

EXPERIMENTAL

Materials.

2-Furoic acid (**1a**), m.p. 133-134°, Matheson, Coleman and Bell and thiophene-2-carboxylic acid (**1b**) m.p. 127-128°, (Aldrich Chemical Co.) were used as received. Deuterium oxide (>99%) was supplied by Columbia Organic Chemicals Company. A Parr Instrument Company Monel Bomb was employed.

Hydrogen-Deuterium Exchange.

Method A. Exchange at H-5.

Deuterium oxide (16 ml.) was added to an equimolar mixture of 0.008 M of **1a** or **1b** and sodium carbonate. The solution having $pD \sim 10$ was heated in a bomb at 165°. After cooling, the reaction mixture was acidified with dilute hydrochloric acid and the precipitate was collected. Recrystallization from proteo water gave the corresponding carboxylic acid-5-*d*. NMR analyses were obtained on methylene chloride solutions. Results are summarized in Table I. Mass spectral analysis of **2a** showed $d_0 = 8.0\%$, $d_1 = 86.2\%$, and $d_2 = 5.8\%$; **2b** showed $d_0 = 3.6\%$, $d_1 = 95.0\%$, and $d_2 = 1.4\%$.

Method B. Exchange at H-3,5.

2-Furoic acid-0-*d* or 2-thiophenecarboxylic acid-0-*d* (2.0 g.) was heated in a bomb at 250°. The product obtained from the cooled bomb was dissolved in methylene chloride for nmr analysis. Prior to nmr analysis of **2a**, the solid was gently warmed to remove furan formed by decarboxylation. Results are given in Table I. The dideuterated products were recrystallized from proteo water before mass spectral analysis: **3a** showed $d_0 = 59.9\%$, $d_1 = 34.6\%$, $d_2 = 5.5\%$; **3b** showed $d_0 = 46.2\%$, $d_1 = 43.6\%$, $d_2 = 10.2\%$.

Acknowledgment.

Partial support by the National Science Foundation (grant GP 9488) is gratefully acknowledged.

REFERENCES

- (1) A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953.
- (2) S. Gronowitz, *Advan. Heterocycl. Chem.*, **1**, 2 (1963).
- (3) Sadtler Standard Spectra, NMR No. 633M, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.
- (4) *Ibid.*, NMR No. 523M.