which separated was reduced with stannous chloride in dioxane by the method of Sandin and Fieser.[1] This yield of almost pure 4,9-dimethyl-5,6-benzthiophanthrene, m. p. 158°, was 0.7 g. One crystallization from glacial acetic acid raised the m. p. to 158–159°.

**7,8-Benz-4,9-thiophanthrenequinone (IV).**—Following the procedure (b) detailed above, for the isomeric quinone, 3.5 g. of 1-$\alpha$-thenoyl-2-naphthoic acid (I) afforded 0.67 g. of 7,8-benz-4,9-thiophanthrenequinone, m. p. 202–204°.

*Anal.* Calcd. for $C_{16}H_8O_2S$: S, 12.13. Found: S, 11.92, 11.94.[7] A mixture of equal parts of this preparation and a sample of the quinone (m. p. 203–204°, sublimed twice and recrystallized from glacial acetic acid eleven times to constant m. p.) made by the cyclization of 1-$\alpha$-thenoyl-2-naphthoic acid[1] melted at 202.5–203.5°.

**4,9-Dimethyl-7,8-benzthiophanthrene (V).**—The procedure was essentially the same as described for 4,9-dimethyl-5,6-benzthiophanthrene, with the exception that ether was used for the preparation of the Grignard reagent and also that a mixture of equal parts of hydriodic and hydrobromic acids was used for the precipitation of the iodomethyl compound.

**2,3-Dimethyl-9,10-diethylanthracene.**—In this case 2,3-dimethylanthraquinone was added to the Grignard reagent made from ethyl iodide, ether and magnesium. It was found advantageous to use a mixture of hydrobromic acid (sp. gr. 1.4) and hydriodic acid (sp. gr. 1.7) as in the above instance. The reduction with stannous chloride in dioxane proceeded smoothly.

**1,9,10-Trimethylanthracene.**—The melting point of this compound changes on standing. One sample which had been kept for three weeks, melted unsharply at 210° The change is probably a dimerization. In the preparation of the compound it is essential that the reduction reaction mixture be worked up as rapidly as possible and that purification be made through the picrate.

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## Summary

1. The preparation of five *meso*-alkylanthracenes is described.

2. 4,9-Dimethyl-7,8-benzthiophanthrene, an isomer of the active carcinogen 4,9-dimethyl-5,6-benzthiophanthrene, has been prepared.

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[7] Macroanalysis by R. K.

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

# The Identification of Aryl Iodides

BY J. CHARLES NICHOL AND REUBEN B. SANDIN

Many useful procedures have been described for making derivatives of aryl halides.[1,2] Recently Huntress and Carten[3] have used chlorosulfonic acid as a reagent for this purpose and found it to yield excellent results. Of thirty-two aryl halides studied, thirty afforded characteristic arylsulfonyl chlorides which were readily converted to the corresponding arylsulfonamides. However, Huntress and Carten obtained unsatisfactory results with certain iodo derivatives of aromatic hydrocarbons.

The authors of this paper report a study of some aryliodoso chlorides as applied to the characterization of a number of aryl iodides. Aryliodoso chlorides decompose on heating, usually into the iodo compounds and chlorine. There is also the "migration" of chlorine to ring carbon with the formation of hydrogen chloride and chlorine substitution compounds.[4] Phenyliodoso chloride, for example, decomposes at 120–121° giving up chlorine and hydrogen chloride. There are a few instances in the chemical literature where this property has been used in the identification of aryl iodides. Leicester and Bergstrom,[5] working on the thermal decomposition of triphenylselenonium iodide characterized iodobenzene by conversion into phenyliodoso chloride, and further checked by a mixed melting point with a known sample of phenyliodoso chloride. Similarly Ganguly and Le Fèvre,[6] working on the iodo-*p*-cymene formed by the direct iodination of the hydrocarbon, characterized 2- and 3-iodocymene by converting them into the corresponding iodoso chlorides. Their melting points were found to be 97° and 85–87°, respectively, whereas an equal-part mixture melted at about 75°. C. Willgerodt[7] in his monograph lists approximately one hundred and twenty-five iodinated aromatic compounds which have been converted into solid iodosochlorides. Willgerodt's data should prove useful for identification work.

The authors of this paper have found that the iodoso chlorides of some aryl iodides are satisfactory derivatives in that they are prepared easily and quickly, and require no purification. The io-

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[1] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 159–161.

[2] Kamm, "Qualitative Organic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 194–196.

[3] Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).

[4] Ingold, Smith and Vass, *J. Chem. Soc.*, 1245 (1927). See also Brazier and McCombie, *ibid.*, **101**, 968 (1912); Buchan and McCombie, *ibid.*, 137 (1931); Matheson and McCombie, *ibid.*, 1103 (1931).

[5] Leicester and Bergstrom, THIS JOURNAL, **51**, 3587 (1929).

[6] Ganguly and Le Fèvre, *J. Chem. Soc.*, 1697 (1934).

[7] C. Willgerodt, "Die organischen Verbindungen mit mehrwertigem Jod," F. Enke, Stuttgart, 1914.

TABLE I

BENZENE DERIVATIVES

| No. | Dichloride of compound | M. p., ° C. uncor. | | Equivalent weight | | |
|---|---|---|---|---|---|---|
| | | After 10-15 min. | After 1 hr. | After 15 min. | After 1 hour | Calcd. |
| 1 | I | 120-121 | 118-119 | 138 | 138.2 | 137.5 |
| 2 | 1-$CH_3$, 2-I | 91 | 90- 91 | 146.5 | 145.9 | 144.5 |
| 3 | 1-$CH_3$, 3-I[a] | 104-105 | 99-100 | 145.7 | 145.4 | 144.5 |
| 4 | 1-$CH_3$, 4-I[a] | 100 | 96-100 | 146.8 | 153.1 | 144.5 |
| 5 | 1-Cl, 2-I[b] | 96- 97 | 96- 97 | 155.5 | 155.5 | 154.7 |
| 6 | 1-Cl, 3-I[b] | 99-100 | 97- 98 | 155.3 | 157.3 | 154.7 |
| 7 | 1-Cl, 4-I | 115 | 115 | 156.2 | 156.7 | 154.7 |
| 8 | 1-Br, 3-I | 108-109 | 108-109 | 181.4 | 185.1 | 177.0 |
| 9 | 1-Br, 4-I | 124-125 | 123-124 | 178.9 | 181.3 | 177.0 |
| 10 | 1,4-di-I[c] | 147-148 | 146-147 | 203.8 | 201.3 | 200.5 |
| 11 | 1-$C_6H_5$, 4-I | 110 | 108 | 178.8 | 187 | 175.5 |
| 12 | 1,4-di-$CH_3$, 2-I | 87- 89 | 84 | 153.3 | 153.9 | 151.5 |

[a] An equal-part mixture melts at 80-82°. [b] An equal-part mixture melts at 80°. [c] An iodosochloride is produced instead of the expected diiodosochloride.

doso chlorides can also be prepared in good yields. There is also the added fact that iodoso chlorides are good oxidizing agents and ordinarily are reduced practically irreversibly. For that reason they can be titrated quantitatively with standard sodium thiosulfate, after the addition of an acid and potassium iodide.[8] Against these favorable properties are the facts that the melting points or decomposition points of the iodoso chlorides depend upon the rate of heating and also that the iodoso chlorides are not stable over a period of time. However, the authors have obtained consistent results by heating rapidly at a uniform rate, and by carrying out the determinations shortly after the preparation of the derivative.

In Table I are collected the authors' experimentally determined decomposition temperatures and equivalent weights of the iodoso chlorides of some of the more common aryl iodides. Of fourteen aryl iodides studied, twelve afforded iodoso chlorides which were considered to be of value in characterization work. Unsatisfactory results were obtained with *o*-bromoiodobenzene and 4-iodo-1,3-dimethylbenzene. The results obtained at the end of fifteen minutes and at the end of one hour of standing indicate that the iodoso chlorides vary in stability. The color of the iodoso chloride varies from pale yellow (2-iodo-1,4-dimethylbenzene) to bright yellow (*p*-diiodobenzene).

## Experimental

By a melting point of an iodoso chloride is meant that temperature at which the melting point tube begins to fill with gas and liquid. All melting points were determined using the apparatus described by Shriner and Fuson.[9] The rate of heating was 20° per minute and the melting point tube was introduced into the bath liquid at a temperature 20° below the melting point of the compound.

**Preparation of Iodoso Chlorides.**—One gram of the solid aryl iodide or 1 cc. of the liquid compound is dissolved in 3 cc. to 15 cc. of dry chloroform, depending on the solubility. After cooling to 0° a slow current of dry chlorine is passed through the solution. Usually the iodoso chloride separates rapidly as yellow crystals and in a pure condition. If the separation of crystals does not occur, the addition of 10 cc. of low boiling ligroin invariably brings it about. The crystals are filtered by suction, washed with ligroin and air dried for ten minutes while still on the suction funnel. During this time suction is maintained.

**Determination of Equivalent Weights.**—The freshly precipitated and air-dried iodoso chloride (0.5 to 1.0 g.) is placed in a 250-cc. Erlenmeyer flask, along with 50 cc. of water, 10 cc. of chloroform, 10 cc. of glacial acetic acid and a small excess of solid potassium iodide. The liberation of iodine it is rapid and it is readily titrated with standard sodium thiosulfate.

## Summary

The possibility of identifying aryl iodides by means of their iodoso chlorides has been pointed out. Out of the fourteen aryl iodides examined, twelve gave what are believed to be satisfactory melting points and equivalent weights.

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[8] Sandin, *Chem. Rev.*, **32**, 257, 259 (1943).

[9] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 85-87.