

reproducible to $\pm 0.1^\circ$. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250-cc. receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to ensure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified carbon dioxide through the system, the solvents are distilled with a steam-bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0° . From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart, Fig. 2, paper VII, the experimental precipitation point is then corrected to standard conditions, *viz.*, 28.55% alcohol and 0.85% rubber. This is the s. p. p. Including experimental errors and corrections, the s. p. p. determination is correct within $\pm 0.2^\circ$.

Summary

1. Fractional precipitation has been used to determine and isolate the constituents of the rubber hydrocarbon.
2. A "standard precipitation point" has been devised and its use advanced as a physical constant of rubber.
3. The presence of a single component, amounting to more than 50% and characterized by a standard precipitation point of 35° , has been demonstrated.
4. The presence of highly soluble portions, of indeterminate s. p. p., has been shown.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

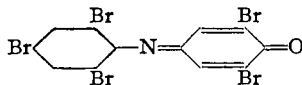
THE OXIDATION OF SYMMETRICAL TRIBROMOANILINE BY CHROMIC ANHYDRIDE IN ACID SOLUTION. II. MECHANISM¹

BY W. H. HUNTER AND CARYL SLY

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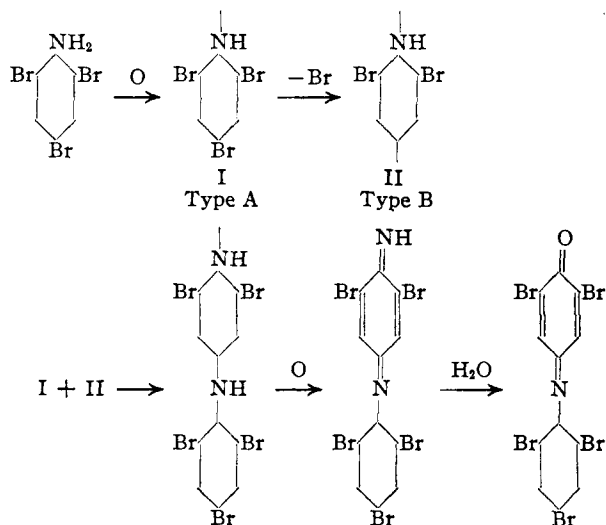
In some unpublished work performed in this Laboratory by A. G. Mayers (now deceased), it was found that symmetrical tribromoaniline, dissolved in a mixture of acetic and dilute sulfuric acids, on oxidation with chromic anhydride gave a compound with the molecular formula $C_{12}H_4ONBr$, and the structural formula



¹ Abstracted from a thesis submitted by Caryl Sly to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

Brominated N-phenylquinoneimines have been prepared by Smith and Orton² by first brominating *p*-hydroxydiphenylamine and then oxidizing with chromic anhydride. However, no reference could be found relative to the formation of such compounds by the oxidation of halogenated anilines.

Consideration of the probable mechanism for the formation of the above compound by oxidation of symmetrical tribromoaniline led to two widely divergent views of the reaction. Goldschmidt³ has shown in the oxidation of anilines that a radical of the type $C_6H_5NH\cdot$ is first formed, which may react as such or be further oxidized to the type $C_6H_5N\cdot$. This latter radical in his opinion was responsible for the formation of azobenzene and quinone diimine by the oxidation of aniline. The radical $C_6H_5NH\cdot$ is the nitrogen analog of the type A radicals which result during the oxidation of *sym*.-trihalogenated phenols.⁴ Using the type A and type B radicals predicated in the case of the halogenated phenols the reaction becomes



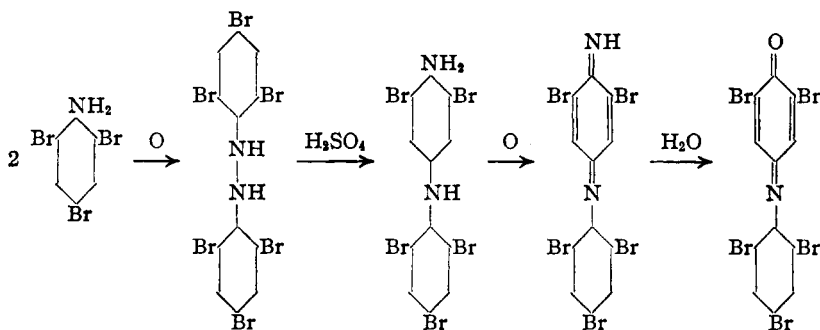
The alternative mechanism assumed the formation of *sym*.-hexabromohydrazobenzene, a *p*-semidine rearrangement of this derivative with the loss of a bromine atom, oxidation to the quinonediimine and finally hydrolysis to the quinoneimine.

In order to choose between these mechanisms an attempt was made to prepare the pentabromoquinoneimine from *sym*.-hexabromohydrazobenzene. The preparation of hexabromohydrazobenzene presented consider-

² Smith and Orton, *J. Chem. Soc.*, **93**, 314-326 (1908).

³ Goldschmidt, *Ber.*, **55**, 3216 (1922).

⁴ Hunter and Levine, *THIS JOURNAL*, **48**, 1608 (1926); Hunter and Morse, *ibid.*, **48**, 1615 (1926).



able difficulty despite the fact that it had been previously reported by Pechmann and Nold.⁵

Production of the desired hydrazo derivative from *sym*.-tribromonitrobenzene was not successful because at least one bromine was lost in alkaline reduction, a condition already observed by other workers.⁶ Eventually 2,4,6,2',4',6'-hexabromoazobenzene was prepared by oxidizing *sym*.-tribromoaniline in pyridine solution with potassium permanganate.

In the light of our work it is extremely doubtful if Pechmann and Nold had the hexabromohydrazobenzene. Instead, it is probable they had the 2,4,2',4'-tetrabromohydrazobenzene, since the reduction of hexabromoazobenzene according to their directions gave as the main product this tetrabromohydrazobenzene. The fact that we had the tetrabromohydrazo derivative was not at first recognized because Zincke⁷ had reported the corresponding azo compound as melting at 179°, as compared with a melting point of 211° for the oxidation product of our compound. The identity of the substance, however, was established by analysis, by reduction to 2,4-dibromoaniline, and by the fact that 2,4-dibromoaniline could be oxidized with permanganate to the compound melting at 211° and then reduced back to the 2,4-dibromoaniline. Both the hexabromoazobenzene and the tetrabromoazobenzene were readily reduced to the hydrazo state by zinc dust and acetic acid, the former without loss of bromine.

All of our attempts to cause the benzidine or semidine rearrangement of the hexabromoazobenzene or hexabromohydrazobenzene met with failure. Using the azo derivative, Jacobson's method⁸ or Witt's method⁹ gave only reduction products. With the hydrazo derivative, concentrated hydrochloric acid or 65% sulfuric acid¹⁰ caused only oxidation and reduction to

⁵ Pechmann and Nold, *Ber.*, **31**, 564 (1898).

⁶ Jackson and Bentley, *Am. Chem. J.*, **14**, 364 (1892).

⁷ Zincke and Kuchenbecker, *Ann.*, **330**, 54 (1904).

⁸ Jacobson, *Ann.*, **287**, 105, 110, 128 (1895).

⁹ Witt, *Ber.*, **27**, 2382 (1894).

¹⁰ Meyer, *Ber.*, **53**, 2035, 2045 (1920), reports that sulfuric acid caused rearrangement in a similar case where hydrochloric acid failed.

the azo compound and the substituted aniline. Tauber's method¹¹ of treating the hydrazo compound with a reducing agent and a mineral acid gave only reduction to the aniline. Similar results were obtained in the case of the tetrabromoazobenzene and tetrabromohydrazobenzene. The usual tests¹² for *o*- and *p*-semidine rearrangement products were negative.

As a final test for the formation of pentabromoquinoneimine from *sym.*-hexabromohydrazobenzene, the hydrazo compound was added to the reaction mixture which had oxidized *sym.*-tribromoaniline to the pentabromoquinoneimine. Here the only reaction was one of oxidation to hexabromoazobenzene.

In view of these results it seems probable that the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride involves the same reaction mechanism as that previously postulated for the oxidation of symmetrically halogenated phenols, with the intermediate formation of the N analogs of the type A and type B radicals.

Experimental Part

2,4,6,2',4',6'-Hexabromoazobenzene.—Twenty grams of *sym.*-tribromoaniline was dissolved in a mixture of 90 cc. of pyridine and 46 cc. of water and the solution heated to 75°. To this solution 40 g. of finely pulverized potassium permanganate was added in small portions, shaking after each addition until the permanganate color had disappeared. The copious precipitate of manganese dioxide was filtered off, washed with cold water, dried and thoroughly extracted with chloroform. The chloroform solution was evaporated to dryness, and the resulting solid suspended in 100 cc. of acetic acid held at 80°. The insoluble purple precipitate was pure hexabromoazobenzene, m. p. 212–213° (uncorr.); yield, 40%.

A 20% yield was obtained by heating 1 g. of *sym.*-tribromoaniline, 5 cc. of pyridine and 1 cc. of 17% sodium hypochlorite solution, diluting with 50 cc. of water and treating the insoluble precipitate as above.

Pechmann and Nold⁶ described the compound as red needles, but in every case our product was a dull violet color, although solutions of it were red. The substance is readily soluble in hot chloroform or benzene, moderately soluble in these solvents cold and practically insoluble in either hot or cold alcohol, acetic acid, ether, and acetone.

Anal. Calcd. for $C_{12}H_4N_2Br_6$: Br, 73.17, N, 4.27. Found: Br, 73.17; N, 4.29.

2,4,2',4'-Tetrabromoazobenzene.—Using the same procedure described for the hexabromo derivative, 20 g. of 2,4-dibromoaniline dissolved in a mixture of 40 cc. of pyridine and 40 cc. of water was treated with 40 g. of potassium permanganate. The dried mixture of manganese dioxide and azo derivative was extracted with 200 cc. of benzene until no further coloration of the benzene resulted. On cooling the benzene solution a considerable portion of the azo compound crystallized as red needles. These were filtered off, the mother liquor evaporated to 50 cc. and 100 cc. of hot 95% alcohol added; yield, 40%; m. p. 211° (uncorr.).

Fifty to sixty per cent. yields were also obtained by reducing *sym.*-hexabromoazobenzene suspended in alcohol with zinc dust and ammonium chloride and then oxidizing the product thus formed in acetic acid with chromic anhydride.

¹¹ Tauber, *Ber.*, **25**, 1022 (1892).

¹² Witt and Schmidt, *ibid.*, **25**, 1017 (1892), and Ikuta, *Ann.*, **243**, 281 (1887); *Ber.*, **27**, 2707 (1894).

The substance crystallizes in red needles from benzene, is very soluble in either hot chloroform or benzene, slightly soluble in hot acetic acid and practically insoluble in alcohol.

Anal. Calcd. for $C_{12}H_6N_2Br_4$: Br, 64.26; N, 5.62. Found: Br, 63.74, 63.61; N, 5.63, 6.03.

2,4,2',4'-Tetrabromohydrazobenzene.—Two and one-half grams of tetrabromohydrazobenzene dissolved in a boiling mixture of 40 cc. of benzene and 5 cc. of acetic acid was stirred vigorously with 1 to 3 g. of zinc dust, added in small portions. The excess zinc was filtered from the colorless solution and the filtrate evaporated to 5 cc. One cc. of water and 5 cc. of acetic acid were added, and the solution chilled, giving colorless needles of m. p. 123–124° (uncorr.); yield, 80%. Reduction with stannous chloride gave 2,4-dibromoaniline.

Anal. Calcd. for $C_{12}H_6N_2Br_4$: Br, 64.00; N, 5.60. Found: Br, 63.70; N, 5.99.

N,N'-Diacetyl-2,4,2',4'-tetrabromohydrazobenzene.—One gram of tetrabromohydrazobenzene was added to 25 cc. of cold acetic anhydride and the mixture allowed to stand for two days, then heated to 40° and cooled. The azo derivative which had formed was filtered off and the excess acetic anhydride destroyed with hot water. The insoluble material after treatment with water was recrystallized from dilute alcohol as colorless crystals, m. p. 178–179°C. (uncorr.); yield, 40%.

Anal. Calcd. for $C_{16}H_{12}O_2N_2Br_4$: Br, 54.80. Found: Br, 54.22.

Rearrangement Experiments.—All of our attempts to rearrange either the hexabromohydrazobenzene or the tetrabromohydrazobenzene met with failure. Mineral acids without a reducing agent present and at elevated temperatures gave only the azo

TABLE I
REARRANGEMENT EXPERIMENTS ON HEXABROMOHYDRAZOBENZENE

| Reaction of 1 g. of hexabromohydrazobenzene and | Hexabromoazo- benzene, g. | Sym.- tribromo- aniline, g. | Recovered, % |
|--|------------------------------|-----------------------------------|-----------------|
| 20 cc. concd. HCl, sealed tube, 130° | 0.46 | 0.51 | 97 |
| 20 cc. 66% H ₂ SO ₄ , sealed tube, 150° | .43 | .52 | 95 |
| 25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. SnCl ₄ , 80° for 12 hrs.; stood for 3 days | .40 | .55 ^a | 95 |
| 25 cc. abs. alcohol, 10 cc. 66% H ₂ SO ₄ , 80° for 12 hrs., stood for 3 days | .42 | .52 ^a | 94 |
| 30 cc. cold abs. alcohol, 1 g. SnCl ₄ ·H ₂ O, 5 cc. concd. HCl, stood for 48 hrs. | .93 | .05 | 98 |
| unchanged hydrazo | | | |

^a Contained small amounts of unchanged hexabromohydrazobenzene.

TABLE II
REARRANGEMENT EXPERIMENTS ON TETRABROMOHYDRAZOBENZENE

| Reaction of 1 g. of tetrabromohydrazobenzene and | Tetrabromoazo- benzene, g. | 2,4-Dibromo- aniline, g. | Recovered, % |
|---|-------------------------------|-----------------------------|-----------------|
| 10 cc. concd. HCl, sealed tube, 130° | 0.45 | 0.47 | 92 |
| 10 cc. 66% H ₂ SO ₄ , sealed tube, 100–130° | .45 | .42 | 87 |
| 25 cc. abs. alcohol, 10 cc. concd. HCl, 1 g. SnCl ₄ , 80° for 12 hours, stood for 3 days | .48 | .40 | 88 |
| 25 cc. abs. alcohol, 10 cc. 66% H ₂ SO ₄ , 80° for 12 hrs., stood for 3 days | .47 | .46 | 93 |
| 25 cc. abs. alcohol, 1 g. SnCl ₄ ·2H ₂ O, 5 cc. concd. HCl, stood for 48 hrs. | .85 | .12 | 97 |
| unchanged hydrazo | | | |

derivative and the aniline, while in the cold, stannous chloride in the presence of hydrochloric acid gave the aniline along with the unchanged hydrazobenzene.

The tables indicate the conditions of attempted rearrangement and the products isolated.

Summary

1. A study of the properties of *sym.*-hexabromohydrazobenzene has shown that it cannot be responsible for the formation of a pentabromoquinoneimine obtained by the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride. It is, therefore, probable that N analogs of the type A and type B radicals postulated in the oxidation of *sym.*-halogenated phenols play the important role.

2. *Sym.*-hexabromohydrazobenzene and 2,4,2',4'-tetrabromohydrazobenzene do not undergo the benzidine type of rearrangement. Instead they oxidize and reduce to the corresponding azo and aniline derivatives in the presence of a mineral acid without a reducing agent; in the presence of a reducing agent they are split to the anilines.

3. A method for the preparation of azo compounds is described.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

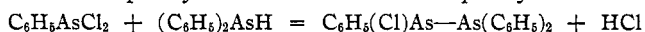
THE INTERACTION OF PHENYLARSINES WITH PHENYLHALOARSINES¹

BY F. F. BLICKE AND L. D. POWERS

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Several years ago it was announced by Steinkopf and Smie² that phenyldichloroarsine and diphenylarsine react to form triphenylchlorodiarsyl.



Since we wished to prepare triphenylhydroxydiarsyl,^{2a} hydrolysis of the corresponding chloro compound suggested itself as a preparative procedure. Phenyldichloroarsine and diphenylarsine were allowed to react in the proportions used by the above-mentioned investigators but instead of triphenylchlorodiarsyl, arsenobenzene and diphenylchloroarsine were obtained in yields which correspond closely to those calculated from equation A.³

¹ This paper represents one part of a dissertation submitted to the Graduate School by L. D. Powers in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² Steinkopf and Smie, *Ber.*, **59**, 1459 (1926).

^{2a} It is of interest to note that Wieland and co-workers [*Ber.*, **44**, 898 (1911); *ibid.*, **48**, 1118 (1915)] were unable to obtain the corresponding nitrogen analog $\text{R}_2\text{N}-\text{NR}(\text{OH})$.

³ The very unsharp melting point (164–179°) of the "triphenylchlorodiarsyl" obtained by Steinkopf and Smie indicates that these investigators really had a mixture of compounds. The identity of the material obtained by them was based on the result