

**Table 1.** The effect of ATP and AMP on the  $^{14}\text{C}$ -thiamine uptake by non-proliferating thiamine deficient cells of *L. fermenti*. Incubation mixture: sodium chloride 0.15 M, ascorbic acid 0.03 M,  $\text{MgCl}_2$  0.02 M, variable buffer 0.02 M, ATP or AMP 0.02 M,  $10^8$  cells/ml,  $^{14}\text{C}$ -thiamine  $2 \times 10^{-6}$  M, total volume 5 ml. Incubation for 20 min at  $37^\circ\text{C}$ . Radioactivity counted by the liquid scintillation method.<sup>3</sup>

Buffer	Relative uptake of radioactivity			
	In the absence of exogeneous energy	In the presence of ATP <sup>a</sup> (Sigma)	ATP <sup>a</sup> (Fluka)	AMP <sup>b</sup> (Sigma)
K-phosphate pH 5.5	100	250	190	220
K-phosphate pH 6.8	100	40	120	140
Tris-HCl pH 6.8	100	115	127	110
Tris-HCl pH 6.8, without $\text{MgCl}_2$	100	270	276	220

<sup>a</sup> disodium salt

<sup>b</sup> sodium salt

In certain cases a depression of the thiamine uptake was observed instead of a stimulation. There were also certain differences between the preparations of ATP obtained from Sigma and from Fluka. The effect of AMP was, in most cases, essentially similar to the effect of ATP, except when ATP exerted a depressing effect on the uptake. It must therefore be concluded that the stimulating effect of ATP, observed under certain conditions, does not depend on this compound as an energy carrier. Rather, it seems that the stimulating effect may depend on some contaminant, which is presumably present both in the ATP and in the AMP preparations. It is interesting to note in this connection a report by Lorand *et al.*<sup>4</sup> according to which different commercial preparations of crystalline ATP disodium salt were hydrolyzed to widely varying degrees by myofibrillar ATPase. The authors suggest that the observed variations may depend on the varying  $\text{Ca}^{2+}$  content of the respective preparations.

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1. Neujahr, H. Y. *Acta Chem. Scand.* **17** (1963) 1902.
2. Neujahr, H. Y. *Acta Chem. Scand.* **20** (1966). *In press.*
3. Neujahr, H. Y. and Ewaldsson, B. *Anal. Biochem.* **8** (1964) 487.
4. Lorand, L., Demovsky, R., Meisler, J. and Molnar, J. *Biochim. Biophys. Acta* **77** (1963) 679.

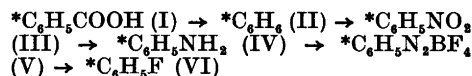
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## Preparation of a Mixture of Mono- $^{13}\text{C}$ -fluorobenzenes

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The preparation of the statistical mixture of 1-, 2-, 3-, and 4- $^{13}\text{C}$ -fluorobenzenes has been performed according to the following scheme:



$^{13}\text{C}-\text{C}_6\text{H}_6$ : Starting from 1.969 g (15 mmoles) of (I) (55 % enriched in  $^{13}\text{C}$ ) 1.11 g (14.3 mmoles) of (II) was obtained using the method of Ref. 1.

$^{13}\text{C}-\text{C}_6\text{H}_5\text{NO}_2$ : 1.11 g (14.5 mmoles) of (II) was nitrated by the method of Ref. 3 using a mixture of conc.  $\text{HNO}_3$  (1.35 ml) and conc.  $\text{H}_2\text{SO}_4$  (1.35 ml) at  $50^\circ$ , (optimal temp.). After washing with  $3 \times 300$  ml  $\text{NaOH}$  (1 M) and  $3 \times 300$  ml  $\text{H}_2\text{O}$  and drying over 0.2 g anhydrous  $\text{CaCl}_2$ , the product was distilled at  $22^\circ\text{C}$  using vacuum-line technique. The fraction in the vapour pressure range from 1.5–0.6 mm Hg consisted of 1.47 g (12 mmoles) of (III).

$^{13}\text{C}-\text{C}_6\text{H}_5\text{NH}_2$ : 0.86 g (7.0 mmoles) of (III) was dissolved in 10 ml methanol. 150 mg 10 % Pd on C was added. While continuously stirred this mixture absorbed 470 (calc. 500) ml  $\text{H}_2$  in 3 h. 0.5 g molecular sieves 'A5' was now added to remove water. After the removal of methanol *in vacuo* the residue was distilled on the vacuum-line. The fraction in the vapour pressure range from 2.0–0.9 mm Hg at

22°C was collected. Yield of IV: 0.50 g (5.44 mmoles).

$^{13}\text{C}-\text{C}_6\text{H}_5\text{N}_3\text{BF}_4$ : (IV) was converted to (V) using a modification of Flood's method (Ref. 2). A mixture of 0.50 g (5.44 mmoles) of (IV), 1.38 ml conc. HCl and 1.38 ml  $\text{H}_2\text{O}$  was cooled to  $-8^\circ\text{C}$  and maintained at this temperature during the preparation. A diazotization was effectuated by adding 0.4 g (5.8 mmoles)  $\text{NaNO}_2$  in 1.1 ml water. Afterwards 0.1 g (1.02 mmoles)  $\text{Na}_2\text{CO}_3$  was added under magnetic stirring. When all was dissolved 0.66 g (6.10 mmoles)  $\text{NaBF}_4$  in 3 ml water was added. The mixture was stirred for 10 min and filtered. After washing with 1 ml water and 1 ml methanol at  $0^\circ\text{C}$  and drying *in vacuo* over  $\text{P}_2\text{O}_5$ , 0.60 g (3.16 mmoles) of (V) was obtained.

$^{13}\text{C}-\text{C}_6\text{H}_5\text{F}$ : Following Ref. 2 (V) was decomposed to (VI) on the vacuum-line at  $110-117^\circ\text{C}$ . All the volatile reaction products were passed through a trap cooled to *ca.*  $-80^\circ\text{C}$ . Here (VI), all higher boiling substances, and part of the  $\text{BF}_3$  condensed. After removal of  $\text{BF}_3$  the residue was distilled. 0.24 g (2.54 mmoles) of (VI) was collected at a vapour pressure of 55 mm Hg at  $22^\circ\text{C}$ . The over-all yield of this five-step-preparation was *ca.* 15 %.

In the infrared spectrum of (VI) in the liquid phase, all absorption bands could be attributed to fluorobenzene or  $^{13}\text{C}$ -fluorobenzenes. Isotope effects could be observed in the regions of CF-stretching vibrations at  $1200\text{ cm}^{-1}$  and CH-stretching vibrations at  $3020\text{ cm}^{-1}$ .

Microwave studies of the isotopic species are in progress.

1. Bak, B., Christiansen, J., Lipschitz, L. and Tormod Nielsen, J. *Acta Chem. Scand.* **16** (1962) 2318.
2. Flood, D. T. *Org. Syn. Coll. Vol.* 2 p. 295, (1955).
3. Vogel, A. I. *Textbook of Practical Organic Chemistry*. Longmans, Green & Co. 1957, p. 525.

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## Hydrothermal Preparation of some Rare Earth Trihydroxides and Rare Earth Oxide Hydroxides

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Hydrothermal methods have been used in the preparation of oxide hydroxides of holmium, erbium, and ytterbium.<sup>1</sup> Microcrystals of  $\text{Ce}(\text{OH})_3$ ,  $\text{Tb}(\text{OH})_3$ ,  $\text{Dy}(\text{OH})_3$ ,  $\text{Ho}(\text{OH})_3$ ,  $\text{Er}(\text{OH})_3$ ,  $\text{Tm}(\text{OH})_3$ , and  $\text{DyOOH}$  were prepared using similar methods. Hydrothermal preparation of rare earth trihydroxides and rare earth oxide hydroxides has been reported previously by other authors.<sup>2-5</sup> Recently hydrothermal preparation of these compounds has been intensively investigated by Klevtsov and Sheina.<sup>6</sup> The unit cell parameters which they report were calculated from powder patterns obtained with 57.3 mm and 114.6 mm Debye-Scherrer cameras. Since a Guinier camera of 114.6 mm diameter was used in the investigation reported here, and since the data processing by the author is probably more elaborate, the author considers his data to be of greater precision than other previously reported.

Microcrystals of the rare earth trihydroxides and rare earth oxide hydroxides were formed by treating freshly precipitated rare earth hydroxides with water or a sodium hydroxide solution in a 20 ml pressure bomb lined with pure silver. The balanced pressure technique was used. Table 1 gives the experimental conditions. The reaction products were identified from Guinier powder patterns. A quadruple camera of the de Wolff type was used. Purified sodium chloride was used as internal standard. The powder patterns had sharp lines and a reasonable precision in the determination of the unit cell dimensions was obtainable. The powder patterns were indexed by using a GIER-ALGOL least squares program which gives the powder lines the weight  $\sin 2\theta$  and permits changes of the unit cell parameters step by step. The unit cell parameters obtained from the X-ray diffraction data for  $\text{Ce}(\text{OH})_3$ ,  $\text{Tb}(\text{OH})_3$ ,  $\text{Dy}(\text{OH})_3$ ,  $\text{Ho}(\text{OH})_3$ ,  $\text{Er}(\text{OH})_3$ , and  $\text{Tm}(\text{OH})_3$  are listed in Table 2. The unit cell parameters are compared with