in the 2 or 4 positions (cf. Table 1, No. 6 to 9) may be rationalized on the view that a nitro group decreases the electron density by delocalization. The possibility of a primary steric factor may not exist.

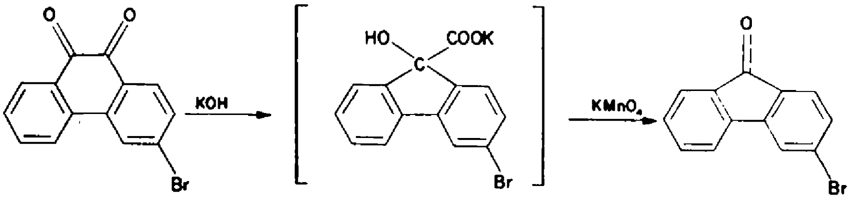
The catalytic influence of peroxides on the reaction and the qualitative observation that the rate of the reaction increases with increasing the concentration of the reactants (unpublished observation) suggests a bimolecular rate-determining step. Perhaps this step consists of hydrogen abstraction from the σ complex XVII by bromine atoms.

It would be logical to enquire whether reactions of other canonical forms particularly XV are realized. The photochemical reaction of I with sulphur dioxide to form 9,10-hydroquinone sulphate (XIX)[20] and addition of I to olefins to form *p*-dioxanes (XX)[21] probably involves XV in the transition state. The electronic transitions responsible for these reactions and the nature of the intermediary species await a more detailed study. The reaction (I) with aldehydes in the presence of UV radiation to form acyl derivatives of 9,10-hydroquinone (XXI) may also result from an excited state similar to XV.[22,23]

Structure of the products

The structure of II and III have been established by earlier workers[5,24] by degradation experiments. We have however confirmed the structure of II by converting it into 3-bromo fluorenone (XXII) by a ring contraction, followed by oxidation procedure as shown:

Chart 3



II

XXII

The structure of XXII was established by unambiguous synthesis from 2-amino-4'-bromobenzophenone (XXVI) prepared by the sequence shown in Chart 4.

The acid chloride (XXIV) and the amide (XXV) have the pseudo structure, in chloroform solution. Although these compounds have been described earlier,[25] the described properties of these compounds differ from those of the present work. The structure of XXV is based on its elemental analysis, IR spectrum, and conversion to 2-bromoanthraquinone. The earlier workers report a m.p. of 184–184·5° for the amide whereas we find m.p. 210–211°. These workers have reported only bromine

---

[20] G. O. Schenck, *Naturwissenschaften* **40**, 229 (1953); G. O. Schenck and G. A. Schmidt-Thomes, *Liebig's Ann.* **584**, 199 (1953).

[21] A. Schonberg and A. Mustafa, *J. Chem. Soc.* 387 (1944); 2126 (1948).

[22] H. Klinger, *Liebig's Ann.* **249**, 137 (1889).

[23] A. Schonberg and R. Moubasher, *J. Chem. Soc.* 1430 (1939).

[24] J. Schmidt and G. Ladner, *Ber. Dtsch. Chem. Ges.* **37**, 3571 (1904).

[25] H. F. Miller and G. B. Bachmann, *J. Amer. Chem. Soc.* **57**, 2443 (1935).

Chart 4

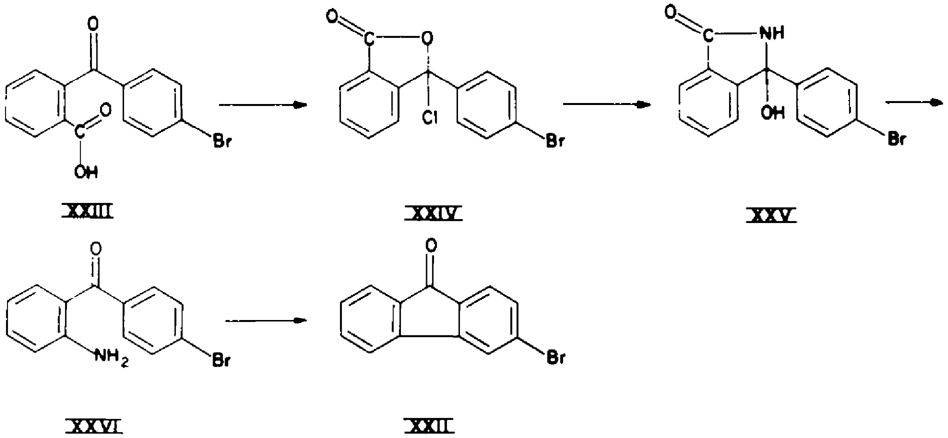
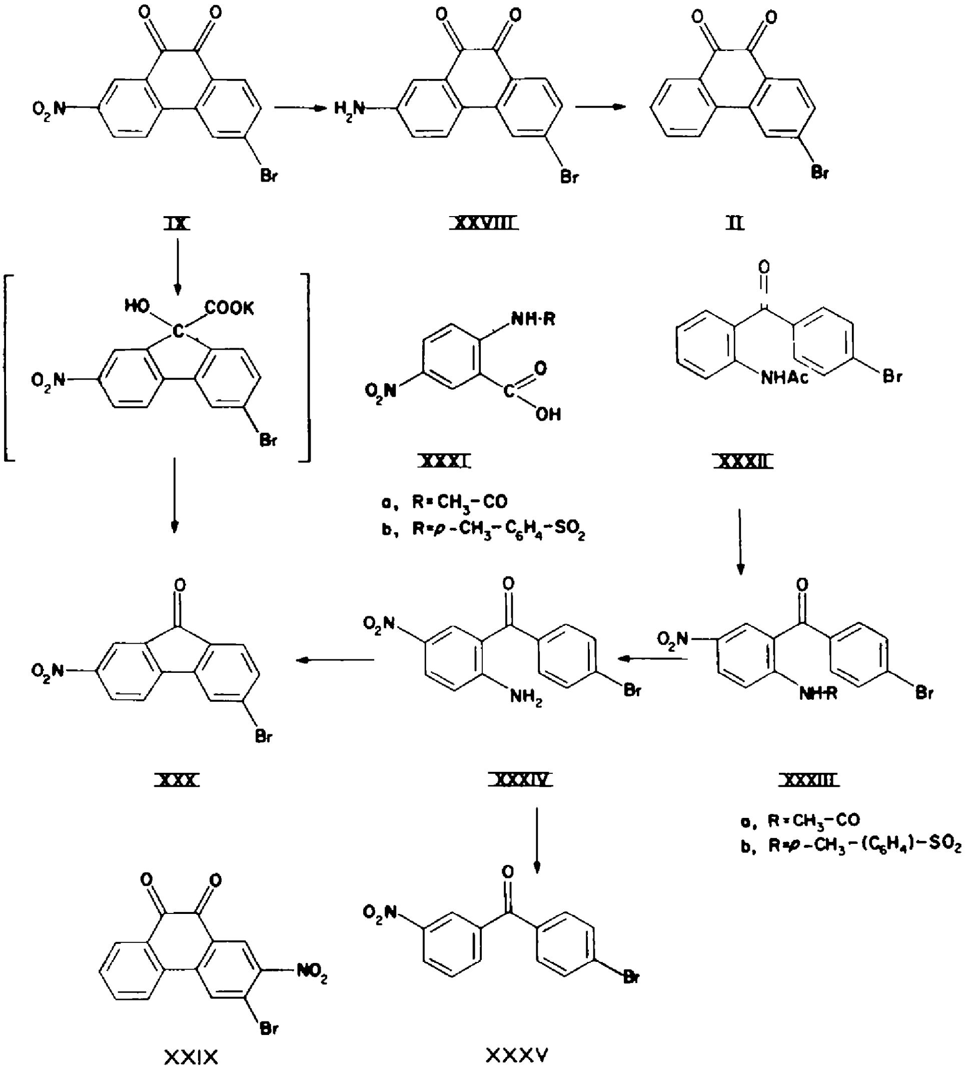


Chart 5



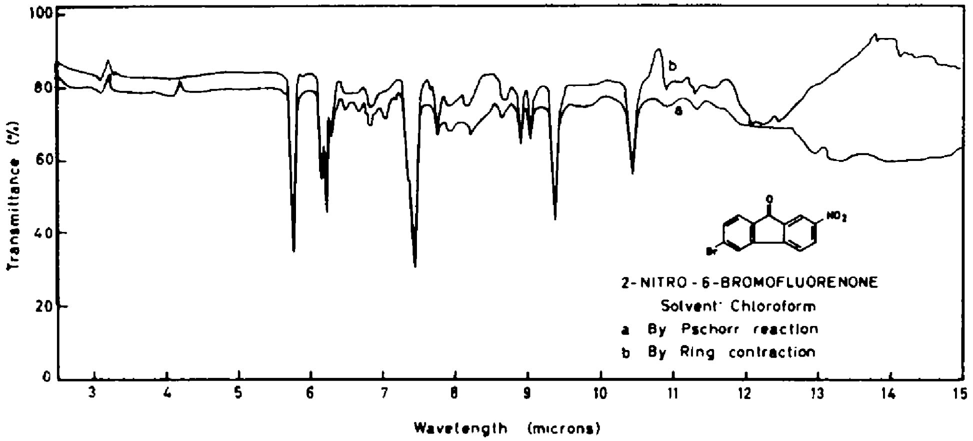

100
80
60
40
20
0
Transmittance (%)
3
4
5
6
7
8
9
10
11
12
13
14
15
Wavelength (microns)
a
b
O
NO2
Br
2-NITRO-6-BROMOFLUORENONE
Solvent: Chloroform
a By Pschorr reaction
b By Ring contraction

FIG. 6

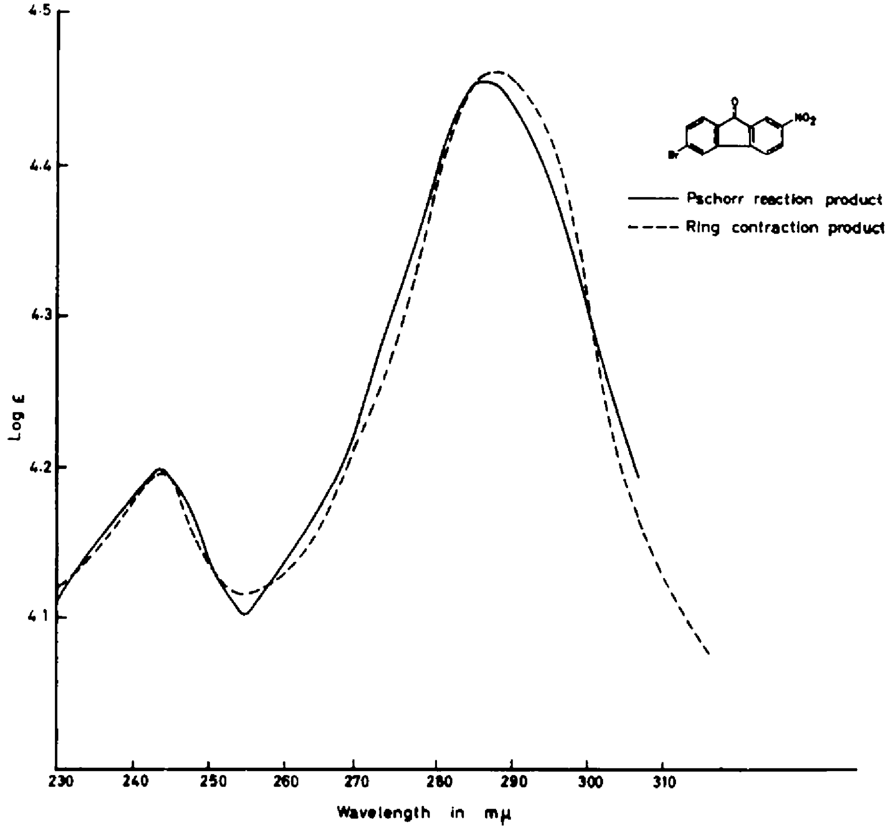

4·5
4·4
4·3
4·2
4·1
Log ε
230
240
250
260
270
280
290
300
310
Wavelength in mμ
O
NO2
Br
Pschorr reaction product
Ring contraction product

FIG. 7

analysis for the amide, which would not differ from that of the parent acid. We do not believe that the discrepancy could have arisen due to the amide being in two tautomeric forms, i.e. open and the cyclic forms.[26]

The Hofmann reaction of the amide did not proceed smoothly. Generally a substantial amount of the amide was hydrolysed to the acid resulting in poor conversion to the amine.[27] The Pschorr reaction of XXVI yielded a product which was identical in all respects (m.p., mixed m.p. and IR spectrum) with the product obtained from II.

The structure of 6-brom o-2-nitrophenanthrenequinone (IX) was established by degradation as well as by synthesis. It was reduced to the aminohydroquinone (XXVII), by tin and hydrochloric acid and oxidized by air to 2-aminoquinone (XXVIII). Diazotization and reduction furnished II. The formation of II itself did not constitute an adequate proof for the structure of IX, because 2-nitro-3-bromophenanthrenequinone (XXIX) could also yield II by the same sequence of reactions. To decide between the two possibilities (IX and XXIX), the material was treated with alkali and oxidized to a fluorenone derivative. The fluorenone was found to be identical with 2-nitro-6-bromofluorenone (XXX) prepared by synthesis. The identity was established by mixed m.p. of the ketones and of the oximes, and comparison of IR and UV spectra (Figs. 6 and 7).

We planned to prepare XXXIIIb by the reaction of the acid chloride of XXXIb with bromobenzene. Two methods of synthesis of XXXIb were tried without success. Nitration of acetylanthranilic acid yielded 5-nitroacetylanthranilic acid in 60–66% yield. Hydrolysis with concentrated hydrochloric acid gave 5-nitroanthranilic acid in 98% yield. Attempts to prepare the tosyl derivative by both the pyridine, as well as the alkali method did not succeed. Nitration of tosylanthranilic acid yielded a product whose elemental analysis did not correspond to XXXIb. Finally, we succeeded in preparing XXXIIIa by nitrating XXXII. To rule out the unlikely possibility of the nitro group entering the ring having the bromine atom, the nitro product was hydrolysed and deaminated to bromonitrobenzophenone which was shown to be 3-bromo-4′-nitrobenzophenone (XXXV) by comparison with an authentic sample. Pschorr reaction of the amine (XXXIV) furnished 2-nitro-6-bromofluorenone m.p. 264–265°. The UV and IR spectra and m.p. of the compound were identical with that of the product obtained from IX. Mukherjee and Watson[28] brominated VIII in acetic acid at 140° for 2 hr and obtained a monobromo derivative as reddish yellow plates, m.p. "above 300°." By repetition of their procedure, we have obtained a greenish brown material, m.p. 305–307° (dec), which was shown to be identical with IX by mixed m.p. determination and comparison of the m.p. and mixed m.ps of the quinoxaline derivatives and the derived diphenic acids. Consequently the product of Mukherjee and Watson has structure IX.

2-Bromo- and 2,7-dibromo derivatives have been prepared from the corresponding nitro compounds, through the amines or by pressure reaction from I.[29] It has been possible to obtain these compounds directly from I by bromination in the presence of silver nitrate.

---

[26] Unpublished observations with K. M. Kamath.

[27] We have examined this reaction in great detail and the results will be published separately.

[28] K. C. Mukherjee and E. R. Watson, *J. Chem. Soc.* 109, 617 (1916).

[29] J. Schmidt and E. Junghans, *Ber. Dtsch. Chem. Ges.* 37, 3558, 3567 (1904).

TABLE 2

No.	Starting material	Product	Conc. of compound in moles/l. of nitrobenzene solution	Conc. of bromine in moles/l. of nitrobenzene solution	Temp. °C	Time hr	Conditions	Reference
1.	I	II	0·12	0·27	110	10	Nonphotochemical	4
2.	I	III	0·81	3·3	100	5·5	Nonphotochemical	4
3.			0·25	1·2	80–85	1·5	Dark	Present work
4.	I	II	1	1·2	50–60	1	Photochemical	Present work
5.	I	III	0·67	1·4	50–60	1·5	Photochemical	Present work
6.	I	II	1	1·2	80–85	0·25	Photochemical	Present work

EXPERIMENTAL

All m.ps are uncorrected. Many of the UV spectra recorded were taken by G. Srinivasan on DU Beckmann Spectrophotometer.

General procedure for bromination

The carbonyl compound (0·01 mole), dry nitrobenzene (10 ml), dry Br_2 (1·1 ml, 0·02 mole) and benzoyl peroxide (100 mg) were placed in a flask fitted with a Liebig condenser carrying a $CaCl_2$ guard tube and a thermometer dipping inside the reaction mixture. This apparatus was enclosed in an asbestos box, fitted with a 75 watt tungsten lamp. By the adjustment of the distance of the flask from the lamp, the temp of the reaction mixture could be varied between 50–85°. At the end of the reaction period, the contents of the flask were treated with steam and the residue was crystallized. In cases where bromination did not proceed the recovery of the starting material ranged from 70 ± 10%. The identity of the material was checked by mixed m.p. determination with the starting material. Further details of the experiments are given in Table 1 and 2 or in the description of individual procedures.

3-*Bromophenanthrenequinone* (II)

A mixture of phenanthrenequinone (I, 2·1 g), dry nitrobenzene (10 ml) and dry Br_2 (6 ml; dried over conc. H_2SO_4) and benzoylperoxide (100 mg) was exposed to the tungsten lamp. Within about 10 min, evolution of gas bubbles could be seen. The temp of the reaction mixture was 70 ± 5°. After about 1 hr the evolution of gas became imperceptible and clusters of needles gradually separated. The nitrobenzene was then removed by steam distillation. The residue (2·5 g; 86%), m.p. 225–240°, crystallized from acetic acid in yellow needles (1·5 g), m.p. 264–266°. Lit.[4] m.p. 268–269°.

By warming the quinone on a water bath with *o*-phenylenediamine in acetic acid, a *quinoxaline* derivative was prepared; m.p. 251–252·5°, Lit.[4] m.p. 249°.

In a similar experiment with half the quantities, at 80–85° the reaction was complete in about ¼ hr. Yield after 3 crystallizations from acetic acid was 0·4 g, m.p. 254–258°.

Reaction in the absence of light

A mixture of I (500 mg), benzoyl peroxide (50 mg) and nitrobenzene solution of bromine (2·5 ml, 1·2 M) was heated in the absence of light (by covering with black cloth). Evolution of HBr stopped after 1½ hr. The reaction mixture was worked up as before yielding 360 mg crystals, m.p. 245–252° (shrinking at 230°). Recrystallizations from acetic acid yielded yellow needles, m.p. 261–264°, undepressed when mixed with authentic specimen of II.

3,6-*Dibromophenanthrenequinone* (III)

A mixture of I (2·1 g), Br_2 (1·1 ml), nitrobenzene (15 ml) and benzoyl peroxide (100 mg) was exposed to the tungsten lamp. The evolution of gas became imperceptible after about 1½ hr and the colour of Br_2 disappeared from the reaction mixture. On cooling to laboratory temp clusters of brown crystals were separated by filtration, washed with alcohol and dried (2·7 g). The mother liquor was treated with alcohol (25 ml) and cooled in ice. A second of the crop of crystals was obtained (0·4 g), total yield: 3·1 g (83%), m.p. 259–276°. Crystallizations from nitrobenzene furnished orange needles, m.p. 285–286°; Lit.[4] m.p. 286–287°. Quinoxaline derivative was prepared from acetic acid; m.p. 333–334°; Lit.[4] m.p. 333–334°.

Effect of variations of conditions

Carbon tetrachloride as solvent. A solution of Br_2 (0·5 ml) in 25 ml of dry CCl_4, was refluxed with I (500 mg) and benzoyl peroxide (50 mg) for 6 hr. Evolution of HBr was not observed. The reaction mixture was cooled to 25° and filtered. The residue (m.p. 205–206°) was dissolved in saturated $NaHSO_3$ aq. (II is insoluble under these conditions) and regenerated with Na_2CO_3, yield 0·4 g yellowish orange crystals, m.p. 205–208°, undepressed when mixed with authentic sample of I.

N-*Bromosuccinimide as brominating agent.* A suspension of I (2·1 g), N-bromosuccinimide (1·8 g), benzoyl peroxide (200 mg) in 30 ml dry benzene was exposed to a 75 watt lamp for 2½ hr without additional heating. Again it was refluxed on a water bath for 1½ hr and filtered hot. The residue was washed with hot benzene, and recrystallized from benzene in shining orange flakes, 0·3 g, m.p. 204–205°. The benzene mother liquor and first filtrate were boiled with water, benzene layer was separated, dried and concentrated. A further quantity of orange yellow flakes was obtained, 1·2 g, m.p. 198–200°. Both the products dissolved in saturated $NaHSO_3$ aq., and their m.p.'s were undepressed when mixed with pure I.

Reaction in the absence of benzoyl peroxide. A mixture of I (1·05 g), and dry nitrobenzene solution of bromine (5 ml, 1·2M) was taken in the usual apparatus and exposed to light from the tungsten lamp at 80°. Even after 1½ hr there was no evolution of gas. The reaction mixture was cooled to 25° and treated with 20 ml alcohol and the solid separated was filtered off, m.p. 190–193°. All the solid dissolved in $NaHSO_3$ aq. and was regenerated by treatment of the solution with Na_2CO_3. The nitrobenzene–alcohol mother liquor was steam distilled and the residue also treated with $NaHSO_3$ aq. Most of the material dissolved and was regenerated as usual, m.p. 198–200°.

Acetic acid as solvent. Phenanthrenequinone (I, 1·05 g), Br_2 (1·0 ml), acetic acid (10 ml) and reduced Fe powder (200 mg) were refluxed 12 hr. The reaction mixture was diluted with excess water and filtered. The residue was boiled (with sat. $NaHSO_3$ aq.) and filtered. From the filtrate was obtained after acidification and boiling 0·5 g of an orange solid, m.p. 198–200° (undepressed when mixed with I).

2-*Bromofluorenone* (VII)

A mixture of fluorenone (1·8 g, 0·01 mole), dry nitrobenzene (10 ml), Br_2 (1·1 ml, 0·02 mole) and benzoyl peroxide (100 mg) was exposed to the tungsten lamp as usual. After 3 hr no more HBr was evolved. The reaction mixture was treated with alcohol and cooled in a freezing mixture. The solid was separated and washed with ice-cold alcohol. Crystallization from alcohol yielded 1·05 g yellow crystals, m.p. 134–140°. A further quantity of 0·4 g was recovered from the mother liquor by cooling in ice. Evaporation of the mother liquor yielded a dark residue which on crystallization from alcohol furnished 0·9 g of the material, total yield 2·35 g (90%). Recrystallization from alcohol gave yellow crystals, m.p. 142–143°; lit.[30] 142–143° for 2-bromofluorenone and 165·5°[31] for 3-bromofluorenone. It was observed that bromination could be brought about in the absence of light and peroxide but with only slight warming of the reaction mixture. The product was the same as prepared under the previous conditions. Both these products were identical with 2-bromofluorenone (mixed m.p.) and different from 3-bromofluorenone (depression of mixed m.p.).

2-*Nitrophenanthrenequinone* VIII

Nitration procedure was essentially that of Courtot.[30] The isolation of VIII has been carried out differently. Phenanthrenequinone (20 g), and HNO_3 (sp. gr. 1·39–1·40, 600 ml) were taken in a round

[30] Ch. Courtot, *Ann. Chim.* (10) **14,** 5 (1930).

[31] P. J. Montagne and T. M. van Charante, *Rec. Trav. Chim.* **32,** 164 (1913).

bottomed flask with a thermometer dipping in the reaction mixture and boiled vigorously for 25 min (when larger quantities were used the reaction mixture was distilled). The temp of the dark red solution rose from 100 to 120°. Under no circumstances was the temp allowed to rise to 125° and above. The final volume of the liquid on cooling was about 450 ml and sp. gr. 1·40. It was kept at room temp for 12 hr, during which period clusters of thick reddish orange crystals formed. These were separated by filtration or by decantation and washed with small quantities of ice-cold dil. HNO_3, and water and dried, yield 10 g (42%), m.p. 256–258°; lit.[30] 258°.

The reddish brown mother liquor was diluted with water and the solid consisting of a mixture of VIII and XII furnished more VIII when crystallized according to the procedure of Courtot.[30]

2-*Nitro-6-bromophenanthrenequinone* (IX)

Peroxide catalyzed reaction. 2-Nitrophenanthrenequinone (2·5 g, 0·02 mole), dry nitrobenzene (10 ml), dry Br_2 (1·1 ml, ca. 0·04 mole) and benzoyl peroxide (100 mg) were taken in a round bottomed flask and exposed to the tungsten lamp as usual. After 2 hr, absolute ethanol (25 ml) was added to the reaction mixture and cooled in ice. Golden yellow glistening plates that separated were collected and dried at 110°, yield 2·8 g, (80%) m.p. 311–312°. A further quantity could be recovered from the mother liquor, but it was very impure. The bromo compound recrystallized from nitrobenzene in glistening plates, m.p. 318–318·5°. (Found: N, 4·15. $C_{10}H_6O_4NBr$ requires: N, 4·22%). The quinone gives a brown solution in conc. H_2SO_4. A *quinoxaline* derivative was prepared from acetic acid by boiling for 15 min, with *o*-phenylenediamine m.p. 318–318·5° (xylene). (Found: N, 10·76. $C_{20}H_{10}O_2N_3Br$ requires: N, 10·40%). The quinoxaline gives a bright red coloured solution in conc. H_2SO_4.

2-*Nitro-5′-bromodiphenic acid* XXXVI

2-Nitro-6-bromophenanthrenequinone (1 g), glacial acetic acid (20 ml) and H_2O_2 (5 ml, ca. 25%) were refluxed 3 hr. The reaction mixture was diluted with water and filtered. The residue was treated with 3N NaOH and filtered, rejecting a small amount of insoluble material. The alkaline filtrate was acidified, and solid formed was treated with $NaHCO_3$ aq., and then separated from the insoluble material. Acidification of the filtrate gave a material, m.p. 262–264°. Recrystallization from dil. acetic acid yielded transparent shining light-brown cubes, m.p. 271–272°. (Found: N, 3·80. $C_{14}H_8O_6NBr$ requires: N, 3·82%). The $NaHCO_3$ aq. insoluble material was probably the lactone of 4-nitro-5′-bromo-2′-hydroxydiphenyl-2-carboxylic acid or of 4′-nitro-5-bromo-2′-hydroxydiphenyl-2-carboxylic acid. This material was not examined further.

2-*Nitro-6-bromophenanthrenequinone* IX

Bromination in acetic acid solution. The experimental conditions are based on the work of Mukherjee and Watson.[28]

2-Nitrophenanthrenequinone (5 g, ca. 0·025 mole), Br_2 (4 ml) and acetic acid (40 ml) were taken in a closed soda water bottle and heated in an oil bath maintained at 140 ± 5° for 2 hr. At the end of the period the bath was allowed to cool to laboratory temp and the press. released. The dark-coloured reaction mixture was filtered and the solid was washed with water and dried at 110°. The greenish brown solid, m.p. 305–307° (dec) (5·4 g, 77%) was insoluble in organic solvents except in hot nitrobenzene and pyridine. All attempts to remove the extraneous colour by crystallization and norite treatment were unsuccessful. The m.p. of the product was not depressed when mixed with the bromo product IX obtained by radical bromination. It was observed that when the temp of the bath was raised above 150°, an impure product, which could not be recrystallized was obtained. Below 140°, no bromination took place. The quinoxaline derivative prepared as before had m.p. 318–318·5° alone or when mixed with the derivative from the product of photochemical reaction.

A diphenic acid, m.p. 271–272° (acetic acid) was prepared as above by the oxidation of the quinone. Its m.p. was undepressed when mixed with XXXVI.

3-*Bromofluorenone* XXII

By ring contraction of II. Well-powdered II (90 mg) was added to a mechanically stirred boiling solution of $KMnO_4$ (0·5 g) and KOH (4 g) in water (10 ml). Heating and stirring were continued

1 hr. The reaction mixture was cooled and filtered. The residue was suspended in water and enough $NaHSO_3$ added and the mixture boiled to dissolve all dark material. The resulting suspension of yellow crystals was filtered off, washed with water, dried and crystallized from benzene to yield a product (20 mg); m.p. 163–164°; lit.[31] m.p. 165·5°. The m.p. was not depressed when mixed with a specimen of 3-bromofluorenone prepared as described herein under.

2-(4′-*Bromobenzoyl*)-*benzamide* (XXV)

2-(4′-Bromobenzoyl)-benzoic acid (XXIII) was prepared by the method of Ullman and Sone.[32] To a suspension of the acid (36 g; 0·125 mole) in dry benzene (100 ml), PCl_5 (27 g, 0·125 mole) was added. A vigorous reaction started in the cold. In about 2 hr a clear solution was obtained with profuse evolution of HCl. The solvent and $POCl_3$ were removed under water pump suction. The residual jelly was soluble in chloroform. All attempts to crystallize it were unsuccessful. Miller and Bachmann[25] record m.p. 162–163° for the acid chloride XXIV. The IR spectrum showed a single carbonyl band at 5·58 μ, in chloroform solution indicating pseudo acid chloride structure.

A solution of the acid chloride in dry chloroform (150 ml) was added to about 100 ml liquid ammonia, with the tip of the dropping funnel dipping inside the liquid. The ammonia was allowed to evaporate and the residual solid was triturated with Na_2CO_3 aq., filtered, boiled with water, again filtered and the solid dried at 110°. The amide, m.p. 200–202° with softening at 196° was obtained as felt-like crystals (35 g, theoretical yield). After crystallizations from alcohol, needles, m.p. 210–211°, were obtained.

The amide could also be crystallized from xylene or acetone. Miller and Bachmann[25] record m.p. 184·5–185·0. IR spectrum: $\nu_{max}^{CHCl_3}$ 2·8 μ (—OH), 5·83 μ (lactam $>$C=O); ν_{max}^{Nujol} 2·8–3·0 μ (—OH, NH) 5·83 μ (amide $>$C=O), 6·0 μ (ketone $>$C=O). (Found: C, 55·52; H, 3·25; N, 4·82. Calc. for $C_{14}H_{10}O_2NBr$; C, 55·29; H, 3·31; N, 4·61%). The amide (XXV; 100 mg) was heated with fuming H_2SO_4 (5 ml, 20%) at 100° for 1 hr and poured into crushed ice. The solid was collected and crystallized from toluene to yield a product, m.p. 204–205°, undepressed when mixed with an authentic sample of 2-bromoanthraquinone,[33] m.p. 209·6°.

2-(4′-*Bromobenzoyl*)-*aniline* (XXVI)

We did not succeed in preparing the desired amine (by following the directions of Miller and Bachmann[25]). The following procedure was worked out after some experimentation. Sometimes a side product, m.p. 146–148°, was also formed. A detailed study of the Hofmann reaction of substituted *o*-benzoylbenzoic acid amides and the structures of the side products is in progress in this laboratory. Sodium hypobromite was prepared from Br_2 (1·4 ml, 0·025 mole) and ice-cold NaOH (100 ml, 10%). A homogeneous solution obtained from XXVI (6 g, 0·02 mole), NaOH (30 ml, 10%) and alcohol (30 ml), was added to the hypobromite solution, cooled in ice and stirred for 5 min, and refluxed for 1 hr and again cooled in ice. The amine separated as a yellow crystalline cake; 1·7 to 3 g (32–55%); m.p. 89–93°. Recrystallizations from alcohol or benzene–petrol yielded yellow glistening flakes, m.p. 111–113°; lit.[26] m.p. 107° (Found: N, 5·22. Calc. for $C_{13}H_{10}NBr$: N, 5·08%). The mother liquor on acidification yielded 2·1 to 3·9 g (35–65%) of XXIII.

3-*Bromofluorenone* (XXII)

By Pschorr reaction. The hydrochloride of XXVI was prepared by boiling a mixture of the amine (2·76 g) and conc. HCl aq. (60 ml) and water (40 ml). The hot solution was filtered from the insoluble material (0·25 g) and the filtrate was cooled in freezing mixture, when cream coloured crystals of the hydrochloride separated out. The cold suspension was treated with $NaNO_2$ aq. (840 mg in 10 ml water), below 5°. It was stirred for 0·5 hr, allowed to stand for 0·5 hr more and filtered. The clear solution was heated on the water bath 2 hr. The separated yellow solid was collected, washed with water, extracted with 3N NaOH, filtered, and washed again and dried, yield, 1·65 g. On vacuum sublimation and crystallization from benzene, the fluorenone crystallized in yellow needles, m.p. 163–164°; lit.[31] m.p. 165·5°. Acidification of the alkaline solution furnished 0·65 g. of a phenolic material which was not examined further.

---

[32] F. Ullmann and M. Sone, *Ann.* **380**, 337 (1911).

[33] P. H. Groggins, A. J. Stirton and H. P. Newton, *Ind. Eng. Chem.* **23**, 893 (1931).

Conversion of 2-nitro-6-bromophenanthrenequinone (IX) *to 3-bromophenanthrenequinone* (II)

2-*Amino-6-bromophenanthrenequinone* (XXVIII). A mixture of IX (2·0 g), granulated tin (4·0 g), alcohol (70 ml) and conc. HCl (30 ml) and water (30 ml) was heated on a water bath for 3 hr, when most of the tin reacted. The hot straw coloured solution was filtered and the filtrate treated with conc. HCl aq. (100 ml) and cooled in freezing mixture. A separated light yellow solid was collected, dissolved in water and basified with NaOH aq. Air was bubbled through the resulting green suspension, in which excessive frothing was prevented by a layer of benzene. A dark pink solid was collected and dried; yield, 1 g, m.p. > 360°. The amine was sparingly soluble in most organic solvents. It could be crystallized from nitrobenzene in glistening pink needles, m.p. > 360° (Found: C, 54·93; H, 2·94; N, 4·80 $C_{14}H_8O_2NBr$ requires: C, 55·63; H, 2·65; N, 4·64%). A yellow quinoxaline derivative was prepared from acetic acid solution, m.p. > 360°. (Found: N, 11·50; $C_{20}H_{12}N_3Br$ requires: N, 11·23%). A solution of XXVIII (0·3 g) in conc. H_2SO_4 (3 ml) was cooled in freezing mixture and $NaNO_2$ aq. (0·4 ml, 20%) was added, keeping the temp below 5°. After ½ hr, a saturated solution of $NaH_2PO_2 \cdot H_2O$ (3 g) was added slowly and allowed to remain for 24 hr in the freezing mixture. At the end of the period a yellowish orange solid had separated. The solid was collected, purified by vacuum sublimation and crystallization from acetic acid. Orange yellow, glistening plates, m.p. 267–268°, alone or when mixed with a specimen of II prepared by the method of Schmidt and Eitel.[4] A *quinoxaline* derivative prepared from acetic acid, crystallized from benzene m.p. 251–252·5° alone or when mixed with an authentic specimen.

Conversion of 2-nitro-6-bromophenanthrenequinone to 2-nitro-6-bromofluorenone (XXX)

Finely powdered IX (2·0 g) was added gradually with mechanical stirring to a boiling solution containing $KMnO_4$ (10 g), KOH (20 g) and water (200 ml). The reaction mixture was heated and stirred for a further peroid of 1 hr, cooled, diluted and filtered. The residue was suspended in water, and boiled with enough $NaHSO_3$ to react with MnO_2. The yellow solid (1·73 g) left undissolved was collected, dried and crystallized from xylene in yellow glistening flakes, m.p. 264–265°. (Found: C, 51·17; H, 2·26; N, 4·63; $C_{13}H_6O_3NBr$ requires: C, 51·31; H, 1·97; N, 4·61%). An *oxime* was prepared from absolute alcohol and dry pyridine. It crystallized from alcohol in greenish yellow micro crystalline powder, m.p. 256–257° (Found: N, 9·37; $C_{13}H_7O_3N_2Br$ requires N, 8·78%).

5-*Nitroacetylanthranilic acid* (XXXI)

Acetylanthranilic acid was prepared from anthranilic acid by acetylation with acetic anhydride in 96% yield (m.p. 180–182°). Using fuming HNO_3 for nitration, Baly *et al.*[34] reported 85% yield of the nitro derivative. Bogert and Scatchard,[35] however, could obtain the product only in 39% yield. The procedure described below is based on these reports. Optimum conditions have been found after experimentation.

Acetylanthranilic acid (30 g) was added with stirring to HNO_3 aq. (60 ml, sp. gr. 1·5), cooled in the freezing mixture, without allowing the temp to rise above 5°. It was allowed to remain in the freezing mixture for 12 hr, and at the laboratory temp for 1½ hr, and then treated with ice, and the yellowish orange micro crystalline solid was collected, washed and dried in the desiccator; yield, 22·5 to 24 g, (60–66%) m.p. 206–210°. The yield is affected by the period of keeping the reaction mixture at the laboratory temp. If worked up directly after taking out of the freezing mixture, the nitration is not complete. If kept for 4 hr, gummy material difficult to crystallize resulted.

Hydrolysis of the nitro derivative with hot conc. HCl aq. yielded 5-nitroanthranilic acid in 98% yield. Contrary to a previous report it was observed that dilute acid did not hydrolyse the acetyl derivative (cf. 35). 5-Nitroanthranilic acid crystallized in transparent yellow needles from dil. acetic acid, m.p. 268°; lit.[35] 278°.

Tosylation of 5-nitroanthranilic acid in alkali solution did not yield the desired tosyl derivative. It was also not formed when dry pyridine solutions of the reactants were heated on a water bath for 3 hr.

Nitration of tosylanthranilic acid

Tosyanthranilic acid was prepared by the method of Ullmann and Blaier.[36] Strangely the crude

---

[34] E. C. Baly, W. B. Tuck and E. G. Marsden, *J. Chem. Soc.* **97**, 1494 (1910).

[35] M. T. Bogert and G. Scatchard, *J. Amer. Chem. Soc.* **41**, 2065 (1919).

[36] F. Ullman and H. Blaier, *Ber. Dtsch. Chem. Ges.* **35**, 4273 (1902).

product had m.p. 225–227°, which on crystallization from acetic acid changed to 217–218° as reported.[36] Pure, dry tosylanthranilic acid (9·5 g) was added to fuming HNO_3 (50 ml, sp. gr. 1·5), cooled in freezing mixture, keeping the temp below 5°. After standing for 12 hr in the freezing mixture, addition of crushed ice, yielded a cream-coloured solid (sometimes brownish white) which was collected, washed, dried in a desiccator; yield 6 g. It crystallized in light brown transparent needles from dil. acetic acid, m.p. 209–210°. (Found: N, 11·47; 11·53. $C_{14}H_{12}O_8N_2$ requires: N, 8·34%). The analytical results do not correspond to 5-nitrotosylanthranilic acid.

2-(4′-*Bromobenzoyl*)-4-*nitroacetanilide* (XXXIII)

The amine (XXVI; 5 g) and acetic anhydride (10 ml) containing conc. H_2SO_4 (2–3 drops) were warmed on a water bath for ½ hr and then poured into water. The cream yellow solid was collected (yield 5 g). It crystallized from alcohol in transparent needles, m.p. 143·5–144·5°. (Found: C, 57·20; H, 3·80; N, 4·33. $C_{15}H_{12}O_2NBr$ requires: C, 56·58; H, 3·80; N, 4·40%). Powdered XXXII (1·5 g) was added to HNO_3 aq. (obtained by mixing 4·5 ml of acid, sp. gr. 1·50 and 4·5 ml of acid, sp. gr. 1·42), cooled in freezing mixture, keeping the temp below 0°. After allowing to remain in the freezing mixture for 1½ hr and at room temp for 3 hr, crushed ice was added to the reaction mixture. A light yellow solid (750 mg, m.p. 197–198°) was obtained. It crystallized in white silky needles from alcohol (norite), m.p. 206–207° (400 mg). Recrystallizations from alcohol yielded product, m.p. 207–208°. From the mother liquor, impure material, m.p. 60–80° (250 mg) was obtained. (Found: N, 7·80. $C_{15}H_{11}O_4N_2Br$ requires: N, 7·71%).

2-(4′-*Bromobenzoyl*)-4-*nitroaniline* (XXXIV)

A mixture of the acetyl compound (XXXIII; 300 mg) and conc. H_2SO_4 (2 ml) was heated on a water bath for 5 min, when a clear solution was obtained. Dilution with water yielded yellow solid, 250 mg, m.p. 190–194°. Crystallizations from alcohol yielded yellow crystals, m.p. 201·5–202°. (Found: C, 49·43; H, 2·63; N 9·03. $C_{13}H_9O_3N_2Br$ requires: C, 48·60; H, 2·80; N, 8·73%)

2-*Nitro-6-bromofluorenone* (XXX)

By Pschorr reaction. The amine (XXXIV; 200 mg) was dissolved in conc. H_2SO_4 (2 ml), and water (2 ml) was added to obtain a slurry. It was cooled in freezing mixture and treated with $NaNO_2$ aq. (0·3 ml, 30%) drop by drop, keeping the temp below 0°. It was kept at the same temp for 1 hr, with occasional shaking, and then heated on a water bath for 1 hr. The solid formed was collected, treated with 100 ml 10% NaOH, and filtered. The residue (60 mg), m.p. 260–265° (softening at 245°) was sublimed in vacuum (0·5 mm) at 180° and crystallized from xylene, m.p. 264–265° alone or mixed with a sample obtained by the degradation of IX. The oxime prepared as before (from alcohol and pyridine) had m.p. 256–257°, alone or when mixed with the specimen prepared above.

2-(4′-*Bromobenzoyl*)-4,6-(?)-*dinitroacetanilide* (XXXVII)

The acetyl compound (XXXII; 0·5 g) was added to HNO_3 (1 ml, sp. gr. 1·5), cooled in freezing mixture and left for 24 hr at 0°, and treated with crushed ice. A yellowish brown solid was obtained m.p. 174–182°. It was boiled with alcohol and filtered. The micro crystalline solid (0·4 g, m.p. 188–190°) after 3 crystallizations from acetic acid, yielded brown rhombic crystals, m.p. 198–199·5°. (Found: C, 44·24; H, 2·41; N, 10·53. $C_{15}H_{10}O_6N_3Br$ requires: C, 44·12; H, 2·45; N, 10·29%).

2-(4′-*Bromobenzoyl*)-4,(6)(?)-*dinitroaniline* (XXXVIII)

The acetyl derivative (XXXVII; 1·4 g), conc. HCl (20 ml), and acetic acid (10 ml) were refluxed for 2 hr. The reaction mixture was diluted with water and the solid collected, yield 1·1 g, m.p. 213–215°. On recrystallizations from ethyl acetate, light brown crystals, m.p. 220–221°, were obtained. (Found: C, 42·77; H, 2·48; N, 11·83. $C_{13}H_8O_5N_3Br$ requires: C, 42·7; H, 2·18; N, 11·48%). A good deal of experimentation was necessary to arrive at conditions for the preparation of the mononitro derivative XXXIII. Mild conditions did not nitrate the acetyl derivative XXXII, whereas more concentrated acids led to the dinitro derivative, or to gums which could not be crystallized.

2-*Bromophenanthrenequinone* (IV)

To a mixture of I (2·1 g, 0·01 mole), acetic acid (50 ml) bromine, (0·5 ml, 0·01 mole), HNO_3 (5 ml) and water (5 ml), $AgNO_3$ aq. (1·78 g, 0.01 mole in 10 ml water) was added drop by drop. The reaction mixture was refluxed ½ hr and then cooled. The residue was washed with hot acetic acid to dissolve out all organic material. The combined acetic acid solutions deposited reddish-orange crystals on cooling. Recrystallization from acetic acid gave glistening red needles, m.p. 233–234°; yield 0·5 g; lit.[29] m.p. 233–234°. The combined filtrates on dilution with water yielded an orange solid, m.p. 165–185° (1·7 g). Crystallizations from acetic acid raised the m.p. to 202–203°; m.p. was not depressed when mixed with pure I.

2,7-*Dibromophenanthrenequinone* (V)

A solution of $AgNO_3$ (3·4 g) in water (20 ml) was added to a mixture containing I (2·1 g), acetic acid (50 ml), HNO_3 (20 ml, sp. gr. 1·42) and Br_2 (1·1 ml). The reaction mixture was refluxed ½ hr and filtered. The residue was extracted with hot acetic acid to dissolve out all red material. The combined filtrates were cooled, when red crystals (0·6 g) were deposited. On crystallization from acetic acid red needles, m.p. 323°, were obtained; lit.[29] m.p. 323°.

Phenanthrenequinone-bromine complex (VI)

A suspension of finely powdered I (300 mg) in dry CCl_4 (30 ml) was mixed with a solution of Br_2 (1·2 ml) in the same solvent (10 ml) and stirred 1 hr. It was cooled in ice for 40 hr, and the orange-red needles deposited (300 mg) were separated, m.p. 170–175°, with shrinking at 165°. (Found: Br, 30·24%. $C_{14}H_8O_2Br$ requires: Br, 43·43%).

Acknowledgment—I thank Prof. D. K. Banerjee for his interest in this work and Dr. M. K. Subrmanian for his help in the preparation of Fig. 5.