NOTES

SYNTHESIS OF 1-DEUTERIOALDEHYDES

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The report of Filby and Gunther(1) on the preparation of o-nitrobenzaldehyde-1-d by a modified Brown-Subba Rao reduction(2) prompted us to disclose an earlier synthesis of nonanal-1-d for mass spectral(3) and infrared spectral studies, which is simpler and more economical of deuterium.

Filby and Gunther treated o-nitrobenzoyl chloride with lithium tri-t-butoxyaluminodeuteride (which they prepared from lithium aluminum deuteride and deuterated t-butyl alcohol) at -80° for 24 hours and then hydrolyzed the mixture with D_2O ice. We treated nonanoyl chloride with commercially available lithium tri-t-butoxyaluminodeuteride (Ventron Corporation,* Alfa Products, Beverly, Ma.) at -67° for 1 to 2 hours and then hydrolyzed the reaction mixture with ordinary ice.

Mass spectrometric analysis of the prepared nonanal-1-d indicated the presence of one deuterium per molecule and limited its location to the first or second carbon atom(3). The nuclear magnetic resonance spectrum showed that the nonanal-1-d had better than 98% isotopic purity. The aldehydic proton, which appears at $\delta 9.7$ in nonanal, was completely absent in the spectrum of nonanal-1-d.

Infrared spectroscopy further confirmed the presence of deuterium on the carbonyl carbon. The C-H stretching frequency in the carbonyl group appeared at 2723 cm^{-1} in nonanal. In nonanal-1-d this peak was completely absent, but a new peak appeared at 2066 cm^{-1}. The shift in the frequency $\nu C\text{-}H/\nu C\text{-}D = 2723/2066 = 1.31$. Nakanishi(4) places this ratio at about 1.36. The C=O stretching frequency in nonanal is at 1734 cm^{-1}. In the deuterated nonanal this frequency shifted to 1722 cm^{-1}.

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* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

PREPARATION OF NONANAL-1-d

Freshly distilled nonanoyl chloride (1.24 g, 0.0069 mole) in freshly distilled diglyme (15 ml) was placed in a dry 100-ml 3-necked round-bottomed flask equipped with a dropping funnel, a Hershberg stirrer and a low-temperature thermometer. A slow stream of dry nitrogen was passed through the apparatus during the reaction. Lithium tri-t-butoxyaluminodeuteride (1.99 g, 0.0078 mole) was suspended in freshly distilled diglyme (15 ml) in the dropping funnel. The reaction flask was cooled to -67° in a Dry Ice-acetone bath, and the deuteride suspension was added with stirring at that temperature for 1 hour. The flask was allowed to warm to room temperature for 0.75 hour, and 1 hour later its contents were poured onto ice and acidified with 1:1 hydrochloric acid. The mixture was extracted with three 50-ml portions of ether, and the combined ether extracts were washed with three 30-ml portions of ice water to remove much of the diglyme. The ether solution was dried over anhydrous sodium sulfate. The solution was filtered, the ether was removed by distillation and the remaining liquid (1.72 g) was placed on a column of Adsorbosil CAB (30 g) prepared in hexane:ethyl ether (95:5) in a 50-ml Pyrex burette. The column was developed with the same solvent mixture, and the deuterated nonanal appeared in the first four 25-ml fractions. These fractions were combined, and the solvent was removed by distillation to yield nonanal-1-d (0.55 g, 0.0039 mole) in 56% yield. The deuterated nonanal can be purified further through the bisulfite addition product(5) or by preparative gas liquid chromatography.

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