

Law (1921) Department.

(Education)

Ordinary SERIES.

<i>Letter</i>
G.O. No. <i>787</i>
DATED <i>23-5-21</i>

INDEXED

[Despatch Abstract.]

College of Engineering, Madras-- Professor of Technical
Chemistry-D. Surrendranath Dhar-appointment-Govt. of India
addressed.

PAPERS PUT UP WITH CURRENT No. _____

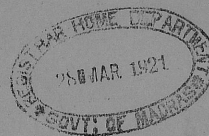
Papers of the department to which the current belongs.

Number.	Date.	Original (=O.) or spare copy (= S.O.)	Remarks. (In this column such of the papers as have been removed for copying, printing, etc., should be marked with a cross.)	Initials of Referencee with date in token of return to Reference department.

Papers of other departments.

Department.	Number	Date.	Original (=O.) or spare copy (= S.O.)	Initials with date of (1) Referencee acknowledging returns of the paper concerned or (2) Despatcher to denote the return of the papers to the department concerned.

All communications should be
addressed to the Secretary to the
Government of India, Public
Works Department, by title
NOT by name.



GOVERNMENT OF INDIA.

PUBLIC WORKS DEPARTMENT.

Establishments.

Delhi, the 24 March 1921.

A copy of the undermentioned paper is forwarded to the
Government of Madras for information.

By order,

Deputy Secretary to the Government of India.

Paper forwarded.

Letter from the India Office No.J.& P.706, dated the
24th February 1921, and enclosures.

32
INDIA OFFICE,

LONDON.S.W.I.

24 February 1921.

J.& P.706

Subject: Indian Educational
Service: Candidature of
Dr.Surendra Nath Dhar.

Dear Sir,

With reference to my letter of the 10th inst.J.& P.
706, I forward, for information, copy of the further papers
noted in the margin, on the subject of the candidature

From Dr.Dhar 15th February, with	)	of Dr.Surendra Nath Dhar for appointment
printed enclosures + letter of	)	
introduction for Sir A.Earle.	)	to the Indian Educational Service.
To Dr.Dhar 17th February	)	
From" " 18th " with	)	It will be seen that Dr.Dhar has
enclosures.	)	
From Board of Education dated	)	now expressed preference for the vacant
22nd February with enclosure.	)	
-----		Professorship of Technical Chemistry at

the College of Engineering, Madras,

The letter from the Board of Education shows that there
is at present no other candidate forthcoming here, and further
that Professor Thorpe, who, in the letter previously forwarded,
had testified to Dr.Dhar's general fitness for appointment to
the Indian Educational Service, considers him specially fitted
for the particular post at Madras.

Yours faithfully,

Secretary.

To

The Secretary to the Judicial & Public Department,
Government of India,
Education Department.

True copy

Superintendent, Govt. of India, P.W.D.

43
Northbrook Society,

21, Cromwell Road,

S.W.7.

15th February 1921.

To The Private Secretary to
Sir William Duke,
The Under-Secretary of
State for India.

Dear Sir,

I shall feel highly obliged if you kindly arrange a personal interview for me with Sir William Duke, at his early convenience.

I am a Government of India Scholar and a London D.Sc. in Chemistry.

I have been a candidate for the Indian Educational Service and intend to see Sir William Duke with a letter of introduction from Sir Archdale Earle who was the Chief Commissioner of the Province I come from.

Yours faithfully,

(Sd) S.N.Dhar.

YARLET,

WALTON ON THE HILL,

SURREY.

13th February 1921.

My dear Duke,

This is to introduce to you Mr. Surenda Nath Dhar, who is a candidate for the Indian Educational Service. He is ^a London D.Sc. I got him a State Scholarship from Assam and so take an interest in him.

If you can help him in any way I shall be obliged. He says that there is a vacancy now in the Madras Indian Educational Service.

Ever yours etc.

(Sd) A. Earle.

To S.N. Dhar, Esq.

5 4
INDIA OFFICE,

LONDON, S.W.1.

17th February 1921.

Dear Sir,

With reference to your letter of the 15th Sir William Duke hopes to be able to see you if you call here at 12 o'clock to-morrow, Friday.

Yours truly,

(Sd) W.D.Croft.

NORTHBROOK SOCIETY,

21, CROMWELL ROAD,

LONDON, S.W.7.

18th February 1921.

To The Under-Secretary of
State for India,
Public Department,
India Office.

Sir,

On the 26th of January 1921, I wrote to the Director of Public Instruction, Assam, requesting him to consider my candidature for the Indian Educational Service particularly in connection with the two vacancies, one in Rangoon and another in the Engineering College, Madras. Now I request you to note that of these two posts I prefer the Madras one. I am writing the same to the Director of Public Instruction, Assam.

I have the honour to be, Sir,

Your most obedient servant,

(Sd) Surendra Nath Dhar.

To The Director of Public Instruction,
Assam.

Sir,

I have already got my name registered through you as a candidate for the Indian Educational Service, and I further request you to be so good as to register my name as a candidate not only for Educational but also for any other post on the Imperial grade for which I may be considered fit.

65
I prefer Educational employment, and I should like to go to any of the semi-Government Universities such as Dacca, Lucknow etc. And if it is possible for you to recommend me to wherever any such vacancy occurs I should request you to do that. Being so far from India I fail to be in touch with Indian affairs.

I learn from the Board of Education here that there are at present two vacancies for a Chemist, one in Rangoon, and another in the Engineering College, Madras.

I hope and request that my case be favourably considered.

I have the honour to be, Sir,
Your most obedient Servant,
Surendra Nath Dhar,

21, Cromwell Road,
London, S.W.

Dated
26th January 1921.

To Director of Public Instruction,
Assam.

Sir,

Section of Dr. Dhar 26/1/21
Admission
I have the honour to supply you with some additional information regarding my qualifications.

After getting the Degree of Doctor of Science from the University of London, I visited almost all the important educational centres in the United Kingdom. Then I went to the Continent, with the permission of the Secretary of State for India, for a tour I had been there from October 1920 to January 1921, and have studied the organisation and working of (1) Universities, (2) Technical Institutes and (3) some Chemical Industries in France, Switzerland, Italy and Germany.

During my tour in the United Kingdom and on the Continent I availed myself of the opportunity of discussing important problems in scientific education with many master minds in Europe, so I am in a position to organise and to build up a chemical laboratory or a chemical Institute - either educational or industrial - in a most modern and thoroughly scientific way.

With the help of some very distinguished professors of Europe I had an opportunity to see some chemical industries, particularly colour industry, and I studied all the processes from start to finish together

7 6
together with the practical application of dye stuffs to all kinds of materials.

I have visited many places of Art and Culture as well, such as Paris, Rome, etc.

I have learnt German which is indispensable for higher study and research in Chemistry, and I am now learning French also.

As before, I have been carrying on research under Professor J.F.Thorpe, C.B.E., F.R.S., in the Royal College of Science.

I have the honour to be,
Sir,
Your most obedient Servant,

P? S.N. Dhar

Dated

26th January 1921.

21, Cromwell Road,
London, S.W.

DEMI OFFICIAL LETTER FROM BOARD OF EDUCATION TO INDIA OFFICE

DATED 22ND FEBRUARY 1921.

We wrote to all the Professors of Chemistry who were likely to be in touch with men in industry and as a result had six names mentioned to us. To all these were sent notice of the post, only three replied to say that they were not prepared to consider the post.

It is unlikely that any English candidate of suitable qualifications will be forthcoming. Neither for Dacca or Rangoon were there any English candidates of merit.

I enclose Professor Thorpe's recommendation.

Yours sincerely,

(Sd) A.E. Twentymen.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

(ROYAL COLLEGE OF SCIENCE)

SOUTH KENSINGTON,

LONDON, S.W.7.

February 7th 1920.

Dear Mr. Twentymen,

*Thank

87
Thank you for your letter of the 5th referring to the post of Professor of Technical Chemistry which is now vacant in the Madras College of Engineering.

+ I have no hesitation in strongly recommending my student Mr. Surendra Nath Dhar for the post. He has taken his degree of D.Sc. in the University of London and has done some valuable and important research work here, the results of which he has published. He has moreover visited some of the larger chemical works on the Continent and is in touch with the most recent applied Chemical practice although he has not been actually engaged in a chemical works. +

Yours faithfully,

Jocelyn Thorpe.

Dhar you will remember was a candidate for the Dacca post and was interviewed by the Committee.

True Copy

A. B. G. M. M. M.

Supetintendent, Govt. of India, P.W.D.

Ind

NOTES.

Law (24) Sept

Professorship of Technical Chemistry
in the College of Engineering, Madras.

[C. No. 1533A] From the Govt of India, P.W.D., No. 1602A,
1st 24.3.21

From the Govt of India
Office letter on page 2 of it will be seen
that no other candidate, except Dr.
Suresh Chandra Dhar, is forthcoming for
the post of Professor of Technical Chemistry
in the College of Engineering, Madras.
The file may be sent to the P.W.D.
No. and he may be requested to
state whether Dr. Suresh Chandra Dhar
will be a suitable candidate for the
~~app~~ post and whether he may
be appointed to it.

En 1533A
8.4.21

No No 230
15.4.21

24.3.21

8.4.21

24.3.21

8.4.21

27/4/21

U.O. Reply.

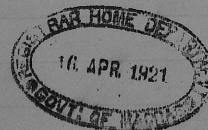
I know nothing about Dr. Dhar except what this
file contains.

Dr. Thorpe recommends his appointment and

states that he was a candidate for the Dacca post and was interviewed by a Committee (presumably a Committee appointed under instructions of the Secretary of State for India). But I find nowhere in the file any statement of the opinion of the Committee on Dr. Dhar's fitness for appointment to the Indian Educational service nor of the opinion of the Secretary of State of his fitness for a post in the Indian Educational service.

There are other qualifications (e.g., *inter alia* Character, ~~experience~~ ^{presence} and teaching ability) necessary for appointment in the Indian Educational Service, qualifications which Dr. Thorpe does not mention in his letter of recommendation and until I know something more than I now do of Dr. Dhar I regret that I am unable to advise Government to recommend his appointment to a post in Madras in the Indian Educational Service.

Encl. N^o 2056 A
18.4.21



Lawl (S) sent.

~~Not to be used for any purpose other than the
the best of Indian law, the said and for
facts, information, and Dr. Dhar.~~

19.4.21

K.A.

NOTES.

Page 3

For the qualifications of Dr. Dhar please see no. 3155 in the list of Indians who have applied to the Board of Education in England for appointment to the D.E.S. This list does not contain any statement of the Board's opinion as to the candidates' fitness for appointment. The Govt. of India's suggestion that this list also should be taken into consideration when making recommendations for filling vacancies may, however, be taken to indicate that the candidates in the list have been approved by the Board of Education.

For order whether the Govt. of India should be addressed for specific information on the points at 'A' & 'B' on page 2 supra.

La
not 4/21
D.P.I. may perhaps see the above. A copy was already furnished him.
20/4/21
5

The D.P.I. is perfectly right in declining to give any opinion against candidates he does not know but the position is exactly similar to all persons recruited in England. In all these cases we have necessarily to depend on the views expressed by professors & authorities in England.

p. 2 of p. no. 443
19.5.19

p. 1 — do

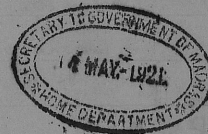


2. In our letter dated 28 May 1920 we asked for an officer in touch with the most recent applied chemical practice. The present letter is the issue thereof. In view of Mr. Morpe's Shinglestunel, we may ask India to obtain Mr. Dhar's services.

May 3/5/21

M 1. Mr. Dhar's observations seem to suffice & to sufficient as the P.D. India may be ordered sent to Mr. Dhar.

H2 Jm. 6.13.5.21

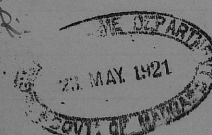
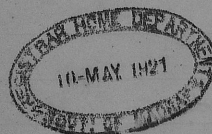
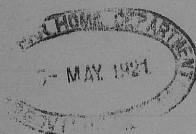


A draft letter to India is submitted.

27.5.21

19.5.21

27.5.21



B87
C.125
P.

18/5/21

O. E. K. L. S.

Letter No. 787 of 23/3/21

RECEIVED
27 MAR 1921

Caution
15/3/21

The Secretary to the Govt.
of India,
P. W. D.

Sir,

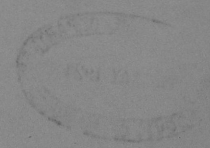
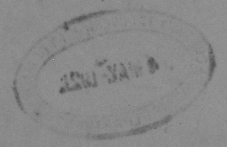
With reference to Mr.
Hadow's endorsement no. 1602A,
dated the 24th March 1921, forwarding
papers relating to the candidature
of Dr. Surendra Nath Dhar for
appointment to the I.E.S. and
the continuance of my letter no. 1466 of 3rd March 1920,
I am directed to state that
this Govt. are willing to take
Dr. Dhar into the I.E.S. in
this Presidency. ~~and I am~~ accordingly
to request that his service
at an early date
may be obtained for employment
as Professor of Technical
Chemistry in the College
of Engineering, Madras.

I have etc.

15/5/21

19/5/21

H-3-110893
7820



Dr. Surendra Nath Dhar
Professor of Technical Chemistry.
His appointment to the above position
is hereby addressed.

To Sir William Duke, G.C.D. E., K.C.S.I.
With best compliments
S. Dhar

SOME NITRO-DERIVATIVES OF NAPHTHALENE AND
ANTHRAQUINONE.

14



BY

SURENDRA NATH DHAR.

From the Transactions of the Chemical Society, 1920. Vol. 117.

15

CXI.—*Some Nitro-derivatives of Naphthalene and Anthraquinone.*

By SURENDRA NATH DHAR.

THE present study was undertaken mainly with the view of preparing some nitro-compounds for halogenation in the manner dealt with in the previous paper. One remarkable fact has, however, been brought to light in connexion with the nitration of anthraquinone.

It is well known that when anthraquinone is nitrated, a mixture of dinitroanthraquinones is formed, and from such a mixture the nitro-compounds can be separated only with very great difficulty, using solvents such as acetone, pyridine, etc. By this method, only the following dinitroanthraquinones have been isolated from different mixtures: 1:5-, 1:6-, 1:7-, 1:8-, 2:6-, and 2:7- (D.R.-P. 167699).

It will be seen that, of the ten possible dinitro-compounds, the 1:2-, 1:3-, 1:4-, and 2:3-derivatives are missing. It is natural to suspect that some of these four isomerides might be left undetected in the mixtures, because of the unsatisfactory method of separation. It was therefore thought that the new method of bromination might help in detecting the unknown dinitro-compounds, if any. This expectation has been fulfilled.

A mixture of dinitroanthraquinones, obtained by nitrating anthraquinone by the ordinary method, was treated with bromine in a sealed tube, and the product was found to be a mixture of

1:2. (m. p. 268°), 1:3. (m. p. 210°), 1:5. (m. p. above 360°), and 2:6. (m. p. 285°) dibromoanthraquinones.

Attempts were then made to isolate the corresponding four dinitro-compounds. As a result of nitration under different conditions with different proportions of nitric and sulphuric acids, four dinitro-compounds have actually been obtained, but only two of them have been identified, and characterised as 1:5- and 1:3- dinitroanthraquinones respectively.

By the nitration of 1:8-dinitronaphthalene, Will (*Ber.*, 1895, 23, 378) obtained only one of the two possible tetranitronaphthalenes, and characterised it as the 1:3:6:8-tetranitro-derivative; but in the present work both the tetranitro-compounds have been isolated, so that the new compound is necessarily 1:2:6:8-tetranitronaphthalene. Two trinitro- β -naphthoic acids have been obtained by the nitration of β -naphthoic acid.

It may here be stated that nitric acid has been found to be a useful solvent for nitro-compounds in general. By using this, not only are costly solvents avoided, but the separation of different nitro-compounds and their purification are accomplished with very great ease.

EXPERIMENTAL.

Anthraquinone Series.

Ten grams of anthraquinone were added gradually to a mixture of 250 grams of concentrated sulphuric acid and 250 grams of nitric acid (D 1.42) with shaking. The solution was kept over the steam-bath for about an hour, when yellow needles were obtained, which were collected over asbestos. The substance melted at 312–317°, and was found to be a mixture of dinitro-compounds. It was heated with two molecular proportions of bromine and a trace of iodine in a sealed tube for six hours between 250° and 300°. From the product, four different dibromoanthraquinones were separated by means of laborious fractional crystallisation. The crude product yielded an insoluble residue when boiled with alcohol. From the alcoholic solution two substances separated on fractional crystallisation. The less soluble one melted at 268° and proved to be 1:2-dibromoanthraquinone (Found: Br=44.21. Calc.: Br=43.71 per cent.), and the more readily soluble one, which melted at 210°, to be 1:3-dibromoanthraquinone (Found: Br=43.96). The insoluble residue yielded two other substances when fractionally crystallised from benzene. The more readily soluble one melted at 285°, and was 2:6-dibromoanthraquinone (Found: Br=43.98), and the less soluble one, which did

not melt up to 360°, was 1:5-dibromoanthraquinone (Found: Br=44.87).

Twenty-five grams of anthraquinone (sublimed) were mixed with concentrated sulphuric acid in a mortar, and the mixture was washed with sulphuric acid into a large flask. A further quantity of sulphuric acid was added to make the total amount of acid 300 c.c., and 400 c.c. of nitric acid were then added to the mixture. The flask was kept over the steam-bath for six hours, when yellow crystals precipitated. These were filtered over asbestos and washed with nitric acid and then with water. The substance was further purified by boiling with nitric acid. It did not melt up to 360°, and was identified as 1:5-dinitroanthraquinone (Found: N=9.31. Calc.: N=9.39 per cent.).

When boiled with sodium methoxide, it gave a dimethoxy-compound which melted at 236° (1:5-dimethoxyanthraquinone melts at 238° (D.R.-P. 167699), and when heated in a sealed tube with bromine and iodine a dibromo-compound was obtained which did not melt up to 300°.

1:3-Dinitroanthraquinone.—From the filtrate and washings of 1:5-dinitroanthraquinone another dinitro-compound was obtained by precipitation with water. It crystallised from nitric acid in yellow needles (5 grams) melting at 240° (Found: N=4.2. $C_{14}H_8O_4N_2$ requires N=9.39 per cent.).

When boiled with sodium methoxide it gave 1:3-dimethoxyanthraquinone melting at 155° (Graebe, *Annalen*, 1906, 349, 230, gives 150–153°).

3-Nitro-1-aminoanthraquinone.—1:3-Dinitroanthraquinone was reduced with alcoholic ammonium sulphide in the usual way. For each gram of the nitro-compound, 50 to 75 c.c. of alcohol and 20 to 25 c.c. of ammonia were required. The nitroamino-compound crystallised from alcohol in deep red needles which melted at 265° (Found: N=10.48. $C_{14}H_9O_2N_2$ requires N=10.45 per cent.).

3-Nitroanthraquinone-1-azo- β -naphthol.—The nitroamino-compound was diazotised in the usual way and combined with β -naphthol. The product separated from alcohol as a deep red, amorphous substance melting at 235–240° (Found: N=9.98. $C_{24}H_{13}O_3N_3$ requires N=9.92 per cent.).

3-Nitro-1-hydroxyanthraquinone was obtained by diazotising the nitro-amino-compound and warming the solution over the steam-bath for ten hours. It separated as a brick-red, amorphous powder melting at 240° (R. Scholl, *Ber.*, 1904, 37, 4435, gives 247–248°) (Found: N=5.01. Calc.: N=5.20 per cent.).

Very small amounts of two other dinitro-compounds were

obtained from the nitric acid filtrates from 1:5- and 1:3-dinitro-anthraquinones, and they are under investigation.

Nitration of both 1:5- and 1:3-dinitroanthraquinone was tried with mixtures of sulphuric and fuming nitric acids in various proportions by boiling over a sand-bath under reflux, but in each case the substance decomposed completely.

Naphthalene Series.

1:2:6:8-Tetranitronaphthalene.—Five grams of 1:8-dinitronaphthalene were dissolved in a mixture of 25 c.c. of concentrated sulphuric acid and 25 c.c. of nitric acid (D 1.5). The solution was kept over the steam-bath for about four hours, when about 2 grams of a white powder were obtained. The substance does not melt up to 300° (Found: N=18.20. $C_{10}H_4O_8N_8$ requires N=18.18 per cent.).

From the filtrate about 2 grams of 1:3:6:8-tetranitronaphthalene were obtained, which was purified by crystallisation from nitric acid.

Trinitro- β -naphthoic Acid.—Two grams of β -naphthoic acid were dissolved in 40 c.c. of concentrated sulphuric acid, and 25 c.c. of nitric acid (D 1.42) were added to the solution. On keeping the solution* overnight, needles melting at 220° separated (Found: N=13.58. $C_{11}H_5O_8N_3$ requires N=13.68 per cent.).

From the filtrate another trinitro-compound, much in excess of the first, was obtained as a yellow precipitate on the addition of water. It melted and decomposed at 215° (Found: N=13.47. $C_{11}H_5O_8N_3$ requires N=13.68 per cent.).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
(ROYAL COLLEGE OF SCIENCE),
LONDON.

[Received, June 24th, 1920.]

To Sri William Duke S.C.D. & K.C.S.I.
With best Compliments
V. S. Dhar.

A COMPARATIVE STUDY IN THE XANTHONE SERIES.
PART I.



BY
SURENDRA NATH DHAR.

From the Transactions of the Chemical Society, 1920. Vol. 117.

19

CXVIII.—A *Comparative Study in the Xanthone Series. Part I.*

By SURENDRA NATH DHAR.

IN the series of investigations of which this is Part I, it is intended to compare xanthone with other compounds having similarities in structure or properties. In the first place, such a comparison is attempted with anthraquinone, which has the greatest similarity to xanthone. No comparative study seems to have been made systematically by anyone except Hertzog (*Monatsh.*, 1891, **12**, 161), who found that euxanthone is more stable than quercetin (a flavone), and Graebe and Eichengrün (*Ber.*, 1891, **24**, 967), who compared some hydroxyxanthenes with certain hydroxyanthraquinones and hydroxybenzophenones. Other attempts at a comparison of xanthone with anthraquinone with respect to the colouring properties of their hydroxy-derivatives are evidenced from a few isolated instances. Thus Graebe and Aders (*Annalen*, 1901, **318**, 365) showed the similarity of the hydroxyl group in position 1 in both the series. A. G. Perkin and Everest

have incidentally raised the same question ("The Natural Organic Colouring Matters," pp. 126-127). They compare alizarin with 3:4-dihydroxyxanthone, but, as a matter of fact, 1:2-dihydroxyxanthone, and not the 3:4-derivative, corresponds with alizarin. Attempts are being made to synthesise 1:2-dihydroxyxanthone, and the results will be communicated in due course. At the same time, a systematic comparison is being attempted in the following directions: (1) nitration; (2) direct displacement of nitro-groups by halogens, methoxy-group, etc., and certain other important reactions with nitro-compounds, such as Skraup's synthesis, Doebner and Miller's and Knorr's syntheses, etc.; (3) halogenation; (4) mobility of halogen atoms; (5) migration of diazo-groups.

It is interesting to note that xanthone has been found to be much more reactive than anthraquinone. Thus with nitric acid alone, xanthone gives two dinitroxanthones (α and β), whereas anthraquinone gives a mononitro-derivative only (*Ber.*, 1883, 16, 363). Again, quite a number of tri- and tetra-nitroxanthones have very easily been prepared, whilst no such polynitro-derivatives of anthraquinone are known, and further nitration of the dinitro-compounds has not yet been effected.

Xanthone seems not only to be more reactive, but also more stable, although from the structure of these compounds such a fact is quite unexpected. It is well known that when fused with potassium hydroxide, xanthone decomposes into 1:1'-dihydroxybenzophenone, whereas anthraquinone is completely degraded to two molecules of benzoic acid. Similarly, it has been found that when further nitration of 1:5- or 1:8-dinitroanthraquinone is attempted with mixtures of nitric and sulphuric acids, they decompose completely, whilst both α - and β -dinitroxanthones are converted into tetranitroxanthones at an earlier stage of such a treatment, and the products are not decomposed on subsequent treatment. It may also be noted that tetrabromoxanthone is nitrated and not decomposed by such a mixture (Dhar, T., 1916, 109, 740).

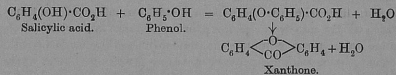
So far as the behaviour of nitroxanthone has been studied, it has been found that the nitro-groups in the xanthone series are much more readily displaced by direct bromination than is the case in the anthraquinone series (see this vol., p. 994).

Skraup's synthesis is effected much more readily in the xanthone series than in the anthraquinone series, and xanthone has also been found to be much more reactive towards halogens than anthraquinone. Thus two hexabromo- and an octabromoxanthone have been prepared, whereas no such corresponding

romo-compounds are known in the anthraquinone series. When treated with bromine in sealed tubes, xanthone gives the 2:7-dibromo-derivative (Graebe, *Annalen*, 1889, 254, 284), whilst anthraquinone gives 1:2-dibromoanthraquinone.

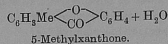
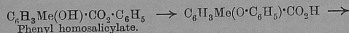
Theory of the Formation of Xanthone.

Strobbach has discussed in detail the various theories put forward to explain the formation of xanthone (*Ber.*, 1901, 34, 4135). He attacked mainly the theories of Graebe and Seifert, and, after proving them incapable of explaining all the experimental facts then known, he tried to establish a new theory of his own, together with a few empirical rules. One thing is, however, common to all the theories, and that is the supposition that phenol does not take part in the formation of xanthone or its derivatives. On the other hand, if phenol is supposed to take part in the reaction, the formation of xanthone becomes very simple and does not necessitate the supposition of various intermediate products, the existence of which is doubtful, or any transposition of groups which Strobbach was compelled to make. Thus, in order to ascertain whether phenol takes part or not, experiments were made on the preparation of xanthone from salicylic acid, using in each case an equimolecular proportion of phenol. It is remarkable that the yield of xanthone in each case was just double when phenol was employed. That phenol actively takes part in the reaction and raises the yield in such a remarkable and systematic way is proved beyond doubt by the facts that when nitrobenzene is used instead of phenol, no increase in the yield of xanthone is effected, and when *o*-nitrophenol is used, 4-nitroxanthone is obtained. The formation of xanthone may therefore be explained thus:



When only salicylic acid is used, half is decomposed into phenol, and traces of phenol can actually be detected in such experiments. The use of a dehydrating agent increases the yield by removing the water formed in the reaction. When acetic anhydride is used, the first reaction is most probably the acetylation of the phenolic group, and this seems to be an important factor in the yield. That is why *o*-acetoxybenzoic acid gives xanthone, and the yield is not affected in the least whether acetic anhydride is used or not.

Now the formation of xanthone from phenyl salicylate, as well as all the other typical instances cited by Strohbach, may be explained by this theory, and the yield is necessarily poor when neither the phenolic groups are acetylated nor any dehydrating agent is used. Thus the formation of xanthone from phenyl salicylate proceeds according to Graebe's first two equations (*loc. cit.*), and the liberated salicylic acid and phenol are not wasted, as he has supposed, but give xanthone again, although the yield in such a case is quite inappreciable, as will be shown in the experimental part (p. 1061). The formation of 5-methyl- and 4:5-dimethyl-xanthone from phenyl homosalicylate supplies another instance in support of this theory. Thus:



The water formed here hydrolyses one molecule of the ester, giving phenol and homosalicylic acid, which may give a further amount of the same methylxanthone, but the main reaction takes the following course. One of a pair of homosalicylic acid molecules gives *o*-cresol, just as salicylic acid gives phenol, and the condensation takes place in the usual way, giving 4:5-dimethyl-xanthone. It is interesting to note that, according to Graebe's theory, only 5-methylxanthone, and according to Strohbach's theory, only 4:5-dimethylxanthone, is possible, and according to Seifert's theory none of these is possible, whereas, according to the present theory, both products can be formed. The other instances cited in Strohbach's paper may be explained similarly.

After elucidating the mechanism of the formation of xanthone, a few experiments were made in order to ascertain whether the change takes place gradually or suddenly, and in the case of a sudden change to find the temperature at which it takes place. The temperature of the reaction mixture was therefore recorded, particularly carefully when a single substance was used. The results show conclusively that the conversion takes place gradually, as there was no sudden change in the temperature. Attempts have also been made to synthesise xanthone by various other methods, and it has been found that the condensation of *o*-chlorobenzoic acid with phenol (Ullmann's method) gives most satisfactory results, the yield of xanthone being almost theoretical and the process very simple.

o-Thiolbenzoic acid condenses with benzene and its simple deriv-

atives in the presence of sulphuric acid, giving thioxanthone and its derivatives (*Annalen*, 1896, **149**, 250), but salicylic acid does not condense with benzene or its derivatives either under these conditions or under the influence of phosphoryl chloride or with acetic anhydride in sealed tubes.

Fluorescence of Xanthone and its Derivatives.

The fluorescence of the two nitroxanthones (2- and 3-) is rather unexpected, as it is generally found that the introduction of a nitro-group destroys the fluorescence (Ullmann, *Annalen*, 1907, **355**, 312). Still more striking is the fact that the colour of the fluorescence is deeper in the case of the nitro-compounds. Thus xanthone shows only blue fluorescence, whereas 2- and 3-nitroxanthone show greenish-blue and green fluorescence respectively. Very few di-derivatives of a fluorescent substance are found to be fluorescent, and of all the di-derivatives described in this paper, only dichloroxanthone is fluorescent.

Nitroxanthones.

Only four nitro-derivatives of xanthone have been described. One (3-nitroxanthone) was prepared by Ullmann by condensing 2-chloro-4-nitrobenzoic acid with phenol (*Annalen*, 1904, **355**, 341), and 2:4-dinitroxanthone was prepared by Mayer (*Ber.*, 1909, **42**, 1132) by a similar method. The other two (α - and β -dinitroxanthones) were prepared by Perkin (T., 1883, **43**, 1870) by the direct nitration of xanthone with nitric and sulphuric acids. By a slight modification of this method, these compounds were obtained in a purer condition (T., 1916, **109**, 746), but it has now been found that they can be prepared from xanthone by treating it with nitric acid alone. As has been stated, xanthone differs from anthraquinone in its remarkable capacity for yielding nitro-derivatives, and the number of these has been increased from four to fifteen, and it is expected that many more can be prepared without difficulty. Two methods have mainly been employed, namely, nitration and synthesis by Ullmann's method (*loc. cit.*).

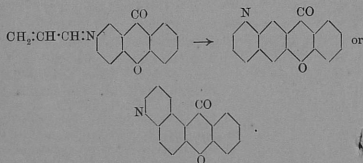
3-Nitroxanthone, which had previously been obtained only by synthesis, has now been prepared by the careful nitration of xanthone. The other three isomeric mononitroxanthones have been obtained by synthesis. 4-Nitroxanthone is formed when salicylic acid and *o*-nitrophenol are heated with acetic anhydride, but it has not been possible to obtain this compound by the condensation of *o*-chlorobenzoic acid with *o*-nitrophenol. The remarkable fact has been observed that nitroxanthones are much more

easily nitrated than xanthone itself under the same condition. Whereas xanthone gives only dinitroxanthones, 1- and 4-nitroxanthone give tetranitroxanthones, and 2- and 3-nitroxanthone give trinitroxanthones. As many as six tetranitroxanthones have been prepared from lower nitroxanthones with very great ease. The orientation of these tetranitro-compounds is still under investigation, but they have been distinguished from each other mainly by their bromination products. By this method it has been found that the α_1 - and β_1 -tetranitro-compounds are identical, and two of their nitro-groups are so stable that they are not removed by bromine, even when heated at 300° for twenty-six hours (this vol., p. 995).

Further nitration of some of these tetranitroxanthones (α_1 -, α_2 -, and β_2 -) has been attempted by boiling them with mixtures of sulphuric acid and fuming nitric acid in various proportions, but without success.

A New Heterocyclic Type.

Skraup's reaction was utilised by F. Mayer (*Ber.*, 1909, 42, 3064) in order to fuse a pyridine ring on to a thioxanthone nucleus. He obtained thereby one thioxanthoquinoline from 2-aminothioxanthone, but he neither studied this compound thoroughly nor extended this reaction to any other member of the thioxanthone or xanthone series. It was therefore proposed to study this reaction, particularly in the xanthone series, with the expectation of obtaining a series of tetracyclic compounds where one pyridine ring would be united with a pyrone ring together with two benzene rings:



It will be seen that the pyrone ring is protected on both sides by benzene rings, whereas the pyridine ring is protected only on one side. Accordingly, the respective stability of these pyrone and pyridine rings can be usefully studied.

It has been found, as expected, that an aminoxanthone, when treated with glycerol and sulphuric acid, gives a heterocyclic compound exactly of the type represented above. The reaction takes place with such great readiness that it is sufficient to use the nitro- instead of the amino-derivative. This naturally simplifies the synthesis considerably, and Dey and Goswami (*T.*, 1919, 115, 531) have noticed the same fact in similar syntheses in the coumarin series. In this way, β -dinitroxanthone gives *nitroxanthoquinoline*. The utilisation of the other nitro-group for fusing another pyridine ring to the already existing tetracyclic nucleus, as well as the synthesis of this type of tetracyclic compounds from other nitro-derivatives of xanthone, are under investigation.

Action of Sodium Methoxide on Nitroxanthones.

One remarkable reaction of the nitroanthraquinones is the ease with which a nitro-group is displaced by a methoxy-group. All the known dinitroanthraquinones have been converted into their corresponding dimethoxy-compounds by boiling them with sodium methoxide. Although xanthone behaves like anthraquinone in many important reactions, it differs entirely in this particular case. None of the nitro-groups of α - or β -dinitroxanthone is displaced by a methoxy-group when treated with sodium methoxide, but the corresponding nitroxanthidrols are produced. These substances dissolve in alkali hydroxide as well as in concentrated acids with distinctive colours.

Colour in solutions of

Substance.	NaOH.	H ₂ SO ₄ .	HCl.	HNO ₃ .	CH ₃ ·CO ₂ H.
α -Dinitroxanthidrol	Yellow	Deep yellow	Yellow	Pink	Orange-red
β -Dinitroxanthidrol	"	"	Pale yellow	"	"

Although xanthidrol is quickly converted into an ether, these dinitroxanthidrols do not undergo this reaction, perhaps because of the influence of the nitro-groups. When boiled with mild oxidising agents, they are converted into the original nitroxanthones.

Halogenation.

Three different methods have been employed for the preparation of halogen derivatives of xanthone, namely: (1) direct halogenation; (2) synthesis according to Ullmann's method (*Annalen*, 1907, 355, 359), and (3) direct displacement of the nitro-group by halogen.

Chloroxanthones.

2-Chloroxanthone was prepared by Ullmann (*loc. cit.*; compare Ullmann and Wagner, *Annalen*, 1910, **371**, 388) while studying the condensation of *o*-chlorobenzoic acid and its derivatives with phenol, 3-chloroxanthone was synthesised by Gomberg and Cone (*Annalen*, 1909, **370**, 142) by a similar method, and octachloroxanthone was prepared by Steiner (*Monatsh.*, 1915, **36**, 175) whilst studying the chlorination of cyclic ketones by means of antimony pentachloride. It is proposed to study the chlorination of xanthone systematically by all the three methods mentioned above, but at present attention has mainly been confined to the second method, by which all the possible isomeric monochloroxanthones have been synthesised.

Chlorination.—The direct chlorination of xanthone has not yet been carried out systematically, and the only method that has been tried is by dissolving xanthone in acetic acid and passing chlorine into the solution, using a trace of iodine as a catalyst. The products are 3-chloroxanthone and a *dichloroxanthone*; the latter can easily be obtained pure, but it is very difficult to remove the last traces of it from the former.

Ullmann's Synthesis.—Of the four possible monochloroxanthones, 2- and 3-chloroxanthone were synthesised by Ullmann and by Gomberg and Cone respectively (*loc. cit.*). The other two isomerides have now been prepared.

Bromoxanthones.

Bromination.—When xanthone in acetic acid solution is heated with one molecule of bromine and a trace of iodine, 3-bromoxanthone is obtained (Dhar, T., 1916, **109**, 745; compare *Annalen*, 1909, **370**, 142), but when concentrated sulphuric acid is used as a solvent instead of acetic acid, the product is 2-bromoxanthone. Each of these bromo-compounds when heated with bromine passes easily into the same dibromo-derivative, and therefore when a slight excess of bromine is used in the preparation of a monobromo-compound, dibromoxanthone is always formed. This is the main product of the direct bromination of xanthone when the operation is carried on under different conditions and with different catalysts. One striking fact in connexion with the direct bromination of xanthone is that although xanthone is brominated in sulphuric acid solution by liquid bromine, it is not attacked by a mixture of potassium bromide and potassium bromate in sulphuric acid solution.

Synthesis.—2-Bromoxanthone has also been synthesised from *o*-chlorobenzoic acid and *p*-bromophenol, and 4-bromoxanthone has been obtained by a similar method.

Direct Displacement of Nitro-group by Bromine.—By this method, several bromoxanthones have been prepared. The method serves as the only means of preparing certain bromo-derivatives, and there is a remarkable economy of bromine as the whole amount of bromine enters the nucleus.

EXPERIMENTAL.

Xanthone.

One hundred grams of salicylic acid when boiled with 100 grams of acetic anhydride and distilled gave only 20 grams of xanthone (compare Graebe, *Annalen*, 1889, **254**, 280). The yield was not improved by an increase in the amount of acetic anhydride or by extending the period of heating, nor was it affected appreciably when different samples of the materials were used. It was, however, raised to 40 per cent. of the salicylic acid used by the addition of a molecular proportion of phenol to the mixture. Thus a mixture of 50 grams of salicylic acid and 50 grams of phenol, when boiled for six hours with 100 grams of acetic anhydride and distilled, yielded 20 grams of xanthone. In all these cases the yield is extremely poor when no acetic anhydride is employed, and acetic acid has no effect at all.

When *o*-acetoxybenzoic acid is similarly boiled either alone or with acetic anhydride, it yields xanthone equivalent to 20 per cent. of its salicylic acid content.

Mononitroxanthones.

1-Nitroxanthone.—*m*-Nitrophenol (1.6 grams) was dissolved in 20 c.c. of methyl alcohol containing 0.4 gram of sodium. *o*-Chlorobenzoic acid (1.5 grams) was then added to the solution, and also a trace of copper powder. The alcohol was evaporated, and the dry, brown substance began to soften at about 100°; the temperature of the bath was raised to 110°, when the contents of the vessel melted to a dark brown liquid which solidified partly at about 140°. When cool, the contents were powdered and heated on a steam-bath for ten minutes with 15 c.c. of concentrated sulphuric acid. The solution was cooled, poured into water, and the precipitate collected. The substance crystallised from alcohol in slender, brown needles melting at 210° (Found: N=5.99. $C_{15}H_7O_4N$ requires N=5.80 per cent.).

It shows no fluorescence in concentrated sulphuric acid solution, but gives a yellow colour only.

2-Nitroxanthone.—*p*-Nitrophenol (4.2 grams) was dissolved in 20 c.c. of methyl alcohol, and 0.7 gram of metallic sodium was then added to the solution. When it was clear, 4.7 grams of *o*-chlorobenzoic acid were added, and a trace of copper powder was introduced as a catalyst. The alcohol was evaporated off slowly, and then the temperature of the bath was raised very slowly to 140°, when the orange-brown, hard mass melted to a viscous liquid of the same colour. After some twenty minutes, the colour began to change, and the liquid then became converted into a greyish-red, jelly-like substance. The temperature was very cautiously raised to 160°, when the dark-coloured substance solidified. The whole mass, however, bursts into flame at about this temperature if more than one atomic proportion of sodium is taken or if the temperature is raised suddenly. The substance, when cool, was powdered and heated on a steam-bath with 50 c.c. of concentrated sulphuric acid for twenty-five minutes. The solution, when cool, was poured into water, and the precipitate was collected (7 grams). The substance crystallised from alcohol in slender, brown needles melting at 200° and dissolving in sulphuric acid with a greenish-blue fluorescence (Found: N=5.56. $C_{15}H_8O_4N$ requires N=5.80 per cent.).

3-Nitroxanthone.—This was first prepared by Ullmann (*loc. cit.*) by the condensation of 2-chloro-4-nitrobenzoic acid with phenol. It has, however, been possible to obtain this compound directly from xanthone by nitration in the following way. Six grams of xanthone were dissolved in 12 c.c. of concentrated sulphuric acid, and 1.4 c.c. of nitric acid (D 1.500) added with shaking. Much heat was developed. The solution was kept overnight and then poured into water, the precipitate (about 7 grams) being collected and washed with water. About 2 grams of the substance, which did not dissolve in alcohol, consisted of β -dinitroxanthone. From the alcoholic solution, yellowish-white needles were obtained, which were found to contain traces of xanthone. The nitro-compound was purified by further crystallisation from alcohol. Traces of xanthone were found still to be associated with it, and could be removed only with very great difficulty, because of the almost equal solubility of each of these compounds in alcohol.

On reduction, traces of xanthone were removed, as this is insoluble in dilute hydrochloric acid, whereas the amino-compound was obtained as hydrochloride in the solution. The free amino-compound, isolated by precipitation with ammonia, melts at 232° (as given by Ullmann, *loc. cit.*).

When 1 gram of 3-nitroxanthone is dissolved in 10 c.c. of con-

centrated sulphuric acid and 5 c.c. of nitric acid (D 1.42) are added to the solution and the mixture kept overnight, a trinitroxanthone is obtained. This compound is described subsequently.

3-Nitroxanthone dissolves in sulphuric acid with a blue fluorescence much stronger than that shown by xanthone itself.

4-Nitroxanthone.—A mixture of 50 grams of salicylic acid and 50 grams of *o*-nitrophenol was boiled with 100 grams of acetic anhydride for ten hours and then distilled. Some tarry matter passed over at a very high temperature. This was boiled with alcohol with the addition of animal charcoal, and from the filtrate about 2.5 grams of yellow needles were obtained melting at 127° (Found: N=5.71. $C_{15}H_8O_4N$ requires N=5.80 per cent.). The compound dissolves in sulphuric acid with a green colour and without fluorescence. It is remarkable that no xanthone could be traced in the distillate. Attempts were made to condense *o*-nitrophenol with *o*-chlorobenzoic acid by Ullmann's method, but without success.

Dinitroxanthones.

α - and β -Dinitroxanthones are ordinarily obtained by nitrating xanthone with a mixture of nitric and sulphuric acids. They have also been prepared by nitrating xanthone with fuming nitric acid alone.

When 2 grams of xanthone are dissolved in 5 c.c. of nitric acid (D 1.500) and the solution is heated on a water-bath for about ten minutes, fine needles of β (or 2:7)-dinitroxanthone precipitate, and from the solution α -dinitroxanthone is obtained by precipitation with water and purification with nitric acid. Similar results are obtained with weaker nitric acid (D 1.42), but the quantity of acid should be proportionately greater, namely, 10 c.c. for each gram of xanthone, and the mixture should be heated for about three hours.

β (or 2:7)-Dinitroxanthone.—One gram of 2-nitroxanthone was dissolved in a cold mixture of 25 c.c. of nitric acid (D 1.42) and 25 c.c. of concentrated sulphuric acid. The solution was kept overnight, and then poured into water. The yellow precipitate (1.5 grams) was collected and crystallised from nitric acid, when it was obtained in white needles melting at 254°. When mixed with 2:7-dinitroxanthone (m. p. 262°), it melted at 254–260° (Found: N=9.79. Calc.: N=9.81 per cent.). From the nitric acid filtrate a trinitroxanthone was obtained (see below).

2:4-Dinitroxanthone.—This compound was prepared by Mayer (*loc. cit.*) by the condensation of sodium phenoxide and 2-chloro-3:5-dinitrobenzoic acid. It can also be prepared by condensing 2:4-dinitrophenol with *o*-chlorobenzoic acid in the following way.

2:4-Dinitrophenol (1.25 grams) and sodium (0.17 gram) are dissolved in methyl alcohol (20 c.c.), and to the clear solution *o*-chlorobenzoic acid (1.2 grams) and a trace of copper powder added. After evaporating the alcohol, the yellow residue melts partly at 160° and solidifies in a few minutes. It is cooled, powdered, and heated again to 160°, when it melts and resolidifies as before. This process is repeated about ten times, when the condensation is complete, and the substance does not melt on heating to 160°. If the temperature of the bath is raised with the view of completing the reaction in one operation, the whole mass suddenly inflames at about 200° without melting. After the completion of the condensation, the powdered substance is heated on a steam-bath with 20 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution is poured into water and the precipitate is collected. The substance, when decolorised with animal charcoal in alcoholic solution, crystallises from this solvent in yellow needles melting at 206° (Found: N=9.91. Calc.: N=9.81 per cent.).

Trinitrooxanthones.

2:3:7-Trinitrooxanthone.—When 2-nitrooxanthone was nitrated (see above), 2:7-dinitrooxanthone was the first product, and from the nitric acid filtrate a yellowish-white precipitate was obtained by adding water. After being boiled with alcohol to remove impurities, it melted at 205° (Found: N=12.74. $C_{15}H_8O_8N_3$ requires N=12.63 per cent.). The same trinitrooxanthone was obtained when 6 grams of 2:7-dinitrooxanthone were dissolved in 50 c.c. of concentrated sulphuric acid, 1.2 c.c. of nitric acid (D 1.500) added, and the solution was heated on a water-bath for twenty-four hours. The unchanged dinitro-compound was crystallised from nitric acid and collected, and the filtrate on concentration gave yellow needles melting at 205°.

This compound was also obtained by nitrating 3-nitrooxanthone.

Dinitromonoaminooxanthone.—The trinitro compound was reduced with alcoholic ammonium sulphide, and the product separated from alcohol as a dark brown powder melting and decomposing at 230° (Found: N=14.55. $C_{13}H_8O_6N_3$ requires N=14.43 per cent.).

Dinitrooxanthoneazo-β-naphthol.—The dinitroaminooxanthone was diazotised in the usual way and coupled with β-naphthol. The azo-compound separates from alcohol as a dark red, amorphous powder melting at 270° (Found: N=12.25. $C_{23}H_{12}O_7N_4$ requires N=12.28 per cent.).

Trinitrooxanthone.—Two grams of xanthone were dissolved in 7 c.c. of concentrated sulphuric acid with the aid of heat, and 2 c.c. of nitric acid (D 1.500) added to the cooled solution. The latter was then kept over the steam-bath, when a copious precipitate appeared in a few minutes consisting of yellow, glistening needles, which were filtered through asbestos and washed with dilute nitric acid, and finally with water. The substance dissolves freely in cold nitric acid (D 1.42). It melts at 225°, and is not identical with the trinitro-compound previously mentioned (Found: N=12.72. $C_{15}H_8O_8N_3$ requires N=12.63 per cent.).

Dinitromonoaminooxanthone.—This was obtained by reducing the trinitro-derivative with alcoholic ammonium sulphide in the usual way. It was obtained as a yellow powder melting at 290° (Found: N=14.47. $C_{13}H_8O_6N_3$ requires N=14.43 per cent.).

Tetranitrooxanthones.

1-Tetranitrooxanthone.—This compound was obtained by dissolving 0.5 gram of 1-nitrooxanthone in 5 c.c. of concentrated sulphuric acid and adding 2.5 c.c. of nitric acid (D 1.42). The solution, on keeping overnight, deposited yellowish-white needles melting at 250°. It is evidently different from α₁, α₂, or β₂-tetranitrooxanthones, which do not melt at 300° (Found: N=14.64. $C_{13}H_4O_{10}N_4$ requires N=14.89 per cent.).

4₁-Tetranitrooxanthone.—Half a gram of 4-nitrooxanthone was dissolved in 5 c.c. of concentrated sulphuric acid, and 2.5 c.c. of nitric acid (D 1.42) were then added gradually with shaking. At the first addition of nitric acid a violent reaction ensued, and the reaction vessel was cooled. After keeping the mixture for a few days, a reddish-yellow precipitate was obtained, which did not melt at 300° (Found: N=15.32. $C_{13}H_4O_{10}N_4$ requires N=14.89 per cent.).

4₂-Tetranitrooxanthone.—When the filtrate from the nitro-compound described above was added to water, there was obtained a brown powder, which could not be crystallised from alcohol, benzene, or nitric acid. It melts and decomposes at 200° (Found: N=14.70. $C_{13}H_4O_{10}N_4$ requires N=14.89 per cent.).

α-Tetranitrooxanthone.—Thirteen grams of α-dinitrooxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1.42). The mixture was heated on a steam-bath, when a clear solution was obtained in a few minutes and shining, yellowish-white crystals (10.7 grams) separated in about six hours. These did not melt at 300° (Found: N=14.79. $C_{13}H_4O_{10}N_4$ requires N=14.89 per cent.). This substance when

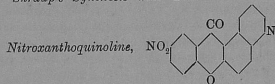
heated with bromine and a trace of iodine in a sealed tube give dibromodinitroxanthone (m. p. 265°) (see this vol., pp. 998—999).

α_5 -Tetranitroxanthone.—From the filtrate from the preceding compound, crystals, in the form of broken plates, were obtained by adding water. They also do not melt at 300° (Found: N=14.69. $C_{19}H_8O_{10}N_4$ requires N=14.89 per cent.).

This substance, when treated similarly with bromine, gives a tetrabromoxanthone (m. p. 255°).

β_5 -Tetranitroxanthone.—Ten grams of 2:7-dinitroxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1.42). The mixture was heated for about six hours, when bright yellowish-white crystals (9 grams) were precipitated. The compound was found to be identical with α_1 -tetranitroxanthone, as both these substances gave the same dibromodinitroxanthone when treated similarly with bromine. From the filtrate, 3.5 grams of shining, white, broken plates were obtained, which did not melt at 300° (Found: N=14.69. $C_{19}H_8O_{10}N_4$ requires N=14.89 per cent.). When this substance is heated with bromine exactly in the same way as the other tetranitro-compounds, a hexabromoxanthone is obtained, which melts at 285°.

Skraup's Synthesis with Dinitroxanthone.



Three grams of 2:7-dinitroxanthone were dissolved in 5 c.c. of concentrated sulphuric acid, and 12 c.c. of glycerol added. The addition of the latter precipitated the nitro-compound. The mixture was heated in a paraffin-bath, and at about 140° it began to froth, when the flask was shaken and the temperature lowered to 110°. Heating was continued for four hours at about 120°, and then for a further two hours at about 140°, when a semi-solid mass resulted. This was then heated for a further three hours until the black mixture became solid. The mass was powdered, and the crude product boiled with water and filtered. The filtrate, on being rendered alkaline, gave an orange-red, colloidal precipitate, which settled on keeping overnight and was collected. The substance separates from alcohol as an orange-red powder, which sinters at 200° and melts at 205—210° (Found: N=9.75. $C_{16}H_8O_4N_2$ requires N=9.59 per cent.). The substance dissolves readily in alcohol, acids, or excess of alkali hydroxide.

Xanthhydrols.

α -Dinitroxanthhydrol.— α -Dinitroxanthone (2.5 grams) was suspended in 100 c.c. of methyl alcohol, and 1 gram of sodium added in small pieces with shaking. The colour of the mixture became first orange, and finally deep red. It was boiled under reflux for half an hour, when a clear, dark red solution was obtained; the boiling was continued for a further period of one and a-half hours, and the solution filtered hot. A yellowish-brown precipitate was obtained on acidifying the solution with hydrochloric acid, and this crystallised from acetic acid in brown needles melting at 185° (Found: N=10.11. $C_{13}H_8O_6N_2$ requires N=9.72 per cent.). The substance dissolves in alcohol and in cold dilute alkali hydroxide, in the latter solvent with a yellow colour. Its solution in concentrated sulphuric or hydrochloric acid is pale yellow, and in nitric acid it dissolves with a pink coloration. When heated with glacial acetic acid, it dissolves to an orange-red solution.

β (or 2:7)-Dinitroxanthhydrol.—This substance was obtained by treating 2.5 grams of 2:7-dinitroxanthone with sodium and methyl alcohol, as in the case of the α -dinitro-compound. It crystallised from alcohol in slender, yellowish-white needles melting and decomposing at 196° (Found: N=9.65. $C_{13}H_8O_6N_2$ requires N=9.72 per cent.). The substance dissolves in cold aqueous alkali hydroxide as well as in concentrated sulphuric acid with a yellow coloration, and in concentrated hydrochloric acid to a pale yellow solution.

Each of these dinitroxanthhydrols, when boiled with a mild oxidising agent, such as a dilute solution of hydrogen peroxide or potassium permanganate, is converted into the corresponding dinitroxanthone.

Chloroxanthones.

1-Chloroxanthone.—*o*-Chlorobenzoic acid (1.6 grams), *m*-chlorophenol (1.4 grams), and sodium (0.4 gram) were dissolved in methyl alcohol (10 c.c.), a trace of copper powder being added as a catalyst. The solution was heated on an oil-bath, and the alcohol evaporated, when the substance melted at about 200° and solidified at about 215°. It was cooled, powdered, and heated on a steam-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water, and the precipitate collected. The substance crystallised from aqueous alcohol in white needles melting at 100°. It dissolves in sulphuric acid with a green fluorescence. In this synthesis, either 1-chloro-

xanthone or 3-chloroxanthone or both may possibly be formed, but only one product was obtained. As it differed from 3-chloroxanthone, which melts at 130° , it must be 1-chloroxanthone (Found: Cl=15.46. $C_{13}H_7O_2Cl$ requires Cl=15.40 per cent.).

1-Anilinoxanthone.—One gram of the substance described above was boiled with 3 c.c. of aniline and a trace of copper powder for six hours. A blue precipitate was obtained by pouring the solution into water acidified with hydrochloric acid. After being purified by extraction with alcohol, it melted at 120° – 125° (Found: N=4.86. $C_{19}H_{13}O_2N$ requires N=4.87 per cent.).

1-Chlorotetranitroxanthone.—Half a gram of 1-chloroxanthone was dissolved in 7 c.c. of concentrated sulphuric acid, and 5 c.c. of nitric acid (D 1.42) were added to the solution with shaking. The solution was kept overnight, when white needles were obtained, which melted at 195° (Found: N=13.70. $C_{13}H_5O_{10}N_4Cl$ requires N=13.69 per cent.). From the filtrate, a white precipitate was obtained, which was too small in amount for any detailed examination.

2-Chloroxanthone.—*p*-Chlorophenol (1.4 grams) was dissolved in methyl alcohol (10 c.c.), and sodium (0.4 gram) and *o*-chlorobenzoic acid (1.6 grams) and a trace of copper powder were added to the solution. The alcohol was evaporated, and the viscous, semi-solid mass was heated to 140° , and kept at that temperature for half an hour, when it darkened. It dried to a black solid mass at 150° . The temperature was further raised to 200° , and then the substance was cooled, powdered, and heated on a water-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water; the precipitate was collected, crystallised from alcohol, and obtained in white needles melting at 165° (Ullmann, *loc. cit.*, gives 171°). It dissolves in sulphuric acid with a blue fluorescence (Found: Cl=15.72. Calc.: Cl=15.40 per cent.).

2-Chlorotetranitroxanthone.—This compound was obtained by nitrating 2-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of substance, 10 c.c. of sulphuric acid and 7 c.c. of nitric acid were used. The substance was obtained in slender, yellowish-white needles melting at 205° (Found: N=13.75. $C_{13}H_5O_{10}N_4Cl$ requires N=13.69 per cent.).

4-Chloroxanthone.—This substance was obtained by the condensation of *o*-chlorobenzoic acid with *o*-chlorophenol in the manner described in the syntheses of 1-chloroxanthone. It crystallised from alcohol in slender, white needles melting at 130° . It dissolves in concentrated sulphuric acid with a green fluorescence (Found: Cl=15.36. $C_{13}H_5O_2Cl$ requires Cl=15.40 per cent.).

4-Chlorotrinitroxanthone.—This compound was obtained by

nitrating 4-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of the substance, 5 c.c. of sulphuric acid and 4 c.c. of nitric acid were used. Brownish-yellow needles were obtained on keeping the reaction mixture overnight. The substance melts at 235° (Found: N=11.14. $C_{13}H_4O_8N_3Cl$ requires N=11.49 per cent.).

4-Chlorodinitroxanthone.—This substance was obtained from the filtrate of the trinitro-compound as a pale yellow powder melting and decomposing at 195° – 200° (Found: N=8.81. $C_{13}H_5O_6N_2Cl$ requires N=8.73 per cent.).

Dichloroxanthone.—Xanthone (7.5 grams) was dissolved in acetic acid (50 c.c.) with the aid of heat. A current of dry chlorine was passed into the solution, which was kept warm by heating the reaction vessel over a steam-bath until approximately one molecular proportion of chlorine was absorbed. A trace of iodine was used as a catalyst. The product (10 grams) crystallised from alcohol in slender, white needles melting at 225° (Found: Cl=26.86. $C_{13}H_6O_2Cl_2$ requires Cl=26.80 per cent.). The substance dissolves in concentrated sulphuric acid with a strong green fluorescence. From the alcoholic filtrate from the dichloroxanthone another product mixed with it was obtained, which appeared to be 3-chloroxanthone from its melting point and chlorine content, but it has not yet been possible to purify it completely.

Dichlorodinitroxanthone.—The dichloro-compound was nitrated in the cold with a mixture of equal volumes of nitric (D 1.42) and concentrated sulphuric acids (100 c.c. for each gram of the substance). On keeping the solution overnight, yellow needles were obtained, which melted at 240° (Found: N=8.10. $C_{13}H_4O_6N_2Cl_2$ requires N=7.88 per cent.).

Bromoxanthones.

2-Bromoxanthone.—*p*-Bromophenol (2.5 grams) and sodium (0.6 gram) were dissolved in methyl alcohol (15 c.c.) and *o*-chlorobenzoic acid (2.3 grams) and a trace of copper powder were added to the solution. It was heated to 160° , when a hard, black mass was obtained. The temperature was raised to 220° , but the substance did not fuse. It was cooled, powdered, and heated over a steam-bath with 25 c.c. of concentrated sulphuric acid for twenty-five minutes. When cool, the solution was poured into water and the precipitate collected. It crystallised from aqueous alcohol in brown needles melting at 150° , and dissolved in sulphuric acid with a yellow colour, but no fluorescence (Found: Br=29.00. $C_{13}H_7O_2Br$ requires Br=29.16 per cent.). 2-Bromoxanthone is also obtained when xanthone is brominated in concentrated

sulphuric acid solution with bromine and a trace of iodine. It is very difficult, however, to isolate the substance in a pure condition, because the last traces of either xanthone or dibromoxanthone, which are always associated with this compound, cannot easily be removed.

2-Bromo- α -tetranitroxanthone.—2-Bromoxanthone (0.7 gram) was dissolved in concentrated sulphuric acid (10 c.c.), and nitric acid (5 c.c. of D 1.42) then added gradually to the solution with shaking. No precipitate was formed after keeping it for a few days. The solution was poured into water, and the precipitate was boiled with alcohol, in which it partly dissolved. From the alcoholic solution, the substance was obtained in slender, brown needles melting at 210° (Found: N=12.02. $C_{18}H_9O_{10}N_4Br$ requires N=12.31 per cent.).

2-Bromo- β -tetranitroxanthone.—The residue of the nitro-compound described above was dissolved in benzene, and crystallised from this solution in brown needles melting at 270° (Found: N=12.21. $C_{18}H_9O_{10}N_4Br$ requires N=12.31 per cent.). When 2-bromoxanthone was heated with bromine (1 or 2 mols.) in acetic acid solution and a trace of iodine, over a sand-bath, a dibromocompound was obtained which melted at 212° . This compound was identified as 2:7-dibromoxanthone by the method of mixed melting points. It is also obtained by brominating xanthone with bromine, using iron filings as a catalyst.

4-Bromoxanthone.—This compound was obtained by condensing *o*-bromophenol with *o*-chlorobenzoic acid in the usual way. It crystallised from alcohol in greyish-white needles melting at 140° . It shows no fluorescence in sulphuric acid solution (Found: Br=29.28. $C_{13}H_7O_2Br$ requires Br=29.16 per cent.).

4-Bromodinitroxanthone.—4-Bromoxanthone was dissolved in the requisite amount of concentrated sulphuric acid in the cold, and nitric acid (D 1.42) was added to the solution (20 c.c. for each gram of the substance). On keeping the solution overnight, yellowish-white needles were obtained, which melted at 295° (Found: N=8.09. $C_{13}H_5O_6N_2Br$ requires N=7.67 per cent.).

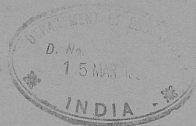
The author takes this opportunity of expressing his thanks to Professor J. F. Thorpe and Dr. M. A. Whiteley for their kind encouragement, and to the Van't Hoff Memorial Fund Committee and to the Chemical Society for Research Grants which met part of the expenses.

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To Sir William Duke ²⁹ G. C. I. & C. S. I. etc.
With best compliments
S. Dhar

EXPERIMENTS ON HALOGENATION. THE DIRECT
DISPLACEMENT OF NEGATIVE GROUPS BY
HALOGEN IN THE AROMATIC SERIES. PART I.
THE DISPLACEMENT OF THE NITRO-GROUP BY
BROMINE.



BY

SURENDRA NATH DHAR.

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CX.—*Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. Part I. The Displacement of the Nitro-group by Bromine.*

By SURENDRA NATH DHAR.

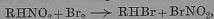
IN the series of which this paper is Part I, it is proposed to investigate the mechanism and conditions which lead to the direct displacement of negative groups by halogen atoms when such groups are attached to the aromatic nucleus, because, although several instances have been recorded of the occurrence of this type of reaction, no systematic study of it appears to have been made. It is evident that if a change of this kind could be definitely controlled and its course clearly established, it would serve as a valuable means for preparing certain aromatic derivatives not otherwise easily obtained.

In the first instance, therefore, it is intended to record certain experiments which have been carried out in connexion with the displacement of nitro-groups by bromine, a change which appears to have been first noted by Kekulé (*Annalen*, 1866, **137**, 169), when he obtained tri-, tetra-, and penta-bromobenzene by heating nitrobenzene with bromine in a sealed tube. Other instances of a similar character have since been published; thus, Meyer (*Monatsh.*, 1915, **86**, 723) found that nitrobenzene under the influence of thionyl chloride gives chlorobenzene, and that *m*-dinitrobenzene when treated with chlorine is converted first into *m*-chloronitrobenzene and finally into *m*-dichlorobenzene (D.R.-P. 108165). Picric acid gives with bromine the same bromodinitrophenol as is obtained when dinitrophenol is brominated (Armstrong, *J. Soc. Dyers*, 1885, **1**, 85). Other instances of the displacement of nitro-groups by halogens in the benzene as well as in the naphthalene series have been recorded by Lobry de Bruyn and Leent (*Rec. trav. chim.*, 1896, **15**, 84), Atterberg (*Ber.*, 1876, **9**, 316, 926, 1734; 1877, **10**, 1841), and Jolin (*Bull. Soc. chim.*, 1877, [ii], **23**, 514). Direct displacement of the nitro-group has also been noticed in the anthracene series. Thus 1-nitroanthraquinone is converted into 1-chloroanthraquinone through the agency of chlorine, and 1:5-dinitroanthraquinone into the 1:5-dichloro-derivative by the same process (D.R.-P. 252578).

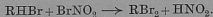
In the present paper are described experiments dealing with the behaviour of certain typical nitro-derivatives of benzene,

naphthalene, anthracene, xanthone, and coumarin towards bromine at a high temperature, when the bromine is present in the proportion of one molecule of the halogen to each nitro-group. These experiments were carried out with the object of settling one of the fundamental points in connexion with the reaction, namely, the reason why it does not stop when all the nitro-groups, or all such as are capable of displacement, are substituted by the halogen, but in many cases proceeds further, leading to the formation of higher halogenated derivatives. Moreover, preliminary experiments showed that not only did further halogenation take place with remarkable ease, but that it was possible by the aid of this reaction to prepare halogen derivatives which could not be obtained by the direct halogenation under known conditions. Examples of this kind are given in the experimental part, the best being that supplied by the formation of octabromoxanthone (p. 999).

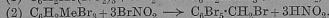
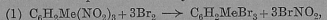
It is evident, therefore, that in this reaction some product is formed which acts as a very much more powerful halogenating agent than the halogen itself, and it is thought that this substance may well be the nitro-derivative of bromine, which might be formed in accordance with the equation



the reaction being completed in accordance with the equation



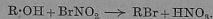
If this is the true explanation of the course of the reaction, it follows that a trinitro-derivative when treated with three molecules of bromine should, if a sufficient number of hydrogen atoms are present in the nitro-derivative, yield a compound containing six atoms of bromine, and that this is actually the case is shown by the behaviour of trinitrotoluene, which is transformed under these conditions into pentabromobenzyl bromide:



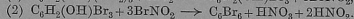
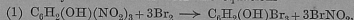
It may be added that this view is supported by the fact that in this and other similar cases the halogenation does not proceed further, even though excess of bromine is used. Similarly, both 1:5- and 1:8-dinitronaphthalene when treated with two molecular proportions of bromine yield the same tetrabromonaphthalene, which must therefore be the 1:(4):5:8-compound, the formation of the substance being in complete accord with the views expressed above.

It would be difficult to predict the reactions which might occur between the substance BrNO_2 and phenols, but it is reasonable to suppose that one of them would be the displacement of the

hydroxyl by bromine and the formation of nitric acid, in accordance with the equation



It is therefore interesting to note that when picric acid is treated with three molecular proportions of bromine, it is converted into hexabromobenzene, although tetrabromo- and pentabromo-phenol are also produced. It is probable, therefore, that the reaction takes place chiefly in accordance with the equations



It is evident that both tetrabromo- and pentabromo-phenol are intermediate products in the reaction, because the yield of hexabromobenzene increases with the temperature of the reaction.

Although in the instances given above the displacement of the nitro-groups and subsequent bromination proceeds smoothly and completely, yet it is evident that the completion of the reaction must depend on two main factors, namely, (a) the stability of the nitro-group, and (b) the tendency for hydrogen atoms present in the molecule of the aromatic substance to be displaced by bromine. It is to be expected that experiment would reveal the operation of these two factors, and that instances would be found in which the reaction would leave nitro-groups in stable positions unattacked and in which the further entrance of bromine atoms would be inhibited. Actually, the experiments carried out with nitro-derivatives of xanthone and coumarin have supplied admirable examples of the operation of both factors, although in every case the course of the reaction can be explained by the general equations given above.

It may be added that all the nitro-compounds mentioned in this paper, excepting those of the coumarin series, have been treated with bromine in the usual solvents, such as acetic acid or nitrobenzene, without result. Compounds of the coumarin series do, however, yield bromo-derivatives under these conditions (see p. 1000). Thus both α_1 - and β_1 -tetranitroxanthone give only dibromodinitroxanthone, and 3:6-dinitrocoumarin gives 3-bromo-6-nitrocoumarin when treated with four and two molecules of bromine respectively. On the other hand, α_2 -tetranitroxanthone gives tetrabromoxanthone, and 1:3- and 1:5-dinitroanthraquinone give 1:3- and 1:5-dibromoanthraquinone, respectively, under the same experimental conditions.

Further experiments, carried out under different conditions, will be necessary in order to determine the order in which the nitro-groups are displaced, and it is hoped that in this way valuable

evidence respecting the position-stability of this group will be forthcoming. Even in the present preliminary experiments, however, there is clear evidence of the remarkable stability conferred on nitro-groups occupying certain positions in an aromatic nucleus. It has been pointed out, for example, by Jordan and Thorpe (T., 1915, 107, 395) that whereas a nitro-group can be introduced into position 6 of the coumarin molecule with remarkable ease, it is a matter of considerable difficulty to introduce this group into position 3. The present experiments show that a nitro-group in position 6 cannot be displaced by bromine, and that one in position 3 is readily displaced. For example, 6-nitrocoumarin with one molecule of bromine yields 3-bromo-6-nitrocoumarin, and 3:6-dinitrocoumarin with two molecules of bromine gives the same 3-bromo-6-nitrocoumarin. Even when the last-named reaction is carried out at a high temperature, the nitro-group is not displaced, the final product being a tetrabromonitrocoumarin.

EXPERIMENTAL.

Benzene Series. The Bromination of Picric Acid.

Three grams of picric acid and 2 c.c. of bromine (3 mols.), together with a trace of iodine, were heated in a sealed tube at 220–250° for six hours. The crude product (4 grams), when treated with dilute alkali, yielded an insoluble residue which, when collected and recrystallised from benzene, was found to be hexabromobenzene, melting at 315° (Found: Br=86·87. Calc.: Br=86·96 per cent.). The precipitate obtained when the alkaline filtrate was acidified, when fractionally recrystallised from alcohol, yielded two substances. The less readily soluble one melted at 225°, and proved to be pentabromophenol (Found: Br=81·61.* Calc.: Br=81·81 per cent.), and the more readily soluble one, which melted at 120°, was tetrabromophenol (Found: Br=78·53.* Calc.: Br=78·03 per cent.).

The same products are obtained when the reaction is carried out at either 130° or at 300°, but the amount of hexabromobenzene formed is much greater at the higher temperature.

The Bromination of 2:4:6-Trinitrotoluene.

Pentabromobenzyl Bromide.—Three grams of 2:4:6-trinitrotoluene, 2 c.c. of bromine (3 mols.), and a trace of iodine were heated in a sealed tube at 200° for eight hours. The crude pro-

* All halogen estimations were made by Robertson's method (T., 1915, 107, 902).

duct (2·5 grams), after being washed with dilute alkali, was crystallised from benzene, when it yielded slender, white needles melting at 320° (Found: Br=84·53. $C_6H_3Br_5$ requires Br=84·80 per cent.). Pentabromobenzyl bromide is sparingly soluble in alcohol, and no precipitate of silver bromide is formed when its solution is treated with freshly precipitated silver hydroxide or alcoholic silver nitrate solution. It appears to be a remarkably stable substance, since it is not oxidised to pentabromobenzoic acid either by alkaline permanganate or by nitric acid in a sealed tube. It remains unchanged when heated in a sealed tube with bromine.

Pentabromobenzyl Alcohol.—This substance was obtained by heating a mixture of 1 gram of pentabromobenzyl bromide, 5 c.c. of absolute alcohol, and 2 grams of potassium acetate in a sealed tube at 200° for eight hours. It crystallises from alcohol in slender needles melting at 175° (Found: Br=79·82. $C_6H_3OBr_5$ requires Br=79·52 per cent.). The compound is sparingly soluble in water, but dissolves readily in alcohol. It sublimes in colourless needles when heated at 100°.

Naphthalene Series. The Bromination of 1:5- and of 1:8-Dinitronaphthalene.

1:(4):5:8-Tetrabromonaphthalene.—Five grams of 1:5-dinitronaphthalene mixed with 2·5 c.c. of bromine (2 mols.) and a trace of iodine were heated in a sealed tube at 200° for five hours. The crude product (6 grams) crystallised from benzene in colourless needles melting at 308°, and the same compound is also obtained from 1:8-dinitronaphthalene under similar conditions (Found: Br=71·88. $C_{10}H_4Br_4$ requires Br=72·06 per cent.).

1:(4):5:8-Tetrabromomononitronaphthalene was obtained by treating the above compound with concentrated sulphuric acid and nitric acid (D 1·42). For 1 gram of substance, 50 c.c. of each acid were used. A yellow precipitate was obtained on keeping the mixture overnight. The substance melts and decomposes at 220° (Found: N=2·83. $C_{10}H_3O_2NBr_4$ requires N=2·86 per cent.).

Hexabromonaphthalene.—This compound was prepared by heating 1·5 grams of 1:2:5:8-tetratritronaphthalene with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at 220° for twenty hours. The crude product (about 2 grams), after being washed with dilute aqueous alkali hydroxide, crystallised from benzene in white needles melting at 280–285° (Found: Br=79·60. $C_{10}H_2Br_6$ requires Br=79·73 per cent.).

1:3:5:8-Tetrabromonaphthalene.—This substance was obtained by heating a mixture of 2 grams of 1:3:5:8-tetratritronaphthalene,

1.5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. The crude product (2.5 grams), after being washed with cold aqueous alkali hydroxide, crystallised from benzene in white needles melting at 310° (Found: Br=72.13. $C_{10}H_4Br_4$ requires Br=72.06 per cent.).

1:3:5:8-Tetrabromonitronaphthalene.—Half a gram of the tetrabromo-compound was dissolved in 50 c.c. of concentrated sulphuric acid, 50 c.c. of nitric acid (D 1.42) were added, and the solution was heated over the steam-bath for one hour. When cold, a yellowish-brown precipitate was obtained by pouring the solution into water; this was collected and washed with water. The substance melts at 205° and does not decompose even at 280° (Found: N=2.76. $C_{10}H_2O_2NBr_4$ requires N=2.86 per cent.).

1:2:6:8-Tetrabromonaphthalene.—This substance was obtained by heating 1.5 grams of 1:2:6:8-tetranitronaphthalene (p. 1004) with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at 220° for twenty hours. The substance was purified and crystallised, as in the case of hexabromonaphthalene, and obtained in yellowish-white, shining needles melting at above 315° (Found: Br=72.26. $C_{10}H_2Br_4$ requires Br=72.06 per cent.).

1:2:6:8-Tetrabromonitronaphthalene was obtained by nitrating the above tetrabromo-compound, as in the case of the 1:3:5:8-tetrabromo-compound. A brownish-yellow substance was obtained which melted at 230° (Found: N=2.64. $C_{10}H_2O_2NBr_4$ requires N=2.86 per cent.).

1:3:6:8-Tetrabromonaphthalene.—This was obtained by heating a mixture of 2 mols. of 1:3:6:8-tetranitronaphthalene, 1.5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. White needles, melting at above 315°, were obtained by purifying the crude product (2 grams), as before (Found: Br=71.74. $C_{10}H_2Br_4$ requires Br=72.06 per cent.).

1:3:6:8-Tetrabromonitronaphthalene was obtained as a brownish-yellow powder by nitrating the tetrabromo-compound, as in the previous cases. The substance melts at 210° (Found: N=2.77. $C_{10}H_2O_2NBr_4$ requires N=2.86 per cent.).

Xanthone Series. The Bromination of Tetranitroxanthones.

In the following experiments a large excess of bromine was used, because preliminary experiments had shown that variation in the amount of halogen beyond the theoretical and in the temperature conditions did not affect the result.

Dibromodinitroxanthone was obtained by heating a mixture of

grams of α_1 -tetranitroxanthone,* 3 c.c. of bromine (11 mols.), and a trace of iodine in a sealed tube at 300° for twenty-six hours. It crystallises from benzene (2 grams) in colourless needles melting at 265°. The same compound was obtained from β_1 -tetranitroxanthone* under similar conditions (Found: Br=36.22; N=6.16. $C_{18}H_4O_2N_2Br_2$ requires Br=36.08; N=6.30 per cent.).

Tetrabromoxanthone.—This substance (about 3 grams) was obtained by heating a mixture of 2.5 grams of α_2 -tetranitroxanthone,* 4 c.c. of bromine (more than 11 mols.), and a trace of iodine in a sealed tube at 300° for twenty-six hours. It is isolated from its solution in benzene (in which it is very readily soluble) as an amorphous, yellow solid melting at 255° (Found: Br=62.36. $C_{18}H_2O_2Br_4$ requires Br=62.50 per cent.). The compound is insoluble in alcohol and soluble in pyridine or acetic acid, but does not crystallise from either of these solvents. It is evidently different from the tetrabromoxanthone previously described (T., 1916, 109, 746), because it cannot be converted into a dinitro-derivative on nitration.

Hexabromoxanthone.—This compound (about 4 grams) was prepared by heating 2.5 grams of β_2 -tetranitroxanthone* with 4 c.c. of bromine (more than 11 mols.) and a trace of iodine in a sealed tube at 200° for thirty hours. It crystallises from benzene in slender, yellow needles melting at 288° (Found: Br=72.01. $C_{18}H_2O_2Br_6$ requires Br=71.63 per cent.). This compound is evidently different from that previously described (T., 1916, 109, 748), because it does not yield a colouring matter when heated with aniline and a trace of copper powder.

Octabromoxanthone.—One gram of tetrabromodinitroxanthone (*loc. cit.*), 3 c.c. of bromine (36 mols.), and a trace of iodine were heated in a sealed tube at 300° for thirty-six hours. The product crystallised from benzene in slender, colourless needles melting at above 315° (Found: Br=77.57. $C_{18}O_2Br_8$ requires Br=77.31 per cent.).

Anthraquinone Series.

1:3-Dibromoanthraquinone was obtained by heating 2.2 grams of 1:3-dinitroanthraquinone, 1 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at 200–250° for seven hours, and at 290° for a further hour. It crystallises from alcohol in canary-yellow needles melting at 210°, as stated by Ullmann and Eiser (*Ber.*, 1916, 49, 2154) (Found: Br=44.16. Calc.: Br=43.71 per cent.).

* The new tetranitroxanthones mentioned in this paper will be described in a later communication.

1:5-Dibromoanthraquinone was obtained by heating 5 grams 1:5-dinitroanthraquinone, 2 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at 300° for four hours. The substance crystallises from benzene in pale yellow needles melting at above 320° (Found: Br=43.48. Calc.: Br=43.71 per cent.).

Coumarin Series.

3-Bromo-6-nitrocoumarin.—Three grams of 6-nitrocoumarin were heated with 2 c.c. of bromine (3 mols.) and a trace of iodine in a sealed tube at 130° for eight hours. The crude product (3.5 grams), after being washed with water, crystallised from alcohol in colourless needles melting at 215° (Found: Br=29.96; N=5.26. Calc.: Br=29.63; N=5.18 per cent.).

This compound is also obtained when 3:6-dinitrocoumarin is treated in a similar manner, or when 6-nitrocoumarin is heated in an open tube with bromine in acetic acid solution.

3:8-Dibromo-6-nitrocoumarin.—This substance was prepared by heating a solution of 4.5 grams of 3:6-dinitrocoumarin in 10 c.c. of acetic acid with 4 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The product, after being washed with alcohol, crystallised from benzene in white needles melting at 220° (Found: Br=45.89; N=4.19. $C_9H_5O_4NBr_2$ requires Br=45.84; N=4.01 per cent.).

3:8:1-Tribromo-6-nitrocoumarin.—This compound was prepared by heating a mixture of 3 grams of 3:6-dinitrocoumarin, 2 c.c. of bromine (3 mols.), and a trace of iodine in a sealed tube at 180° for six hours. The crude product was purified by solution in cold aqueous alkali hydroxide, precipitation by dilute hydrochloric acid, and crystallisation from alcohol; it melts at 200–205° (Found: Br=56.46; N=2.77. $C_9H_3O_4NBr_3$ requires Br=56.08; N=3.26 per cent.). In this reaction a second product was formed which was insoluble in alkali hydroxide, and proved to be tetrabromonitrocoumarin (see below).

3-Bromo-6:8-dinitrocoumarin was obtained by heating 1.5 grams of 3:6:8-trinitrocoumarin dissolved in 5 c.c. of acetic acid with 2 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The crude product, after being washed with cold aqueous alkali hydroxide, separated from alcohol as a yellowish-white solid melting at 130–135° (Found: Br=25.82; N=8.48. $C_9H_3O_6N_2Br$ requires Br=25.40; N=8.87 per cent.).

3:8:1:1-Tetrabromo-6-nitrocoumarin.—A mixture of 1.5 grams of 3:6:8-trinitrocoumarin with 1 c.c. of bromine (4 mols.) and a trace of iodine was heated in a sealed tube at 160° for six hours.

After being washed with dilute alkali, the product crystallised from alcohol in pale yellow needles melting at 260° (Found: Br=63.29; N=2.58. $C_9HO_4NBr_4$ requires Br=63.10; N=2.79 per cent.).

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