# NOTES

## SYNTHESIS OF METHYL-$d_3$ FORMATE*

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In earlier papers of this series (1, 2) Nolin reported the preparation of several deuterated methyl and ethyl acetates from the alkyl iodides and silver acetate. On account of the instability of silver formate the method is not directly applicable to the synthesis of methyl-$d_3$ formate. This ester has now been prepared in moderately good yields by the acid-catalyzed transesterification of methyl-$d_3$ butyrate and *n*-butyl formate:

$$C_3H_7CO_2CD_3 + HCO_2C_4H_9 \rightarrow HCO_2CD_3 + C_3H_7CO_2C_4H_9.$$

The methyl-$d_3$ butyrate was prepared in nearly quantitative yield from methyl-$d_3$ bromide and silver butyrate. The methyl-$d_3$ bromide was in turn prepared by the brominative decarboxylation of silver acetate-$d_3$ in carbon tetrachloride as described in the experimental part rather than by the method reported in reference (3).

It is of interest to compare the mass spectra of methyl and methyl-$d_3$ formates:

| $HCOOCH_3$ | | $HCOOCD_3$ | |
|---|---|---|---|
| 60 | 100 | 63 | 100.0 |
| 59 | 1.86 | 62 | 4.56 |
| | | 61 | 0.1 |

Since the intensity of the 61 peak—due to loss of D—is so small in methyl-$d_3$ formate the peaks at 59 in the spectrum of methyl formate and 62 in the spectrum of methyl-$d_3$ formate must be due to loss of H in the formoxy group rather than in the methyl group.

### EXPERIMENTAL

*Silver Butyrate*

Silver butyrate was prepared by adding a solution of 77 gm. of silver nitrate in 400 ml. of water in small portions to a stirred solution of 40 gm. of *n*-butyric acid in 200 ml. of water containing sufficient aqueous ammonia for neutralization. The salt was recrystallized from boiling water, dried for a day over phosphorus pentoxide in a vacuum desiccator, and stored in an amber bottle. The yield was nearly theoretical.

*Methyl-$d_3$ Bromide*

Silver acetate-$d_3$ (34.0 gm., 0.2 mole) was placed in a 500 ml. four-necked round-bottomed flask equipped with a funnel, a thermometer, a mechanical

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stirrer with a graphite packed gland, and a reflux condenser. Three spiral traps, two of which were cooled in dry ice and carbon dioxide at −78° and the third at −30°C., were connected to the outlet of the condenser. A solution of 11 ml. of dry bromine in 75 ml. of dry carbon tetrachloride was added to the stirred silver salt at the rate of about a drop every two seconds. The temperature of the reaction mixture was kept at 27–30°. Addition of the bromine required about four hours. The reaction mixture was then slowly heated to the boiling point and refluxed from one to one and one-half hours while a current of dry nitrogen was passed in. The contents of the first trap were then distilled into the second. The third trap was generally empty. The crude product was distilled on the vacuum line through ascarite to remove dissolved carbon dioxide and bromine. The distillate was redistilled twice from a bath at −40°C. into a trap cooled in liquid nitrogen. The weight of crude methyl-$d_3$ bromide was 19.0 gm. After another distillation from a trap at −78° the vapor pressure of the product at 0° was 679 mm. There was little change in the vapor pressure of various fractions distilled at 0°C. The yield was 17.5 gm. (89.3% of the theoretical amount). Mass analysis showed a purity of 97.8 mol. % $CD_3Br$ or 99.2 atom % D.

*Methyl-$d_3$ Butyrate*

Silver butyrate (8.3 gm., 0.04 mole) was heated with 4.1 gm. (0.04 mole) of methyl-$d_3$ bromide in a sealed tube for 16 hr. at 80°C. in a rocking furnace. The methyl-$d_3$ butyrate was isolated by attaching the opened tube to a Stock trap cooled in liquid nitrogen on a vacuum manifold and evacuating to a pressure of 0.1 mm. The yield of ester recovered in the trap, $n_D^{20}$ 1.3879, vapor pressure 30 mm. at 22°C., was quantitative. Methyl butyrate prepared in the same way had $n_D^{20}$ 1.3874.

*Methyl-$d_3$ Formate*

A mixture of 4.5 gm. of *n*-butyl formate, 4.1 gm. of methyl-$d_3$ butyrate, and three drops of concentrated sulphuric acid was distilled in a column packed with glass helices. The yield of methyl-$d_3$ formate, b.p. 31–32°C., $n_D^{20}$ 1.3431, was 1.5 gm. (61% of the theoretical). Its mass spectrum gave a deuterium content of 97.6 mol. % or 99.07 at. %.

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