

*Anal.* Calcd. for  $C_{32}H_{26}O_8$ : C, 71.4; H, 4.8. Found: C, 71.2, 71.1; H, 5.7, 5.8.

### Summary

1. 9,10-Dimethyl-2',3',6',7'-tetramethoxy-1,2,5,6-dibenzanthracene, and its 4,8-dicarboxylic acid, have been prepared by the Pschorr reaction from *p*-xylylene-*bis*-(acetic acid) and 6-nitroveratraldehyde.

2. In the diazotization of the intermediate aminodimethylcaffeic acid, cyclization results only

when dioxane is used as the solvent. In aqueous solutions, the amino groups are replaced by hydroxyls.

3. Attempts to prepare the corresponding tetrahydroxydibenzanthracenes by hydrolysis of the methoxyl groups proved unsatisfactory.

4. The dibenzanthracene and its dicarboxylic acid were synthesized for testing as possible carcinogens.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

## The Nitration of Diphenyliodonium Nitrate

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The nitration of diphenyliodonium nitrate has been the subject of considerable research.<sup>3</sup> It is an interesting problem, from the standpoint of the influence of groups present in the benzene ring, on the course of further substitutions. According to Vorländer, Robinson, Ingold and others,<sup>4</sup> the most strongly meta-directing groups are the positive poles directly attached to the benzene ring. For example, phenyltrimethylammonium nitrate is nitrated exclusively in the meta position.<sup>5</sup> In this case the orienting group is  $-\text{N}(\text{CH}_3)_3^+$ . Again, a group may be meta-directing because the group as a whole carries a permanent dipole as in  $\text{NO}_2$ . On the other hand, ortho-para orientation is associated with those radicals which lose electrons to the ring as in the case of the methyl group, or which carry unshared pairs of electrons so that conjugation with the double bonds of the ring is possible as in  $\text{NH}_2$ .<sup>6</sup>

The nitration of a compound such as diphenyliodonium nitrate might be expected to be similar to the nitration of phenyltrimethylammonium nitrate, since the orienting group is  $-\text{IC}_6\text{H}_5^+$ .

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(3) (a) Vorländer and Büchner, *Ber.*, **58**, 1893 (1925); (b) Chalenger and Rothstein, *J. Chem. Soc.*, 1258 (1934).

(4) (a) Vorländer, *Ber.*, **52**, 262 (1919); (b) Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 401 (1926); (c) Goss, Ingold and Wilson, *ibid.*, 2440 (1926); (d) Flürscheim and Holmes, *ibid.*, 1562 (1926); (e) Ingold, *Ann. Repts. Chem. Soc.*, **23**, 130 (1926).

(5) Vorländer and Siebert, *Ber.*, **52**, 283 (1919).

(6) For discussions on the directive influence of substituent groups, see also Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 140 and 1881; Lucas, "Organic Chemistry," American Book Co., New York, N. Y., 1935, p. 360; Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1936, p. 439; Watson, "Modern Theories of Organic Chemistry," Oxford University Press, London, 1937, p. 57.

Vorländer<sup>3a</sup> in his work showed that meta-nitration did take place. By repeated crystallization of the reaction product he isolated pure di-*m*-nitrophenyliodonium nitrate. This gave *m*-iodo-nitrobenzene and *m*-nitrophenol (free from *o*-derivative) with sodium hydroxide. Any *p*- or *o*-compound may thus have been separated. On reading Vorländer's experimental work, the reader might draw the conclusion that nitration occurs almost exclusively in the meta position. Regarding the nitration, Vorländer has this to say: "*p*-Nitro-phenol ist vielleicht in spuren, *o*-Nitro-phenol überhaupt nicht vorhanden, . . . . *o*-Nitro-phenol war nicht einmal durch seinen Geruch nachzuweisen." The experimental work which Vorländer reports gives no indication of ortho-para nitration.

However, the iodine atom in  $-\text{I}(\text{C}_6\text{H}_5)_2^+$  has unshared electrons and is at the same time the positive end of a dipole. On the basis of unshared electrons one might expect the formation of some ortho and para derivatives along with the meta compound. Meta-directing groups usually do not contain unshared electrons in the shell of the atom which is directly joined to ring carbon.<sup>7</sup>

There is also another difference between phenyltrimethylammonium nitrate and diphenyliodonium nitrate to be considered. Since the positive electricity resides at the nucleus of the charged atom, the amount of damping action arising through the passage of the effect, through the

(7) Vorländer, *Ber.*, **58B**, 1893 (1925), has shown that  $-\text{IO}_2$  in which the iodine atom has unshared electrons is meta-directing. Recently, Masson, Race and Pounder, *J. Chem. Soc.*, 1669 (1935), have nitrated iodoxybenzene and have obtained about 99.5% meta-nitration.

successive shells of electrons belonging to the charged atom itself, would be smaller for the former than for the latter compound. On this basis it might be expected that the iodonium compound would show weaker *m*-reactivity.

It was in connection with a study of phenyl derivatives of several elements occupying consecutive or adjacent positions in the periodic table that Challenger and Rothstein<sup>3b</sup> carried out the nitration of diphenyliodonium nitrate. They carried out the nitration under the conditions followed by Vorländer. The composition of the resulting iodonitrobenzenes was determined by thermal analysis and the nitrophenols simultaneously produced were not examined. Their results showed a para-nitration which varied from 14 to 20.2% (average 17.5%). They also definitely isolated *p*-iodonitrobenzene. However, they say that "a method whereby both the nitrated phenyl groups were obtained as halogenonitrobenzenes would have been preferable."

It was with the object of trying to confirm the results of Challenger, especially from the standpoint of the more desirable procedure which he mentions, that the authors of this paper have reexamined the nitration of diphenyliodonium nitrate. In the authors' procedure the nitrated material was isolated as the nitrated iodonium iodide, which was then caused to rearrange into a mixture of iodonitrobenzenes. Both phenyl groups were therefore isolated as halogenonitrobenzenes. The mixture was examined from the standpoint of thermal analysis and also any *p*-iodonitrobenzene was very readily isolated from the mixture because of its limited solubility in ethanol.

The work of the present authors confirms the work of Challenger. Thermal analysis indicates a minimum of 18.5% of para nitration. At least 10% of the reaction mixture can be isolated as pure *p*-iodonitrobenzene and by taking into consideration the solvent effect of the ethanol, the amount of para-nitration can be shown to be at least 14%.

In the rearrangement of the nitrated iodonium iodide, it is believed that it is quite safe in assuming that the meta nitrated material will yield a *m*-iodonitrobenzene, the para nitrated material a *p*-iodonitrobenzene, and so on. In support of this there is the work of Lucas and co-workers<sup>8</sup> which shows that the decomposition of di-

tolyliodonium iodide produces only *o*-iodotoluene and not a mixture of iodotoluenes. Moreover, the authors have not been able to detect the formation of any *p*-iodonitrobenzene as a result of the decomposition of pure di-*m*-nitrophenyliodonium iodide.

### Experimental Part

**Preparation of Materials.**—A method similar to that of Lucas<sup>8</sup> and co-workers was followed for the preparation of the iodonium salts. The reaction between iodosobenzene and iodoxybenzene in the presence of a small amount of silver oxide was found to take place very readily and in a relatively short period of time. Diphenyliodonium nitrate was prepared by adding potassium nitrate to the aqueous extract produced in the above reaction. Care was taken to keep the volumes of solution as small as possible because of the solubility of the iodonium nitrate. The latter compound finally was crystallized several times from water, from which it separated in a pure condition.

Di-*m*-nitrophenyliodonium iodide was made similarly from *m*-nitroiodoxybenzene and *m*-nitroiodosobenzene. In this case, however, the yields were relatively small and the reaction required a longer period of time. The iodide was produced by adding potassium iodide to the aqueous extract of iodonium base. The salt was purified by crystallizing from water, in which it is difficultly soluble. It was shown to be pure by analysis. Vorländer<sup>3a</sup> reports that di-*m*-nitrophenyliodonium iodide melts at 142–144°. The authors have found that the melting point is 158–159°. It should be mentioned here that, usually, by the melting point of an iodonium salt is meant the decomposition temperature, and at this temperature very often the products are in a liquid condition.

**Nitration of Diphenyliodonium Nitrate and Decomposition of the Nitrated Iodonium Iodides.**—Ten grams of diphenyliodonium nitrate was added during five minutes to 50 cc. of nitrating mixture (130 cc. of concentrated nitric acid, 327 cc. of concentrated sulfuric acid), kept cool in an ice-water mixture. The reaction mixture was allowed to stand for about thirty minutes at room temperature, after which it was poured into 1 liter of a mixture of crushed ice and water. The mixture was heated until all of the precipitate had dissolved. Potassium iodide was then added to the clear solution and the very insoluble iodonium iodide was formed. After cooling to room temperature the iodide was filtered off by suction and washed with small quantities of cold water. After air drying, the yield of nitrated iodonium iodide was found to vary from 13.4 to 14.2 g.

The decomposition of the compound was effected by immersing a 250-cc. flask, containing the compound, in a glycerol-bath heated to the required temperature. The rearrangement also could be brought about by holding the flask directly in the low flame of a Bunsen burner. The rearrangement was practically instantaneous and was accompanied by the liberation of some iodine. The main reaction proceeds as follows:  $(m\text{-O}_2\text{NC}_6\text{H}_4)_2\text{I}_2 \longrightarrow 2m\text{-O}_2\text{NC}_6\text{H}_4\text{I}$ .

The rearranged product in some cases was treated directly in the flask with enough boiling ethanol to bring about complete solution. It was filtered immediately and on cooling the filtrate, almost pure *p*-iodonitrobenzene

(8) Lucas, Kennedy and Wilnot, *This Journal*, **58**, 157 (1936)

separated out. A second crystallization from ethanol usually gave crystals melting at 171–172°. The yield of pure *p*-iodonitrobenzene was determined and an estimation of the amount remaining in the solvent was made. For this purpose the solubility in 95% ethanol at 25° was taken as 0.76 g. in 100 cc. of solution. There was also taken into consideration a loss due to a side reaction which liberates iodine. This sometimes was as high as 9%. On this basis, then, the amount of para nitration was calculated to be about 14%.

When the rearranged product was examined from the standpoint of thermal analysis it was first of all shaken up with a dilute solution of sodium thiosulfate. The iodine-free mixture was then extracted with chloroform, the chloroform solution was separated, washed with water, dried and evaporated to dryness. The melting point of the residue was determined and from the tables given by Challenger and Rothstein<sup>3b</sup> the amount of para nitration was calculated to be 19%. In this work it was assumed that no ortho compound was present,<sup>3b</sup> and no attempt was made to fractionate the material prior to a melting point determination.

Pure di-*m*-nitrophenyliodonium iodide was treated according to a procedure similar to the above, and no *p*-iodonitrobenzene could be detected.

Some typical experiments are recorded in Tables I and II.

TABLE I

Experiment	I	II
Yield of nitrated iodonium iodide, g.	13.4	14.2
Yield of <i>p</i> -iodonitrobenzene, g.	1.20	1.34
<i>p</i> -Iodonitrobenzene remaining in solvent, g.	0.60	0.45
Loss due to iodine liberation, g.	0.16	0.16
<i>p</i> -Nitration, %	14.6	13.9

TABLE II

Experiment	III	IV
Yield of nitrated iodonium iodide, g.	13.4	13.7
M. p. of rearranged material	88°	89°
<i>p</i> -Nitration, %	18.5	19.0

### Summary

Diphenyliodonium nitrate has been nitrated and the work of Challenger and Rothstein, which shows that a considerable amount of para nitration occurs along with meta nitration, has been confirmed.

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## The Dipole Moments and Structures of Ozone, Silicobromoform and Dichloroform

BY GEORGE L. LEWIS AND CHARLES P. SMYTH

The structures of the molecules of the three inorganic substances, ozone, silicobromoform and dichloroform contain contributions from several forms among which resonance exists. It has seemed desirable to investigate the relation of each of these structures to its dipole moment.

The dipole moments were obtained in the usual manner from the dielectric constants  $\epsilon$  and the densities  $d$  of solutions of the substances in non-polar solvents by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d}$$

and

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which  $P_{12}$  is the polarization of the mixture, and  $c_1$  and  $c_2$ ,  $M_1$  and  $M_2$ , and  $P_1$  and  $P_2$  are, respectively, the mole fractions, molecular weights and polarizations of the individual components, the subscript 2 referring to the polar substance. The values of  $P_\infty$  obtained by extrapolating the  $P_2 - c_2$  curves to infinite dilution are used to calculate the dipole moment  $\mu$  by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

in which  $MR_D$  is the molar refraction for the D sodium line and  $T$  is the absolute temperature.

### Preparation of Materials

**Heptane.**—Material from the American Petroleum Corporation was used without purification,  $d^{25}_4$  0.67958,  $n^{25}_D$  1.38428.

**Carbon Tetrachloride.**—Purification of this solvent was carried out by standard methods:<sup>1</sup>  $d^{25}_4$  1.58431,  $n^{25}_D$  1.45717,  $\epsilon^{25}$  2.223.

**Oxygen.**—Tank electrolytic oxygen was passed through concentrated sulfuric acid and over phosphorus pentoxide and condensed by means of liquid air:  $d^{-192.5}_4$  1.1937,  $\epsilon^{-192.2}$  1.505.

**Ozone.**—A solution of ozone in liquid oxygen was prepared by passing a stream of purified oxygen through an ozonizer and condensing the product directly in the dielectric cell or the pycnometer surrounded by liquid air. The concentration of the solution was determined by allowing the liquid to evaporate through neutral potassium iodide solution in three gas washing bottles in series into a large aspirator bottle. The volume, measured within 0.1%, was then used to determine the total number of moles of oxygen plus ozone; the mole fraction of ozone was determined iodimetrically with sodium thiosulfate.

**Silicobromoform.**—A pure specimen of silicobromoform was given us by Professor W. C. Schumb of the Massachusetts Institute of Technology.

(1) Williams and Krcchma, THIS JOURNAL, 48, 1888 (1926).