

5. H. W. LEMON. J. Am. Chem. Soc. **69**, 2998 (1947). T. W. CAMPBELL and G. M. COPPINGER. J. Am. Chem. Soc. **73**, 2709 (1951).
6. L. JURD. Arch. Biochem. Biophys. **63**, 376 (1956).
7. KALYANANMAY SEN and P. BAGCHI. J. Org. Chem. **24**, 316 (1959).
8. R. N. JONES, C. L. ANGELL, T. ITO, and R. J. D. SMITH. Can. J. Chem. **37**, 2007 (1959).
9. J. R. CANNON, G. K. HUGHES, E. RITCHIE, and W. C. TAYLOR. Australian J. Chem. **6**, 86 (1953).
10. R. ADAMS (*Editor-in-Chief*). Organic reactions. Vol. I. John Wiley & Sons. 1953. p. 20.

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SYNTHESIS OF DEUTERIATED METHYL BENZOATES AND DIMETHYL PHTHALATES¹

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As part of an investigation (1) of the infrared spectra of carbonyl compounds, the deuteriated methyl benzoates and dimethyl phthalates shown below were synthesized:



For reasons stated in previous communications on deuterated esters (2, 3) the required compounds were prepared from the silver salts and methyl or trideuteriomethyl iodide rather than by esterification. Silver phthalate was more conveniently prepared from aqueous solutions of the ammonium salt and silver nitrate than from the acid and silver carbonate as described by Ekeley and Banta (4). The methyl esters were formed in moderate yield when a suspension of the silver salt was stirred in an ether solution of methyl iodide for a day. Deuterated benzoic and phthalic acids were prepared by the platinum-catalyzed exchange of potassium benzoate and phthalate in deuterium oxide (5). The deuterium content of the compounds was determined by the method of Jones and MacKenzie (6).

EXPERIMENTAL

Tetradeteriophthalic Acid

Phthalic acid (8.3 g; 0.05 mole) was stirred in 100 ml of water and neutralized by the addition of 20% aqueous potassium carbonate. The neutral or slightly alkaline solution was evaporated to dryness under reduced pressure. The residue was dissolved in 40 ml of 99.5% deuterium oxide and the solution was poured into a tube which contained 0.1 g of platinum oxide, and which was constricted at the top near the joint. A stream of deuterium was bubbled through for a minute or two to reduce the oxide to platinum and then the tube was evacuated on the vacuum line, sealed, and heated for 72 hours in a rocking furnace at 130°. At the end of this period, the contents of the tube were poured into a flask for removal of the solvent under reduced pressure. The residue was heated with a second 40-ml portion of deuterium oxide as before. The residue from the second exchange was taken up in 100 ml of water and the solution was acidified with hydrochloric acid. It was filtered hot with the aid of carbon black. On cooling the filtrate, deuteriophthalic acid crystallized out. It was filtered off, washed with a little ice-cold water, and dried. Yield: 7.0 g.

Silver Phthalate

Phthalic acid (1.7 g; 0.01 mole) was mixed with 10 ml of water in a beaker and neutralized with ammonium hydroxide. The solution was heated on the steam bath until free of excess ammonia and diluted with water to about 75 ml. A solution of 4.0 g of silver nitrate in 25 ml of water was then added with stirring. The precipitate of monosilver salt which first formed redissolved. Further addition of silver nitrate solution precipitated the disilver salt, which was filtered off, washed once with water, then with acetone, and dried. The yield was nearly quantitative.

Silver Tetradeteriophthalate

The deuterated silver phthalate was prepared in the same manner from tetradeteriophthalic acid.

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Di(trideuteriomethyl) Phthalate

Silver phthalate (3.78 g; 0.01 mole) was pulverized in a mortar and added to 50 ml of anhydrous ether in which had been dissolved 1.5 ml of trideuteriomethyl iodide. The mixture was stirred under a reflux condenser for 24 hours. The yellow precipitate of silver iodide was filtered off and washed with ether. The ether solution and washings were largely evaporated on the steam bath and the residue was purified by distillation from a Späth bulb in an air bath at 90–100° under 0.1 mm pressure. Yield: 1.5 g (72%), n_D^{20} 1.5122. For ordinary dimethyl phthalate, n_D^{20} is 1.5140. Calc. for $C_{10}H_4D_6O_4$: D, 6.00. Found: D, 6.06.

Dimethyl Tetradeuteriophthalate

This ester was prepared as described above for the methyl-labelled ester, n_D^{20} 1.5132. Calc. for $C_{10}H_6D_4O_4$: D, 4.00. Found: D, 3.99.

Di(trideuteriomethyl) Tetradeuteriophthalate

The totally deuterated ester was also prepared as described above, n_D^{20} 1.5119. Calc. for $C_{10}D_{10}O_4$: D, 10.00. Found: D, 10.24.

Pentadeuteriobenzoic Acid

Sodium benzoate (14.2 g, 0.1 mole) was exchanged as described by Brown and Garnett (5). The yield of deuterated benzoic acid was quantitative.

Methyl Pentadeuteriobenzoate

A suspension of 8.0 g (0.034 mole) of pulverized silver pentadeuteriobenzoate was stirred under reflux for 24 hours with 250 ml of absolute ether and 7.0 g of methyl iodide. The silver iodide was filtered off and washed with ether. The filtrate was evaporated on the steam bath and the residue of methyl pentadeuteriobenzoate was purified by distillation in a Späth bulb. Yield: 4.0 g (82%), n_D^{20} 1.5140. For normal methyl benzoate, n_D^{20} is 1.5160. Calc. for $C_8H_5D_5O_2$: D, 5.00. Found: D, 4.83.

Trideuteriomethyl Benzoate

This compound was prepared in the same manner as the above compound from trideuteriomethyl iodide and silver benzoate. The yield of product, n_D^{20} 1.5150, was 75%. Calc. for $C_8H_5D_3O_2$: D, 3.00. Found: D, 3.00.

Trideuteriomethyl Pentadeuteriobenzoate

The compound was similarly prepared from trideuteriomethyl iodide and silver pentadeuteriobenzoate. The yield of product, n_D^{20} 1.5142, was 75%. Calc. for $C_8D_5O_2$: D, 8.00. Found: D, 7.92.

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1. R. N. JONES and J. B. DI GIORGIO. Unpublished work.
2. M. E. ISABELLE and L. C. LEITCH. *Can. J. Chem.* **36**, 440 (1958).
3. B. NOLIN. *Can. J. Chem.* **31**, 1257 (1953).
4. J. B. EKELEY and C. BANTA. *J. Am. Chem. Soc.* **39**, 764 (1917).
5. W. G. BROWN and J. L. GARNETT. *J. Am. Chem. Soc.* **80**, 5272 (1958).
6. R. N. JONES and M. A. MACKENZIE. *Talanta*, **7**, 124 (1960).

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SYNTHESES INVOLVING IMIDOGEN INTERMEDIATES: PHENANTHRIDINES AND BENZO[c]PHENANTHRIDINES¹

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It has been suggested (1, 2) that the reaction of certain aromatic nitro compounds with ferrous oxalate involves the formation of imidogen intermediates² which could be either

¹Preliminary communication: ref. 1.

²These have also been called azene or nitrene intermediates. Both of these names are now considered unsuitable. Imidogen is used by Chemical Abstracts (Index). We wish to thank Drs. R. L. Shriner and R. S. Cahn for their advice on this matter.