

THE PREPARATION OF BROMOMESITYLENE

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Bromomesitylene has been prepared in the past by several recorded methods. Schramm¹ has prepared bromomesitylene by the bromination of mesitylene in the dark, Fittig and Storer² in daylight. It has also been made by using mesitylene, ligroin, nitric acid and sulfur bromide³. Smith and MacDougall⁴ have reported its preparation by the direct bromination of mesitylene, using carbon tetrachloride as a solvent. This procedure was later published in "Organic Syntheses"⁵. They report yields ranging from 79 to 82 per cent.

No detailed and satisfactory method for the preparation of bromomesitylene in which the direct bromination was carried out in the presence of catalysts and without solvent has ever been recorded. In this study, iron and manganese have been used as catalysts in the direct bromination of mesitylene without additional solvent. In the purification of the bromomesitylene two methods have been used; that suggested by Adkins and McElvain⁶ for the purification of bromobenzene, and that given by Smith for the purification of bromomesitylene.

In the process suggested by Adkins and McElvain the bromomesitylene was washed first with sodium hydroxide solution, then with water, and then fractionally distilled under reduced pressure. In Smith's method of purification, the bromomesitylene was boiled for an hour with sodium ethoxide solution in alcohol, and then was allowed to stand over night. Then the mixture was poured into water, extracted with car-

1 Schramm, Ber. 19, 212 (1886).

2 Fittig and Storer, Ann. 147, 6 (1886).

3 Ger. Pat. 123, 746 [(Frld. 6, 53 (1902))].

4 Smith and MacDougall, J. Am. Chem. Soc. 51 3002 (1929).

5 Marvel, "Organic Syntheses" Vol. XI, John Wiley & Sons, Inc., New York, (1931), p. 24.

6 Adkins and McElvain, "Practice of Organic Chemistry", McGraw-Hill Book Co., Inc., New York, (1933), p. 149.

bon tetrachloride and fractionally distilled under reduced pressure. The sodium ethoxide is used to remove any traces of side chain derivatives.

Experiments

A 250 cc. round bottom flask was provided with a three-hole rubber stopper bearing an adapter, a dropping funnel, and a mechanical stirrer with a mercury seal. The adapter was connected to a reflux condenser set at an angle with the vertical. The upper end of the condenser was connected with a gas absorption train, to absorb the HBr which is evolved during the reaction. In the round bottom flask were placed 45 g of mesitylene and 1 g. of finely divided iron filings or 3 g. of finely divided manganese⁷. The mesitylene used had a boiling point range from 159°-163°C. at 719 mm. and was prepared as described by Adams and Hufferd in *Organic Syntheses*⁸. From the dropping funnel 70 g. of bromine (a slight excess) was gradually added with constant stirring. Care should be taken that the reaction does not become too vigorous. During the time of the addition of the bromine the flask was cooled with ice water. After the vigorous evolution of HBr was over, the reaction product was allowed to stand for 48 hours at room temperature. The reaction mixture was then washed first with sodium hydroxide solution, then with water by shaking in a separatory funnel. It was then dried over fused CaCl₂ and filtered. The filtrate was the crude bromositylene. Two methods of purification for each of the two catalysts, i. e., iron and manganese, were used with separate preparations. In the method suggested by Adkins and McElvain the crude product was fractionally distilled under reduced pressure. The product boiling from 117°-119° (36 mm) was retained and is bromomesitylene. There is a small low-boiling fraction, and also a high boiling fraction. There is also produced a small amount of tarry residue.

In the method of purification given by Smith a solution of sodium ethoxide, prepared by dissolving 6 g. of sodium in 100

⁷ Ducehiez, Gay et Raymond, *Bull. Soc. Chem.*, (4), 15, 737 (1914).

⁸ Gilman, "Organic Syntheses" Collective Volume 1, John Wiley & Sons Inc., New York, (1932), p. 334.

cc. alcohol, was added to the crude bromomesitylene. The whole was then boiled under a reflux for an hour, and then allowed to stand over night. It was then poured into 300 cc. of water and extracted with carbon tetrachloride. The carbon tetrachloride was evaporated on the water bath, and the remaining product fractionally distilled under reduced pressure.

Table I

Yields of Bromomesitylene.

	Adkins and McElvain's method of purification	Smith's method of purification
Fe as catalyst -----	44 g. (59%)	45 g. (61%)
Mn. as catalyst -----	32 g. (41%)	58 g. (75%)

Conclusions

On the basis of this study certain conclusions may be drawn:

1. Smith's method of purification of bromomesitylene is by far the better of the two methods.
2. Manganese shows a greater tendency than iron to form reducible side chain derivatives, while iron forms di and tri bromo derivatives.
3. Manganese is a better catalyst than iron both from the standpoint of quality of product produced, and from the standpoint of yield.
4. The catalytic preparation of bromomesitylene is a good and convenient method.