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## Tritium Distribution in 4-Octene Prepared by Catalytic Hydrogenation

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In our work on hydrogen isotope effects we needed a symmetrical olefin specifically labeled on the double bond with tritium. The simplest way to achieve this seemed to be the preparation of an acetylene and the subsequent catalytic reduction with tritium gas to the corresponding olefin. 4-Octyne was therefore prepared from *n*-propyl bromide and disodium acetylide in liquid ammonia by a procedure which was found to be more practical than the published ones<sup>1,2</sup>. 4-Octyne was then reduced without solvent in the presence of Lindlar catalyst with tritium gas which was produced by electrolysis of tritiated sulfuric acid. The distilled product was pure 4-octene as shown by vapor phase chromatography.

In view of some recent work<sup>3-6</sup> showing that exchange reactions can take place during catalytic hydrogenations, a determination of the specificity of the tritium label in 4-octene was performed. Thus, 4-octene was ozonized in methylene chloride at -75° and the ozonide oxidized with alkaline hydrogen peroxide. Sodium butyrate was isolated from the reaction mixture and after purification, the free acid was checked for radioactivity. The results, given in the Experimental, indicate that in our case 8.82 per cent of the radioactivity in 4-octene is not connected with the hydrogens of the double bond. Together with other evidence<sup>3-6</sup>, this experiment shows that catalytic hydrogenation is not suitable for the preparation of specifically tritium or deuterium labeled compounds.

### EXPERIMENTAL

Radioactivity measurements were accomplished with a Tri-Carb liquid scintillation spectrometer. Tritium source was tritiated water from The Radioactive Centre, Amersham. The purity of volatile compounds was checked by vapor phase chromatography.

#### 4-Octyne

Dry ammonia (1 l.) was condensed in a 2 l. three necked flask equipped with a cold finger type condenser cooled with dry ice-acetone mixture, a stirrer and a gas outlet connected to potassium hydroxide pellets. Sodium metal (11.5 g., 0.5 mole) was added and dissolved under stirring. The gas outlet was then replaced by a gas inlet tube. Acetylene was passed successively through a trap cooled at -75°, a saturated solution of potassium permanganate, concentrated sulfuric acid and into the reaction mixture. The introduction was continued until the blue color disappeared. Additional 11.5 g. of sodium metal were then added together with traces of ferric nitrate. When the blue color turned to brownish-gray (1 to 2 hours), *n*-propyl bromide (123 g., 1 mole) was added and the stirring continued for 6 hours. Ammonia was then left to evaporate and water and ether added. The upper layer was separated, washed with water, dried and the solvent removed

over a column. The residue was fractionated yielding 24.5 g. (44.5%) of pure 4-octyne, b.p. 130°/750 mm.

#### 4-Octene-t

Tritium gas was produced by electrolysis of 20 per cent sulfuric acid (720  $\mu\text{C}/\text{mM}$ ), passed through a trap cooled with liquid air and introduced into a gas buret filled with mercury. A flask containing 800 mg. of 4-octyne and 80 mg. of Lindlar catalyst was then connected to the buret and the reaction started by means of a magnetic stirrer. After the theoretical amount of tritium gas was absorbed, the liquid phase was separated and distilled. Thus, 500 mg. of pure 4-octene-t, b.p. 120–121°/750 mm. was obtained. The specific activity was 7.50  $\mu\text{C}/\text{mM}$ .

#### Butyric acid-t

Tritiated 4-octene was diluted with the non-radioactive olefin to the specific activity of 0.772  $\mu\text{C}/\text{mM}$ . This substance (832 mg.) was dissolved in 30 ml. of methylene chloride, the solution cooled to -75° and subjected to a stream of ozone in oxygen until no more ozone was consumed. The solution was then left to warm up to room temperature and slowly added under stirring to a mixture of 25 ml. hydrogen peroxide (30%) and 100 ml. of a 10 per cent sodium hydroxide solution. After 1 hour of stirring, the mixture was warmed up, methylene chloride distilled off and the stirring continued overnight. The mixture was then acidified, saturated with sodium chloride and extracted with ether. The ether extracts were washed with 1 N sodium hydroxide solution, the alkaline solution acidified, saturated with sodium chloride and extracted with ether. After drying, ether was removed over a column. The residue was dissolved in ethanol and titrated with sodium ethylate in ethanol to methyl red. Ethanol was then evaporated, the residue dissolved in water, the solution acidified, saturated with sodium chloride and extracted with ether. After drying, the solvent was removed and the residue distilled *in vacuo*. Thus, 96.4 mg. of pure butyric acid were obtained.

The specific activity was 0.034  $\mu\text{C}/\text{mM}$  or 0.068  $\mu\text{C}/\text{mM}$  of 4-octene.

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#### IZVOD

##### Raspodjela tritija u 4-oktenu priređenom katalitičkom hidrogenacijom

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Prireden je 4-oktin iz kojeg je katalitičkom hidrogenacijom s tritijem uz Lindlar katalizator dobiven 4-okten. Ozonizacijom ovog olefina i oksidacijom nastalog ozonida dobivena je čista maslačna kiselina, u kojoj je zaostalo 8,82% aktiviteta originalno prisutnog u 4-oktenu. Na osnovu dobivenih rezultata zaključeno je, da katalitičke hidrogenacije nisu pogodne za specifično markiranje spojeva izotopima vodika.

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