

## Isomerization of Alkane Molecular Ions

John L. Holmes,\*† Peter C. Burgers,† M. Yousuf A. Mollah,† and Peder Wolkoff\*†

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, K1N 9B4, Canada, and the Department of General and Organic Chemistry, University of Copenhagen, The H.C. Ørsted Institute, DK-2100, Copenhagen, Denmark. Received April 15, 1981

**Abstract:** The appearance energies of daughter ions for the major low-energy fragmentations, namely, losses of  $C_2H_6$ ,  $CH_4$ , and  $CH_3$ , of pentane and methylbutane radical cations have been measured. These reactions for ions of low internal energy content (rate constants in the range  $10^5$ – $10^7$  s $^{-1}$ ) have been studied by observations of metastable peak shapes. The behaviors of a variety of  $^{13}C$ - and  $^2H$ -labeled compounds were also examined. Hydrogen atoms do not extensively lose their positional identity in any of these fragmentations. For methylbutane, loss of  $C_2H_6$  and  $CH_3$  yielded ionized propene and 2-butyl cations, respectively, at their calculated thermochemical thresholds. Loss of  $CH_4$  proceeded at an energy greater than that calculated for the production of ionized but-2-ene, methylpropene, but-1-ene, or methylcyclopropane. The labeling experiments permitted the separation of the complex Gaussian-type metastable peak for  $CH_4$  loss into high and low kinetic energy release components, each appropriately relating to the generation of different daughter ions via competing mechanistic pathways. Large isotope effects were observed, similar in magnitude to those observed for the loss of methane from the methylpropane radical cation. Ethane elimination is preceded partially (ca. 20–25%) by a 1–2 methyl shift and a concomitant 2–1 H shift; isotope effects associated with this reaction are discussed. For pentane, losses of  $CH_3$  and  $CH_4$  take place at the same energy, corresponding to the calculated threshold for production of the secondary cations;  $^{13}C$  labeling experiments showed that the penultimate C atoms are not lost but that C-3 is lost (46%) in these reactions, with an ease similar to terminal C atom losses (54%). As with methylbutane,  $^2H$  labeling permitted the separation of the metastable peak for methane loss into components having different kinetic energy releases and attributable to the production of different  $[C_4H_8]^+$  daughter ions. Although  $C_2H_6$  loss was observed to take place at energies down to the calculated thermochemical threshold for generation of ionized propene, the appearance energy of the metastable peak was the same as that for  $CH_3$  and  $CH_4$  losses. Labeling experiments showed that the central C atom is not lost in this reaction. Detailed analysis of the observations leads to the conclusion that the  $CH_3$ ,  $CH_4$ , and  $C_2H_6$  eliminations from pentane radical cations are preceded by an isomerization to energy-rich ionized methylbutane.

## Introduction

The state of knowledge and understanding of the energetics and mechanisms of the unimolecular decompositions of alkane radical cations was reviewed in our earlier studies of the fragmentation behaviors of ionized butane and methylpropane.<sup>1–3</sup> In the last few years more information has accrued concerning the unimolecular decompositions of the lower homologous alkanes, and a summary of this new knowledge is presented as an appropriate background to this report on the behavior of the  $C_5H_{12}$  radical cations.

It has been shown by Meisels et al.<sup>4</sup> that the central carbon atom in propane is extruded in the loss of methane from ions of low internal energy. The threshold energies for methane losses involving terminal and central C atoms lie within 0.1 eV of each other, with the former reaction proceeding at the thermochemical threshold for the generation of ionized ethene. The ratio terminal  $CH_4$ :central  $CH_4$  was energy independent from 11.8 to 13 eV and had a value  $10 \pm 3:1$ , appreciably greater than the statistical ratio, 2:1. These observations were for *all* ions fragmenting within the above energy range; for metastable ions, selected by rate constant rather than by energy content, a larger ratio of approximately 50:1 was observed. It was proposed that the extrusion of the central C atom proceeded in a concerted manner involving a transition state tighter than that for terminal methane loss.

With regard to the behavior of butane and methylpropane, it has now been established that the daughter ion generated by methane loss from both isomers is ionized propene<sup>3,5</sup> rather than cyclopropane. The extrusions of C2 and C3 as methyl or methane from butane radical cations are minor processes<sup>2</sup> (ca. 6%) but they proceed at the same threshold energy (to within 0.1 eV) as the terminal C losses.

It was proposed that fragmentations of  $[butane]^+$  ions by loss of  $CH_3$  (to yield 2-propyl cations at the thermochemical threshold) and by loss of  $CH_4$  (at the same threshold as for methyl loss, to yield propene radical cations with excess internal energy) proceeded via concerted reactions rather than by a stepwise mech-

anism in which energy-rich methylpropane radical cations participated.<sup>2</sup>

The very large isotope effects associated with methane loss from deuterium-labeled metastable methylpropane ions<sup>1,2</sup> have been reexamined by Mead et al.,<sup>6</sup> and the results were interpreted in terms of a nonclassical transition state involving a three-center bond.

The normal mass spectra of the higher homologues (hexane, heptane, nonane, and tetradecane), multiply labeled with  $^{13}C$ , recently have been thoroughly studied by Gäumann and his co-workers.<sup>7,8</sup> It is clear from these investigations that loss of  $CH_3$  involves all positions in the chain but with only a minor or no contribution coming from the penultimate C atoms.

The purpose of the present study was to investigate the low-energy fragmentations of the ionized isomers pentane and methylbutane, namely, the losses of  $C_2H_6$ ,  $CH_4$ , and  $CH_3$ . With the use of isotopic labeling and metastable ion measurements, daughter-ion structures and the participation of internal C atoms in these reactions were to be examined in detail. The possible isomerization of  $[pentane]^+$  to  $[methylbutane]^+$  (or their free interconversion) prior to fragmentation will be discussed in the light of all available evidence.

Since the completion of this work, a study of deuterium-labeled  $C_5H_{12}$  isomers has been reported by Wendelboe et al.<sup>9</sup> Their

(1) Wolkoff, P.; Holmes, J. L. *J. Am. Chem. Soc.* 1978, 100, 7346.(2) Holmes, J. L.; Wolkoff, P.; Rye, R. T. B. *J. Chem. Soc. Chem. Commun.* 1979, 544.(3) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B., *Org. Mass Spectrom.* 1980, 15, 149.

(4) Meisels, G. G.; Gilman, J. P.; Hsieh, T., presented at the 28th Annual Conference on Mass Spectrometry and Allied Topics, New York, May 25–30, 1980, and private communication.

(5) Bowen, R. D.; Barbalas, M. P.; Pagano, F. P.; Todd, P. G.; McLafferty, F. W. *Org. Mass Spectrom.* 1980, 15, 51.(6) Mead, P. T.; Donchi, K. F.; Traeger, J. C.; Christie, J. R.; Derrick, P. *J. Am. Chem. Soc.* 1980, 102, 3364.(7) Lavanchy, A.; Houriet, R.; Gäumann, T. *Org. Mass Spectrom.* 1978, 13, 410.(8) Lavanchy, A.; Houriet, R.; Gäumann, T. *Org. Mass Spectrom.* 1979, 14, 79.

\* University of Ottawa.

† University of Copenhagen.

Table I. Relative Metastable Peak Abundances<sup>a</sup> for Ethane Loss from <sup>2</sup>H- and <sup>13</sup>C-Labeled Methylbutanes and Pentanes

compound	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> D	C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> D <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> D <sub>4</sub>
<sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (1b)	22	78 ( <sup>13</sup> CCH <sub>6</sub> )			
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CD <sub>3</sub> ) (2b)	65	21		15	
CD <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (3b)	18	6	1	75	
CH <sub>3</sub> CH <sub>2</sub> CH(CD <sub>3</sub> ) <sub>2</sub> (4b)	1	87	1	8	3 <sup>b</sup>
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CHD <sub>2</sub> ) (5b)	74	12	14		
CH <sub>3</sub> CH <sub>2</sub> CD(CH <sub>3</sub> ) <sub>2</sub> (6b)	82	18			
CH <sub>3</sub> CD <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (7b)	2	15	83		
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CH <sub>2</sub> D) (8b)	84	16			
CD <sub>2</sub> HCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (9b)	20	3	77		
CH <sub>3</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (1p)	52	48 ( <sup>13</sup> CCH <sub>6</sub> )			
CH <sub>3</sub> CH <sub>2</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (2p)	100	<1 ( <sup>13</sup> CCH <sub>6</sub> )			
CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> (3p)		3	83	14	
CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (4p)	74	26			
CH <sub>3</sub> CD <sub>2</sub> CD <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> (5p)		3	54	42 <sup>b</sup>	

<sup>a</sup> Metastable peak areas, normalized to  $\Sigma = 100$ ; all values  $\pm 1$ . <sup>b</sup> Neither of these compounds lost C<sub>2</sub>HD<sub>3</sub> or C<sub>2</sub>D<sub>6</sub>.

results and conclusions will be considered in the appropriate discussion sections of this paper.

### Results and Discussion

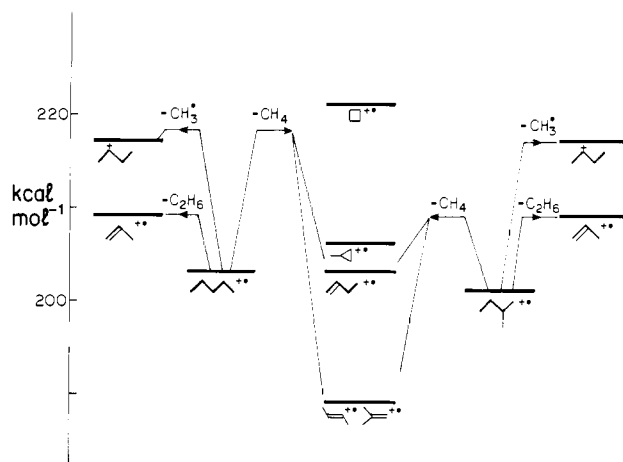
**Energetics.** The energy requirements for the losses of CH<sub>3</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> from pentane and methylbutane are shown in Figure 1. The data from which the figure was drawn are given in the legend.

For both compounds loss of CH<sub>3</sub> takes place at or close to the threshold for the generation of the 2-butyl cation. For pentane a narrow metastable peak of pure Gaussian form<sup>10</sup> was observed for this fragmentation, with an average kinetic energy release,  $\langle T \rangle = 0.81$  kcal mol<sup>-1</sup> (35 meV), similar in magnitude to that observed for the corresponding fragmentation of butane.<sup>1</sup>  $\langle T \rangle = 1.0$  kcal mol<sup>-1</sup> (45 meV), which generates the most stable [C<sub>3</sub>H<sub>7</sub>]<sup>+</sup> species, the 2-propyl cation, at the calculated thermochemical threshold. There is thus no indication that the thermochemically more stable<sup>11</sup> methyl-2-propyl cation is being generated from pentane. For methylbutane only a very weak metastable peak is observed,<sup>1</sup> in keeping with the reaction having a higher energy requirement than the CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> losses.

The loss of CH<sub>4</sub> from pentane has, to within 0.05 eV, the same appearance energy (AE) as for CH<sub>3</sub> loss; this could result from there being a rate-determining step prior to these losses. It can be seen from Figure 1 that at threshold all [C<sub>4</sub>H<sub>8</sub>]<sup>+</sup> isomers except [cyclobutane]<sup>+</sup> are possible daughter-ion structures. The metastable peak for this reaction is possibly of complex Gaussian type, because its shape cannot be described by any simple modification of the equation for a pure Gaussian peak. Criteria for the possible complexity of metastable peaks is discussed in detail elsewhere.<sup>10</sup> It is also associated with a comparatively large average kinetic energy release,  $\langle T \rangle = 2.3$  kcal mol<sup>-1</sup> (100 meV). As will be described below, isotopic labeling experiments lead to the separation of this peak into broad and narrow components, corresponding to the generation of isomeric daughter ions.

Loss of CH<sub>4</sub> from ionized methylbutane takes place with a lower energy requirement than that for pentane, but the threshold nevertheless lies above the thermochemical limits for all [C<sub>4</sub>H<sub>8</sub>]<sup>+</sup> isomers except [cyclobutane]<sup>+</sup>; see Figure 1. The shape of the metastable peak for CH<sub>4</sub> loss from this compound was also of complex Gaussian shape, and the large average kinetic energy release,  $\langle T \rangle = 1.9$  kcal mol<sup>-1</sup> (81 meV) is in keeping with the production of stable daughter ions from the exothermic reactions (see Figure 1). Again, as described below, the peak was separated into large and small kinetic energy release components by isotopic labeling experiments.

Loss of C<sub>2</sub>H<sub>6</sub> from both compounds proceeds at the calculated thermochemical threshold for generation of ionized propene. In



**Figure 1.** Energy diagram showing threshold energies for fragmentations of ionized pentane and methylbutane. Heats of formation ( $\Delta H_f^\circ$ ) for all neutral species and ions from ref 12. Appearance energies (AE) measured in this work (all  $\pm 0.05$  eV): AE[C<sub>4</sub>H<sub>9</sub>]<sup>+</sup> from pentane = 10.98 eV (10.98 eV<sup>12</sup>); from methylbutane = 11.00 eV (11.10 eV<sup>12</sup>). AE[C<sub>4</sub>H<sub>8</sub>]<sup>+</sup> from pentane = 10.98 eV (10.93 eV<sup>12</sup>); from methylbutane = 10.64 eV (10.73 eV<sup>10</sup>). AE[C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> from pentane = 10.60 eV (10.99 eV<sup>12</sup>); from methylbutane = 10.64 eV (10.84 eV<sup>12</sup>). Ionization efficiencies for the latter two reactions rose only slowly with increasing electron energy, but the onset energies were nevertheless clearly defined. Note that for pentane the AE values of the metastable peaks for the three fragmentations, loss of CH<sub>3</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, were the same.

each case a noncomplex Gaussian-type metastable peak is produced:  $\langle T \rangle$  (pentane) = 1.2 kcal mol<sup>-1</sup> (51 meV);  $\langle T \rangle$  (methylbutane) = 0.95 kcal mol<sup>-1</sup> (41 meV). The [C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> daughter-ion structure for pentane was confirmed by a charge-stripping experiment.<sup>3</sup> The relative abundances for  $m/z$  19, 19.5, 20, 20.5, and 21 were 30, 18, 37, 15, and <1; these, within the experimental error,  $\pm 1$ , lie close to the values found for propene:<sup>3</sup> 28, 18, 36, 17, and 1, respectively. Thus, the [C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> daughter ions which are stable up to the time at which they meet the collision gas consist (largely) of [CH<sub>3</sub>CH=CH<sub>2</sub>]<sup>+</sup>; the possible presence of ions having the cyclopropane structure cannot entirely be ruled out (relative abundances for cyclopropane: 35, 19, 38, 7, and <1 respectively).

The AE for  $m/z$  42 from dimethylpropane (loss C<sub>2</sub>H<sub>6</sub>) was measured and was found to be  $\approx 12.6$  eV, corresponding to a value for  $\Delta H_f^\circ$ [C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> of ca. 270 kcal mol<sup>-1</sup>, far above the calculated threshold value for production of ionized propene,<sup>12</sup> 10.8 eV. This result shows that ionized dimethylpropane does not rearrange to its isomers prior to fragmentation.

**Labeled Methylbutanes.** Before the behavior of isotopically labeled pentanes can be discussed with respect to the possibility

(9) Wendelboe, J. F.; Bowen, R. D.; Williams D. H. *J. Am. Chem. Soc.* **1981**, *103*, 2333.

(10) Holmes, J. L.; Terlouw, J. Kk. *Org. Mass Spectrom.* **1980**, *15*, 383.

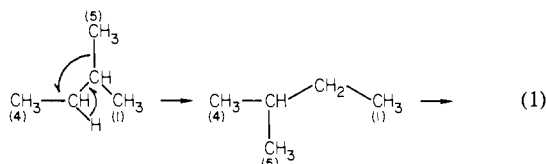
(11) Note that 2-butyl cations can themselves isomerize to the more stable methylpropyl cation: Schold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 7915.

(12) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. ref. data, Suppl.* **1977**, *6*.

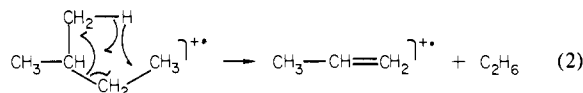
that the isomerization [pentane]<sup>+</sup> → [methylbutane]<sup>+</sup> precedes their fragmentation, it is necessary to describe the behavior of labeled methylbutanes.

**1. Ethane Loss.** The results are presented in Table I. It should be noted that the shapes of the metastable peaks were unaffected by isotopic substitution, and so it may be inferred that only one reacting configuration<sup>10</sup> is involved. It is immediately evident from the results obtained from the <sup>13</sup>C-labeled compound that C atoms other than those in the original CH<sub>3</sub>CH<sub>2</sub>- group also participate in ethane elimination. Isomerization to pentane or neopentane can be ruled out on energetic grounds for fragmentations near threshold (viz., for the former, were isomerization taking place, loss of CH<sub>4</sub> should appear at the same threshold as that for C<sub>2</sub>H<sub>6</sub> loss).

A simple interpretation is that methyl migration occurs as shown in eq 1, leading (in the limit) to a positional mixing of C-1, C-4,



C-5 and of the hydrogen atoms on C-2 and C-3. Thus, for the <sup>13</sup>C compound, the observations may be explained by invoking the presence of 22% of molecular ions **1b**, which have undergone methyl migration, among those fragmenting by loss of ethane in the microsecond time frame. Results for the deuterium-labeled compounds are also presented in Table I. It is evident that complete loss of positional identity of H/D atoms does not precede fragmentation. The observations can largely be quantitatively analyzed by the introduction of isotope effects for specific reactions. Assuming that the elimination reaction has the simple mechanism shown in eq 2, then for compounds **2b**, **3b**, and **4b**



(three related compounds for which the least number of possible isotope effects is required), the following processes were assigned isotope effects.

- (i) H transfer to CH<sub>3</sub>CH<sub>2</sub>- vs. D transfer to CH<sub>3</sub>CH<sub>2</sub>-; isotope effect,  $k_{\text{H}}/k_{\text{D}} = i$ .
- (ii) H transfer to CH<sub>3</sub>CH<sub>2</sub> vs. H transfer to CD<sub>3</sub>CH<sub>2</sub>-; isotope effect,  $k_{\text{H}}/k_{\text{D}} = j$ .
- (iii) Methyl migration reaction, CH<sub>3</sub> transfer to CH<sub>3</sub>CH<sub>2</sub>- vs. CD<sub>3</sub> transfer to CH<sub>3</sub>CH<sub>2</sub>-; isotope effect,  $k_{\text{CH}_3}/k_{\text{CD}_3} = l$ .
- (iv) Methyl migration reaction, CH<sub>3</sub> transfer to CH<sub>3</sub>CH<sub>2</sub> vs. CH<sub>3</sub> transfer to CD<sub>3</sub>CH<sub>2</sub>-, and/or an effect arising from H transfer from CH<sub>3</sub>CH<sub>2</sub> vs. H transfer from CD<sub>3</sub>CH<sub>2</sub>-; isotope effect,  $k_{\text{C}_2\text{H}_5}/k_{\text{C}_2\text{H}_5\text{D}_3} = n$ .

By inspection,  $i$  can be seen to be 3 (compounds **2b**, **3b**, **5b**, and **9b**). Solving the three equations, which express the observed product yields from **2b**, **3b**, and **4b** in terms of  $j$ ,  $l$ ,  $n$ , and  $x$  which represents the fraction of molecular ions which have undergone methyl migration prior to fragmentation in the unlabeled compound, leads to the solution  $j = 1.0$ ,  $l = 3.6$ , and  $n = 0.7$  when  $x = 0.22$ . This latter value is derived from the results from the <sup>13</sup>C-labeled compound, assuming that only one migration step is involved. If a second migration takes place, the net methyl migration is increased only slightly to  $x = 0.26$ . Such a value for  $x$  leads to small changes in  $j = 1.2$ ,  $l = 3.6$ , and  $n = 0.9$ .

A similar approach may be made to the analysis of the results for compounds **5b** and **9b**, if  $n$  is given the value 1.0,  $j = 1.2$ ,  $x = 0.25$ . Note that  $l$  cannot be evaluated for these compounds because the doubly (CHD<sub>2</sub>) substituted compound was not studied. The results on compound **8b** yield  $j = 1.2$  when  $x = 0.26$ , and  $j = 1.1$  if  $x = 0.22$ .

The results on compounds **6b** and **7b** possibly involve further indeterminate isotope effects; for example, the apparent degree of methyl migration in **6b** is 18%. This could result from an isotope

Table II. Relative Metastable Peak Abundances<sup>a</sup> and Kinetic Energy Releases<sup>b</sup> for Methane Loss from <sup>2</sup>H- and <sup>13</sup>C-Labeled Methylbutanes

compound	fragment lost			
	CH <sub>4</sub>	CH <sub>3</sub> D	CH <sub>2</sub> D <sub>2</sub>	CHD <sub>3</sub>
<sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ( <b>1b</b> )	93 (31)	7 <sup>13</sup> CH <sub>4</sub> (30)		
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CD <sub>3</sub> ) ( <b>2b</b> )	90	4	2	4
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CHD <sub>2</sub> ) ( <b>5b</b> )	80 (30)	6 (27)	14 (30)	
CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> (CH <sub>2</sub> D) ( <b>8b</b> )	77	23		
CD <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ( <b>3b</b> )	98	1		1
CH <sub>3</sub> CD <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ( <b>7b</b> )	31 (25)	69 (56)		
CH <sub>3</sub> CD <sub>2</sub> CD(CH <sub>3</sub> ) <sub>2</sub> ( <b>10b</b> )	30 (20)	69 (55)	1	
CH <sub>3</sub> CH <sub>2</sub> CD(CH <sub>3</sub> ) <sub>2</sub> ( <b>6b</b> )	96 (30)	4		
		(50 ± 5)		

<sup>a</sup> Metastable peak areas; normalized to  $\Sigma = 100$ , all values ± 1.

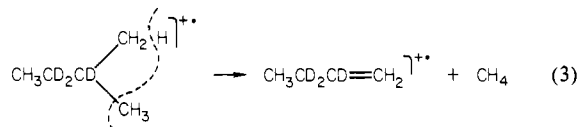
<sup>b</sup> Kinetic energy releases (meV, ± 1) evaluated from peak widths at half-height are shown in parentheses. Peaks were corrected appropriately for contributions from incompletely labeled material and natural <sup>13</sup>C abundances.

effect which acts against CH<sub>3</sub> transfer from >CD- to -CH<sub>2</sub>-, or against H transfer from -CH<sub>2</sub>- to >CD-, or against loss of CH<sub>3</sub>CH<sub>2</sub>D vs. CH<sub>3</sub>CH<sub>3</sub>. Similar problems apply to analysis of the behavior of compound **7b**.

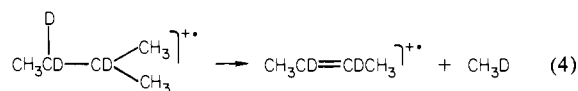
The chief conclusions to be drawn concerning the loss of ethane are that the results can semiquantitatively be interpreted by the simple elimination mechanism shown above, a partial rearrangement involving migration of the branch-methyl group from C-2 to C-3 and isotope effects of unexceptional magnitude. The results in Table I permit the dismissal of other reaction mechanisms such as 1,1 or 1,3 double methyl elimination.

**2. Methane Loss.** The results are presented in Table II. For the methylbutanes the most noteworthy observations were (a) that the metastable peak, which for the unlabeled compound was of complex shape, could be separated into broad and narrow components, and (b) that large isotope effects operated against the loss of [CD<sub>3</sub>] groups vs. [CH<sub>3</sub>] groups in a manner similar to that observed for labeled methylpropanes.<sup>2,6</sup> As with the latter compound the losses of mixed (H, D) methanes made only minor contributions to the overall fragmentation (e.g., compounds **2b** and **3b**). A detailed analysis of isotope effects and the degree of methyl group migration in the deuterium-labeled compounds could not be performed because of the several elimination mechanisms needed to explain the observations.

To begin with, the label positions in compound **10b** will be unaffected by any methyl group migration, and so the loss of CH<sub>4</sub> therefrom is taken as reflecting vicinal methyl group interaction leading to the production of ionized but-1-ene as the daughter ion, i.e., eq 3. However, the possible formation of ionized me-



thylcyclopropane from CH<sub>4</sub> loss cannot entirely be ruled out. The major loss of CH<sub>3</sub>D from **10b** can be attributed to formation of the more stable [but-2-ene]<sup>+</sup> daughter ion (eq 4) in keeping with



the larger kinetic energy release accompanying this reaction (Table II). It is believed that any isotope effects in compounds **7b** and **10b** are small because addition of the metastable peaks leads to a combined peak almost identical with that for the unlabeled compound (e.g., a large isotope effect acting against reaction 4 would lead to an adduct peak which was too narrow). The large and small kinetic energy releases are in keeping with the excess energies of the transition states above the reaction products (see

Table III. Metastable Peak Abundances<sup>a</sup> and Kinetic Energy Release<sup>b</sup> Observations for the Losses of Methyl and Methane from Labeled Pentanes

compound	fragment lost								
	CH <sub>3</sub> ·	<sup>13</sup> CH <sub>4</sub> CH <sub>2</sub> D·	CH <sub>4</sub>	CHD <sub>2</sub> ·	<sup>13</sup> CH <sub>3</sub> D	CD <sub>3</sub> ·	CH <sub>2</sub> D <sub>2</sub>	CD <sub>3</sub> H	CD <sub>4</sub>
CH <sub>3</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (1p)	42 (15)	<0.5							
CH <sub>3</sub> CH <sub>2</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (2p)	23 <sup>c</sup> (15)	19 <sup>c</sup> ← 50 (24)	58 (37)		<0.2				
CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> (3p)	28 (15)	18 ± 2 ← 28 <sup>d</sup> (17)	31 <sup>c</sup>		27 <sup>c</sup> (37)				
CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (4p)	21 (15)		10 ± 2		25 <sup>e</sup> (49)		19 (68)		
CH <sub>3</sub> CD <sub>2</sub> CD <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> (5p)	37 (15)		33 (38)		13 ← 16 (16)		30 (39)		
			4 (23)		22 (55)	19 (15)		5 (24)	13 (65)

<sup>a</sup> Metastable peak areas, normalized to  $\Sigma = 100$ ; all values  $\pm 1$ , except where otherwise indicated. <sup>b</sup> Kinetic energy releases (meV,  $\pm 1$ , for peaks of abundance  $> 20$  units; all weaker peaks  $\pm 10\%$ ) evaluated from peak widths at half-height are shown in parentheses. Peaks were corrected appropriately for contributions from incompletely labeled material and natural <sup>13</sup>C abundances. <sup>c</sup> Proportions calculated using relative peak areas for methyl:methane loss metastable peaks in the unlabeled compound = 0.74. <sup>d</sup> This peak was divided in the proportions shown by trial-and-error summation such that the combined methane-loss peak (CH<sub>4</sub> + CH<sub>3</sub>D + CH<sub>2</sub>D<sub>2</sub>) had the same shape as that for the unlabeled compound. Any net isotope effects are small and the above calculation assumes none. <sup>e</sup> This is a composite peak comprising a broad and narrow component.

Figure 1). Furthermore, the daughter ions for these two compounds were found to have the same AE within experimental error.

Loss of the terminal methyl group is a relatively minor process (compound **1b**), and, in view of the conclusions which were drawn concerning the ethane elimination, the loss of <sup>13</sup>CH<sub>4</sub> from **1b** (Table II) is again interpreted as arising from the methyl migration process preceding fragmentation. This amounts to only 14% (compare 22% prior to ethane loss), but this lower value is in keeping with the threefold greater intensity for the methane loss metastable peak, indicating that this reaction is faster than ethane elimination in the microsecond time frame.

Discrimination against loss of CH<sub>4-n</sub>D<sub>n</sub> clearly depends strongly on the number of D atoms in the departing methyl group, e.g., CHD<sub>3</sub> loss: CH<sub>4</sub> loss from **2b** ( $n = 3$ ) = 0.04. As stated above, CH<sub>3</sub>D loss from **10b** or **7b** involves no isotope effect.

**Pentane: Labeled Molecules.** The discussion of these results will center on the question as to whether the pentane molecular ion isomerizes to that of methylbutane prior to fragmentation. It would appear from the energy diagram that loss of C<sub>2</sub>H<sub>6</sub> from pentane cannot involve isomerization to methylbutane. Now the fragmentations of labeled ions were studied using metastable peak observations on the (usual) assumption that such fragmentations involve only ions of low internal energy content, corresponding to the reaction pathway at the thermochemical threshold measured for long-lived daughter ions (see Experimental Section). To test this hypothesis, the AE's of the metastable peaks for loss of CH<sub>3</sub>·, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> from pentane were measured by a reliable comparative method, in which other metastable peaks of established threshold energy are used as standards.<sup>13</sup> Within experimental error, estimated to be no greater than  $\pm 0.2$  eV, the three metastable peaks were found to have the same AE, 11.0 eV. Thus (see Figure 1) metastable pentane ions fragment at a common threshold, but there is also a lower energy, nonmetastable peak generating C<sub>2</sub>H<sub>6</sub> loss which produces [C<sub>3</sub>H<sub>6</sub>]<sup>+</sup> at the calculated threshold for ionized propene. Note that this latter threshold lies ca. 0.4 eV below that for the metastable peaks, comfortably outside the experimental error of the metastable peak AE measurements.

**Ethane Loss.** As with methylbutane, isotopic substitution produces no change in metastable peak shape for this reaction.

From the results shown in Table I it is seen that C-3 is never involved in ethane loss, compound **2p**, but one of the H atoms from this position is lost, compound **4p**. H/D atoms are not lost in the random statistical ratio, and the results shown in Table I indicate

that positional identity of these atoms is essentially retained. A small degree of H/D mixing is evident from the minor losses of C<sub>2</sub>H<sub>5</sub>D from compounds **3p** and **5p**. These observations on metastable pentane ions are most simply explained by proposing that a rate-determining isomerization to [methylbutane]<sup>+</sup> precedes their fragmentation.

**Methyl and Methane Loss.** Observations on <sup>13</sup>C-labeled pentanes are presented in Table III. The results show that C-2 and C-4 are not lost in metastable fragmentations. Furthermore, these atoms are retained over a wide range of rate constants and internal energies. This was shown by examining ion abundances up to 3 eV above the CH<sub>4</sub>-loss energy (using energy selected electrons and an apparatus whose observational time frame extends to rate constants down to  $\sim 10^3$  s<sup>-1</sup>;<sup>14</sup> also see Experimental Section). For these measurements particular care was taken to ensure the absence of olefinic impurities.<sup>15</sup> Within experimental error and after correction for 8% unlabeled material, <sup>13</sup>CH<sub>4</sub> loss from compound **1p** was less than 1% of CH<sub>4</sub> loss over the above energy range.

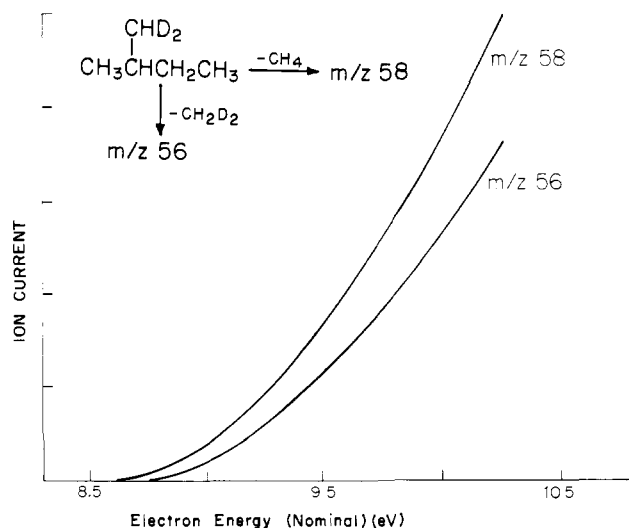
C-3 is eliminated with similar facility to the terminal C atoms in both CH<sub>3</sub>· and CH<sub>4</sub> losses. Such specificity of internal C-atom loss has also been observed in the fragmentation of hexane.<sup>8</sup>

Among the labeled pentanes the metastable peaks for methyl and methane losses may overlap. It was assumed that no kinetic isotope effects were involved and in the calculations of metastable peak abundances for the <sup>13</sup>C compounds the ratio CH<sub>3</sub>:CH<sub>4</sub> loss for the unlabeled compound was used. The results also showed that the metastable peak shapes for eliminations involving terminal C and C-3 are the same. Thus proportional summation of the metastable peaks for the unlabeled compound can also be used to separate the overlapping <sup>13</sup>CH<sub>3</sub>· and CH<sub>4</sub> loss metastable peaks from compound **2p**. The two methods yield the same result, within experimental error.

As with methylbutane, deuterium labeling leads to the separation of the methane-loss metastable peaks into high and low

(14) Holmes, J. L.; Burgers, P. C., in preparation.

(15) It is noteworthy that the first such experiment performed with compound **1p** showed that  $m/z$  56 had an AE appreciably below that for  $m/z$  57, and the two ionization efficiency curves were of different shape, that for  $m/z$  56 having a long "tail". This effect arose from the presence of a trace of C<sub>4</sub>H<sub>8</sub> in the sample. A small drop of bromine was added to **1p** and after a trap-to-trap distillation the AE experiment was repeated yielding the result described in the text. A second treatment with bromine produced no further change in the ionization efficiency curves which now had similar appearance with well-defined onsets. It is concluded that in the synthesis of the <sup>13</sup>C-2 pentane a very small amount of C<sub>4</sub>H<sub>8</sub> was formed, (not visible in the NMR spectrum), presumably in the final reduction step.



**Figure 2.** Ionization efficiency curves for the losses of  $\text{CH}_4$  and  $\text{CH}_2\text{D}_2$  from  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHD}_2$ .

kinetic energy release components, and it is similarly proposed that these correspond to eliminations generating  $[\text{C}_4\text{H}_8]^+$  daughter ions having different heats of formation (see energy diagram, Figure 1).

Note that in contrast to the behavior of methylbutane, deuterium isotope effects are relatively small (compare various labeled methane loss ratios, Table III). This general observation is discussed further below.

**Isomerization of Pentane.** The results for pentane presented above can be explained *either* by proposing that prior to loss of  $\text{CH}_3$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$  the molecular ion isomerizes via a rate-determining step to that of methylbutane, *or* that the fragmentations are concerted reactions analogous to those proposed for butane.<sup>1</sup> The former hypothesis is preferred insofar as it best accommodates all the observations; these will be discussed in turn below.

1. For the isomerization proposal to be valid, an explanation is required for the lack of any major deuterium isotope effect in methane (and methyl) loss from pentane compared with the large isotope effects observed in methane losses from labeled methylbutanes. Accordingly, the following experiment was performed: the abundances of  $m/z$  58 ( $\text{CH}_4$  loss) and 56 ( $\text{CH}_2\text{D}_2$  loss) in their threshold regions for  $\text{CH}_3\text{CH}(\text{CHD}_2)\text{CH}_2\text{CH}_3$ , **5b**, were carefully compared, again using energy selected electrons; the curves are shown in Figure 2. (It also proved necessary to treat this compound with a trace of bromine.<sup>15</sup>) Close to threshold  $m/z$  58: $m/z$  56 (peak heights) is very large, diminishing to ca. 1.3 at electron energies 1 eV above threshold. Note that in this experiment ions are generated having a distribution of internal energies from threshold up to the measured electron-beam energy, and so fragmentations having a large isotope effect always contribute to the total ion current. Thus the isotope effect falls rapidly with increasing internal energy. These observations are certainly compatible with those from the analogous pentane,  $\text{CH}_3\text{CH}_2\text{C}-\text{D}_2\text{CH}_2\text{CH}_3$ , which, on isomerization, will produce **5b** having a *minimum* excess internal energy content of  $\sim 9 \text{ kcal mol}^{-1}$  (0.4 eV), i.e., equal to the difference between the thresholds for methane elimination from ionized methylbutane and pentane (Figure 1). Thus the lack of an isotope effect in these fragmentations for **4p** is compatible with the isomerization hypothesis. The large isotope effects observed in the methane elimination from methylpropane have been discussed in detail by Mead et al.<sup>6</sup> They observed small but significant differences in the threshold energies for loss of  $\text{CH}_3\text{D}$  and  $\text{CD}_4$  from  $(\text{CD}_3)_2\text{CHCH}_3$  but did not investigate the magnitude of the isotope effect at higher internal energies.

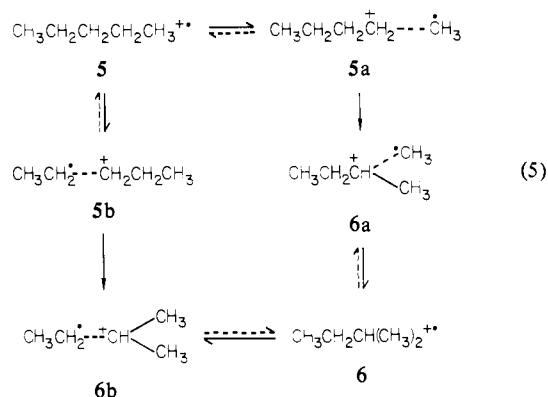
The methyl loss from methylbutane, a higher energy process than methane elimination (Figure 1), appears to have little or no isotope effect.  $m/z$  59 and 57 show roughly equal abundances at internal energies up to a volt above threshold.

2. The observations on the  $^{13}\text{C}$  labeled-pentane **2p** show that the terminal C atoms and C-3 are not lost with equal probability. This may be explained by a methyl migration in the "hot" methylbutane ions (produced by isomerization), as was proposed for methylbutane itself. The  $\text{CH}_3$ ,  $^{13}\text{CH}_3$ , and  $\text{CH}_4$ ,  $^{13}\text{CH}_4$  loss ratios are insensitive to the degree of methyl migration (reaction 1) and within the limits of experimental error represent  $19 \pm 5$  and  $14 \pm 4\%$ , respectively, for this rearrangement.

3. The different  $T$  values for ethane loss from the two isomers deserve comment. That for pentane the kinetic energy release is larger than that for methylbutane can be taken as showing that the former undergoes a rate-determining isomerization to the latter.<sup>16</sup>

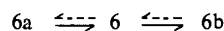
The results on the  $^{13}\text{C}$ -labeled pentanes contrast sharply with those observed for  $^{13}\text{C}$ -labeled butane.<sup>2</sup> In the latter case, internal C atoms were lost as  $\text{CH}_3$  and  $\text{CH}_4$  but only to ca. 6%, whereas losses of C-2 and C-4 in pentane were completely absent. It must be concluded that such eliminations of the penultimate C atoms in pentane involve an energy requirement sufficient to make them wholly noncompetitive with loss of C-3.

The results of Wendelboe et al.<sup>9</sup> must now be discussed with reference to the present work. They studied relative metastable peak abundances for the fragmentation of deuterium-labeled pentanes (**3p**, **4p**, and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CD}_3$ ) and methylbutanes (**4b**, **6b**, and  $\text{CH}_3\text{CH}_2\text{CD}(\text{CD}_3)_2$ ). They made no energy measurements. Their experimental data agree closely with the present results. On the basis of their metastable peak abundance observations they proposed that pentane molecular ions undergo a rate-determining isomerization prior to fragmentation. Their



mechanism invoked the participation of ion-radical complexes as shown in eq 5. (We reproduce their numbering sequence for the species; broken half-arrows designate a reaction slower than its full half-arrow counterpart.)

Although this series of reactions is compatible with their observations, the present labeling experiments show that the reaction sequence cannot be valid, at least for metastably fragmenting ions.



For example, the reversed arrows above require some involvement of C-2 (and C-4) in  $\text{CH}_3$  and  $\text{CH}_4$  losses from ionized pentane (cf. Table III) and some loss of  $\text{CH}_2\text{D}$  from **4p** (Table III). Neither was observed,<sup>17</sup> and so ion **6a** becomes redundant. With the elimination of these possibilities, their mechanism becomes formally indistinguishable from a simple isomerization involving extrusion of C-3 with a concerted H shift from an adjacent  $\text{CH}_2$  group.

Thus the conclusions that we have drawn concerning the losses of  $\text{CH}_3$  and  $\text{CH}_4$  from pentane unfortunately are not complete. It remains to be explained why C-2 and C-4 are not involved in these reactions. The isomerization involving C-3 must proceed via a configuration significantly lower in energy than that available

(16) Williams, D. H. *Acc. Chem. Res.* **1977**, *10*, 280.

(17) Wendelboe et al.<sup>9</sup> did not measure metastable peak shapes, and so loss of  $\text{CH}_2\text{D}$  from **4p** could not be distinguished from  $\text{CH}_4$  loss.

to the penultimate C atoms. Such an energy difference could, for example, be envisaged as arising from nonclassical intermediate states having structures akin to ionized but-2-ene plus neutral methane vs. a (higher energy) ionized but-1-ene plus neutral methane.

The partitioning of the excess internal energy of ions fragmenting by loss of CH<sub>4</sub> deserves comment; it was proposed that the large kinetic energy release processes for pentane and methylbutane resulted from the formation of ionized but-2-ene. For methylbutane, the appropriate  $\langle T \rangle$  is 3.5 kcal mol<sup>-1</sup> (150 meV), and the excess internal energy above threshold corresponding to fragmentations within the metastable time frame is unlikely to exceed ~5 kcal mol<sup>-1</sup>; i.e., in order to achieve the observed metastable peak ratio, only ions of low internal energy can be involved (see Figure 2). The total excess energy for a fragmentation yielding (but-2-ene)<sup>+</sup> is thus ~23 kcal mol<sup>-1</sup> (see Figure 1). The magnitude of  $\langle T \rangle$  indicates that a large proportion of this excess energy is appearing in translational degrees of freedom; for example, use of the Haney and Franklin<sup>18</sup> expression  $\langle E^1 \rangle = \alpha(T)(3n - 6)$  (where  $n$  = number of atoms in the ion and  $\alpha$  is an empirical constant) gives  $\alpha = 0.13$ , compared with the more commonly observed range  $\alpha = 0.4 \pm 0.1$  for ions fragmenting in the metastable time frame.<sup>14</sup>

The behavior of butane is not completely settled.<sup>1-3</sup> In the discussion of the observations on butane,<sup>1</sup> one explanation for the common threshold for CH<sub>3</sub>· and CH<sub>4</sub> losses was that it represented the energy required for rearrangement to the branched isomer via the extrusion of an internal C atom; this explanation was deemed unattractive because the losses of C-2 and C-3 were of minor importance, and it was argued that both fragmentations proceed by concerted reactions (i.e., that methylpropane molecular ions were *not* intermediate species in the [butane]<sup>+</sup> decompositions). The mere absence of any significant isotope effects in the [butane]<sup>+</sup> fragmentations could be explained by an argument similar to that discussed above for pentane. However, if isomerization were indeed taking place, then the small contributions from internal C atoms might, for example, be explained by the hypothesis that energy in the intermediate [methylpropane]<sup>+</sup> is not completely randomized prior to fragmentation; this hypothesis has been used to explain the behavior of the enol of ionized acetone.<sup>19</sup> Such an explanation should certainly be used with reserve because it implies that the quasi-equilibrium theory<sup>20</sup> fails for such systems.

## Experimental Section

**Mass Spectrometric Measurements.** Metastable peak shapes for fragmentations taking place in the first field-free region were obtained at fixed electric sector voltage by sweeping the acceleration voltage of a Kratos MS902S mass spectrometer, under conditions of good energy resolution. The main ion-beam width at half-height was 3–4 V at an acceleration voltage of 7000 V. Kinetic energy releases were calculated in the usual way with correction for the main beam.<sup>10</sup> Average kinetic energy releases were evaluated by established methods.<sup>21,22</sup> The relative abundances of decompositions taking place in the first field-free region were obtained from the areas of the metastable peaks under conditions of good energy resolution and at a single acceleration voltage.<sup>10</sup> They were also measured from the relative metastable peak heights *without* energy resolution but again at a constant acceleration voltage. This latter method is preferred when both intense and weak metastable peaks are to be compared; the greater sensitivity permits a more accurate estimate of weak metastable peak abundances.

All appearance energies (*except* those measured on metastable peaks) were measured with an apparatus comprising an electrostatic electron monochromator<sup>23</sup> together with a quadrupole mass analyzer and mini-

computer data system.<sup>24</sup> Metastable-peak appearance energies were measured as described elsewhere.<sup>13</sup>

**Syntheses of Labeled Compounds.** The purity of and label position in the labeled compounds were checked by NMR spectroscopy. Unless otherwise stated, the deuterated compounds contained  $93 \pm 3\%$  <sup>2</sup>H<sub>n</sub>.

Deuterium-labeled pentanes and methylbutanes were synthesized by reduction of the appropriate bromopentane or bromomethylbutane with LiAlH<sub>4</sub>(D<sub>4</sub>)/NiCl<sub>2</sub><sup>25</sup> or (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnH(D).<sup>26</sup>

**Pentane-3,3,3-<sup>2</sup>H<sub>2</sub>** was prepared by reduction of 3-pentanone with LiAlD<sub>4</sub>. The resulting alcohol was converted via its tosylate to 3-bromopentane-3-<sup>2</sup>H<sub>1</sub>.

**Pentane-2,2,4,4-<sup>2</sup>H<sub>4</sub>** (87% <sup>2</sup>H<sub>4</sub>) and **pentane-2,2,3,3,4,4-<sup>2</sup>H<sub>6</sub>** (80% <sup>2</sup>H<sub>6</sub>) were synthesized similarly starting from 3-pentanone-2,2,4,4-<sup>2</sup>H<sub>4</sub>.<sup>27</sup>

**Methylbutane-1,1,1-<sup>2</sup>H<sub>3</sub>** was prepared by reduction of 2-bromomethylbutane-1,1,1-<sup>2</sup>H<sub>3</sub> which was synthesized from 2-methyl-2-butanone-1,1,1-<sup>2</sup>H<sub>3</sub> (obtained from butanone and perdeuteriomethylmagnesium bromide) and PBr<sub>3</sub> at -10 °C.

**Methylbutane-1,1,1-<sup>2</sup>H<sub>2</sub>** and **-1-<sup>2</sup>H<sub>1</sub>** were obtained by reduction of 2-methylbutanoic acid with LiAlD<sub>4</sub>(H<sub>4</sub>), and the resulting alcohols were treated as above.

**Methylbutane-4,4,4-<sup>2</sup>H<sub>3</sub>** and **methylbutane-4,4,4-<sup>2</sup>H<sub>2</sub>** were prepared similarly starting from isovaleric acid.

**Methylbutane-3,3-<sup>2</sup>H<sub>2</sub>** and **-2,3,3-<sup>2</sup>H<sub>3</sub>** (85% <sup>2</sup>H<sub>3</sub>) were prepared starting from acetone and ethylmagnesium-1,1-<sup>2</sup>H<sub>2</sub> bromide (obtained by reduction of acetic acid with LiAlD<sub>4</sub> followed by bromination). The resulting alcohols were brominated and reduced with LiAlH<sub>4</sub>(D<sub>4</sub>).

**Butane-1,1,1-<sup>2</sup>H<sub>3</sub>** was synthesized starting from acetone-<sup>2</sup>H<sub>6</sub> and ethylmagnesium bromide. The resulting alcohol was treated as above.

**3-Methylbutane-1-<sup>13</sup>C.** Isovaleric-1-<sup>13</sup>C acid was prepared from isobutylmagnesium chloride and <sup>13</sup>CO<sub>2</sub> (90% enriched). Reduction of the acid with LiAlH<sub>4</sub> in refluxing ether for 5 h<sup>28</sup> afforded 3-methylbutanol-1-<sup>13</sup>C, which was converted to 1-bromo-3-methylbutane-1-<sup>13</sup>C. Reduction of the bromide with (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnH yielded the desired product.

**Pentane-2-<sup>13</sup>C.** Propyllithium<sup>30</sup> (1.6 M, 60 mL titrated with diphenylacetic acid<sup>29</sup>) was added over 0.5 h to a dry ice/acetone cooled solution of predried (molecular sieve) acetic-1-<sup>13</sup>C acid (2.5 g, 0.041 M, Merck Sharp and Dohme Canada Ltd., 90% enriched) in dry ether (50 mL). The mixture was stirred at room temperature for 2.5 h, then added dropwise to a vigorously stirred mixture of NH<sub>4</sub>Cl (2.6 g) in ice/water saturated with NaCl. The ether phase was separated and the aqueous phase extracted four times with ether; the combined organic phases were dried, and the ether was removed by careful distillation through a glass-helix column. Distillation of the residue yielded 2-pentanone-2-<sup>13</sup>C, yield 65%. This was dissolved in ether (10 mL) and reduced with LiAlH<sub>4</sub> followed by standard hydrolysis,<sup>31</sup> drying, and careful removal of solvent to give 2-pentanol-2-<sup>13</sup>C in 80% yield. This was converted with PBr<sub>3</sub> to 2-bromopentane-2-<sup>13</sup>C (70% yield). Reduction with Bu<sub>3</sub>SnH gave pentane-2-<sup>13</sup>C in 70% yield.

**Pentane-3-<sup>13</sup>C** was prepared similarly starting with ethyllithium and propionic-1-<sup>13</sup>C acid (90% enriched, generated from ethylmagnesium bromide and <sup>13</sup>CO<sub>2</sub>) but *with the following modifications* of the procedure described above. The ethyllithium was added to an ice-cold solution of propionic-1-<sup>13</sup>C acid. The mixture was agitated for 20 h at room temperature. Subsequent work-up afforded 3-pentanone-3-<sup>13</sup>C in 30% yield.

**Acknowledgment.** We thank Dr. F. P. Lossing for AE measurements and many stimulating discussions. J.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support. P.W. thanks the Danish Natural Sciences Research Council for financial support and Dr. S. Hammerim for stimulating discussions.

**Registry No.** **1b**, 69105-36-8; **1p**, 56986-68-6; **2b**, 81194-28-7; **2p**, 65212-39-7; **3b**, 13264-50-1; **3p**, 33065-47-3; **4b**, 77734-77-1; **4p**, 52092-18-9; **5b**, 81194-29-8; **5p**, 81194-30-1; **6b**, 13221-81-3; **7b**, 81194-31-2; **8b**, 75854-76-1; **9b**, 81205-65-4; **10b**, 81194-32-3; pentane, 109-66-0; 2-methylbutane, 78-78-4; 2-pentanone-2-<sup>13</sup>C, 74889-54-6; 2-pentanol-2-<sup>13</sup>C, 81194-33-4; 2-bromopentane-2-<sup>13</sup>C, 81205-66-5; 3-pentanone-3-<sup>13</sup>C, 6228-79-1.

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