## The Synthesis of Carbon-Isotopic[1] Alkanes: Methane-C$^{13}$, Propane-1-C$^{13}$, *n*-Butane-1-C$^{13}$, *n*-Butane-1-C$^{14}$, Isobutane-1-C$^{13}$, Isobutane-1-C$^{14}$ and Isobutane-2-C$^{13}$

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Studies undertaken in these laboratories on the mechanisms of certain hydrocarbon reactions[2,3,4,5] have necessitated the syntheses of certain isotopic hydrocarbons containing either deuterium, C$^{13}$ or C$^{14}$. Syntheses of the monodeuteroalkanes have been treated separately[6]; this note concerns the syntheses of the several carbon-isotopic alkanes used in these investigations.

All of the compounds, with the exception of *n*-butane-1-C$^{13}$ and isobutane-2-C$^{13}$, were prepared on a 5-20 millimole scale. The reaction schemes are as follows, with the over-all yields indicated[7]:

$$\text{(a)}\quad \mathrm{C^{13}H_3I} \xrightarrow[\mathrm{H^+}]{\mathrm{Mg}} \mathrm{C^{13}H_4}\ (86\%\ \text{yield})$$

$$\text{(b)}\quad \mathrm{KC^{13}N}^{8} \xrightarrow{\mathrm{RBr}} \mathrm{RC^{13}N} \xrightarrow[\mathrm{HCl}]{\mathrm{R'OH,\ H_2O}}$$

$$\mathrm{RC^{13}OOR'} \xrightarrow[\mathrm{H^+}]{\mathrm{LiAlH_4}} \mathrm{RC^{13}H_2OH} \xrightarrow{\mathrm{HBr}}$$

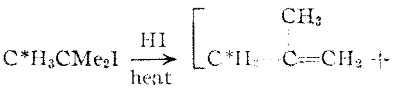
$$\mathrm{RC^{13}H_2Br} \xrightarrow[\mathrm{H^+}]{\mathrm{Mg}} \mathrm{RC^{13}H_3}$$

$$(\mathrm{R = Et,\ Pr},\ 27\%\ \text{yield})$$

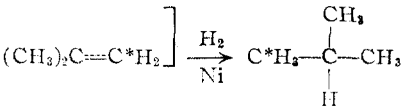
$$\text{(c)}\quad \mathrm{C^{14}H_3OH} \xrightarrow{\mathrm{HI}} \mathrm{C^{14}H_3I} \xrightarrow[\text{allyl Br}]{\mathrm{Mg,}}$$

$$\mathrm{C^{14}H_3CH_2CH{=\!=}CH_2} \xrightarrow[\mathrm{Ni}]{\mathrm{H_2,}} \mathrm{C^{14}H_3CH_2CH_2CH_3}\quad (ca.\ 60\%\ \text{yield})$$

$$\text{(d)}\quad \mathrm{C^*H_3I} \xrightarrow[\mathrm{Me_2CO}]{\mathrm{Mg,}} \mathrm{C^*H_3{-}CMe_2OMgI} \xrightarrow{\mathrm{HI}}$$



$$\mathrm{C^*H_3CMe_2I} \xrightarrow[\text{heat}]{\mathrm{HI}} \left[\mathrm{C^*H_2{=\!=}\overset{\displaystyle CH_3}{\overset{|}{C}}{=\!=}CH_2} + \right.$$



$$\left.\mathrm{(CH_3)_2C{=\!=}C^*H_2}\right] \xrightarrow[\mathrm{Ni}]{\mathrm{H_2}} \mathrm{C^*H_3{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3}$$

$$(\mathrm{C^* = C^{13}\ and\ C^{14}},\ 53\text{-}62\%\ \text{yield})$$

$$\text{(e)}\quad \mathrm{KC^{13}N} \xrightarrow{\mathrm{Me_2SO_4}} \mathrm{MeC^{13}N} \xrightarrow[\mathrm{H_2O,\ HCl}]{\mathrm{EtOH}}$$

$$\mathrm{MeC^{13}OOEt} \xrightarrow{\mathrm{MeMgI}} \mathrm{Me_3C^{13}OMgI} \xrightarrow{\mathrm{HCl}}$$

$$\mathrm{MeC^{13}Cl} \xrightarrow{\text{quinoline}} \mathrm{MeC^{13}{=\!=}CH_2} \xrightarrow[\mathrm{Ni}]{\mathrm{H_2}} \mathrm{Me_3C^{13}H}$$

$$(28\%\ \text{yield})$$

There were no non-isotopic impurities in any of the products (limit of detection mass spectrometrically is approximately 0.1%) except *n*-butane-1-C$^{14}$, which contained small amounts of *n*-hexane and propane.

Analyses of the propane-C$^{13}$ and butanes-C$^{13}$ for the isotopic species[9] and isotopic isomers were made by direct mass spectrometric examination. The data are reproduced in Table I. The methane-C$^{13}$ isotopic composition was found to be 50.0 ± 0.3 atom % C$^{13}$ by burning a sample completely to carbon dioxide and analyzing the latter mass spectrometrically.

The isotopic concentrations of the three radioactive alkane preparations, as determined by use of an ionization chamber, were: *n*-butane-1-C$^{14}$, 0.062 mc./millimole; isobutane-1-C$^{14}$, 0.0026 and 0.077 mc./millimole.

TABLE I

ISOTOPIC COMPOSITIONS OF THE C$^{13}$ ALKANES

| | Mole % | | | |
|---|---|---|---|---|
| | Propane-1-C$^{13}$ | *n*-Butane-1-C$^{13}$ | Isobutane-1-C$^{13}$ | Isobutane-2-C$^{13}$ |
| Alkane-C$_0^{13}$ | 45.7 ± 0.5 | 81.0 ± 0.3 | 50.3 ± 0.5 | 81.5 ± 0.3 |
| Alkane-C$_1^{13}$ | 53.2 ± 0.5 | 18.4 ± 0.2 | 48.2 ± 0.5 | 18.0 ± 0.2 |
| Alkane-1-C$_1^{13}$ | 52.7 ± 0.5 | 16.8 ± 0.2 | 47.7 ± 0.5 | 2.47 ± 0.02 |
| Alkane-2-C$_1^{13}$ | 0.53 ± 0.01 | 1.64 ± 0.02 | 0.51 ± 0.01 | 15.5 ± 0.2 |
| Alkane-C$_2^{13}$ | 1.12 ± 0.02 | 0.52 ± 0.02 | 1.44 ± 0.02 | 0.49 ± 0.02 |
| C$^{13}$ content of the C$^{13}$ reagent[a] used in synthesis | 53.3 | 16.5 | 48.2 | 16.0 |

[a] Calculated from the isotopic species distribution in this table. Values determined should be equal to the C$^{13}$ content of the C$^{13}$ starting materials if there is no isotopic dilution in the course of the synthesis.

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[1] The system of nomenclature used (J. W. Otvos and C. D. Wagner, *Science*, **106**, 409 (1948)) is an extension of that already adopted by the American Chemical Society for deuterium compounds. Occasional obvious departures from the system (*e.g.*, isobutane-1-C$^{13}$ instead of the more proper 2-methylpropane-1-C$^{13}$) have been made for purposes of clarity.

[2] O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **16**, 255 (1948); **17**, 418 (1949).

[3] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **16**, 745 (1948).

[4] D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, *ibid.*, **16**, 993 (1948).

[5] C. D. Wagner, O. Beeck, J. W. Otvos and D. P. Stevenson, *ibid.*, **17**, 419 (1949).

[6] C. D. Wagner and D. P. Stevenson, THIS JOURNAL, **72**, 5785 (1950).

[7] For complete experimental details of these syntheses order Document 3028 from American Documentation Institute, 1719 N. Street, N. W., Wahsington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $2.10 for photocopies (6 × 8 inches) readable without optical aid.

[8] Methyl-C$^{13}$ iodide was not available at the time this pair of isotopic compounds was synthesized. Procedures based upon it as starting material, such as (c), would have been superior to the procedures used.

[9] In this and related reports from this laboratory, the term "isotopic species" and "isotopic isomer" are defined in the following way: Molecules of a given "isotopic species" of a chemical compound all contain the same number of isotopic atoms of a given element. "Isotopic isomers" of the same isotopic species differ only in the positions of the isotopic atoms in the molecules. For example, propane-1,3-C$_2^{13}$ and propane-1,2-C$_2^{13}$ are isotopic isomers of the isotopic species, propane-C$_2^{13}$.