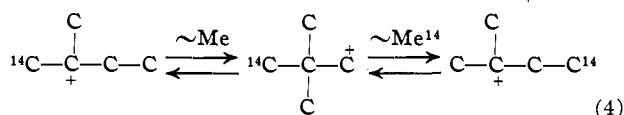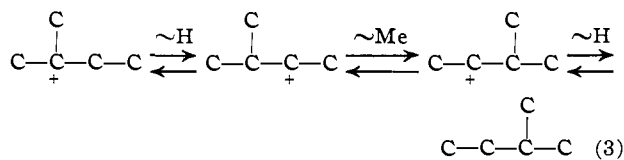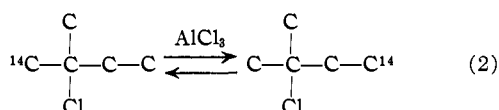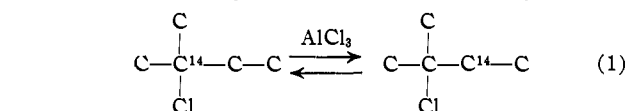# Carbonium Ion Rearrangements. IV. The Reaction of C¹³-Labeled *t*-Amyl Chlorides with Aluminum Chloride; Bimolecular Reactions

By Gerasimos J. Karabatsos, Floie M. Vane and Seymour Meyerson[1]

The reactions of 2-chloro-2-methylbutane-1-C¹³ (57.0% unlabeled and 43.0% monolabeled molecules) and 2-chloro-2-methylbutane-2-C¹³ (42.3% unlabeled and 57.7% monolabeled molecules) with aluminum chloride were studied at 0° for five minutes. Mass spectral and proton n.m.r. analysis shows that the recovered *t*-amyl chlorides contain, in addition to unlabeled and monolabeled molecules, *dilabeled* molecules. The data afford the following conclusions: (a) Isotope-position rearrangements of the *t*-amyl cation occur *via* reaction 3 and *via* bimolecular reactions involving C₁₀-carbonium ions. (b) The six methyl carbon atoms of the C₁₀-carbonium ions become statistically distributed during the course of the reaction while the four non-methyl carbon atoms do not. (c) The carbonium ions involved are classical tertiary and secondary.

It was pointed out[2] that many liquid phase reactions in which intermediate primary carbonium ions have been suggested to arise from rearrangements of secondary and tertiary ones may also be explained in terms of bimolecular reactions not involving primary carbonium ions. The rate of 1 over 2 was found[3] to be 1.55. Had the only path of isotope-position rearrangement been 3, $k_{23}/k_{14}$ should have been two ($k_{23}$ and $k_{14}$ are the rates of C-2, C-3 and C-1, C-4 scrambling, respectively). The data were interpreted in terms of 87% rearrangement *via* 3 and 13% *via* 4, since 4 effects only C-1, C-4

$$C-\overset{\text{C}}{\underset{\text{Cl}}{C^{14}}}-C-C \xrightleftharpoons{\text{AlCl}_3} C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C^{14}-C \quad (1)$$

$$^{14}C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C \xrightleftharpoons{\text{AlCl}_3} C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C^{14} \quad (2)$$

$$C-\overset{\text{C}}{\underset{+}{C}}-C-C \underset{\sim H}{\rightleftharpoons} C-\overset{\text{C}}{\underset{+}{C}}-C-C \underset{\sim Me}{\rightleftharpoons} C-\overset{\text{C}}{\underset{+}{C}}-C-C \underset{\sim H}{\rightleftharpoons} C-C-\overset{\text{C}}{\underset{+}{C}}-C \quad (3)$$

$$^{14}C-\overset{\text{C}}{\underset{+}{C}}-C-C \underset{\sim Me}{\rightleftharpoons} {}^{14}C-\overset{\text{C}}{\underset{\text{C}}{C}}-\overset{+}{C} \underset{\sim Me^{14}}{\rightleftharpoons} C-\overset{\text{C}}{\underset{+}{C}}-C-C^{14} \quad (4)$$
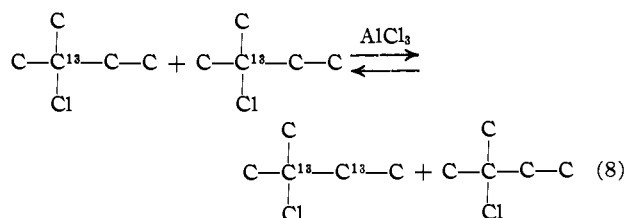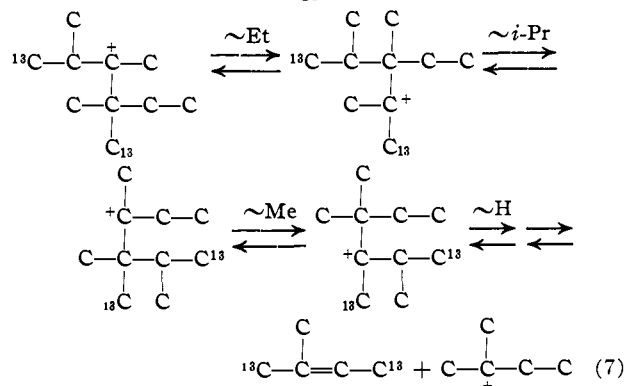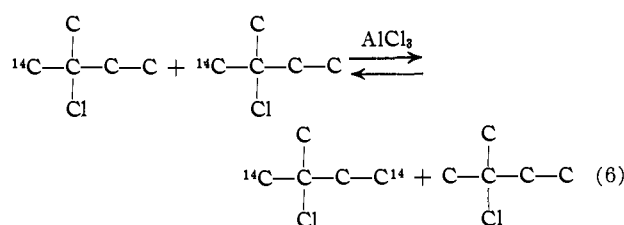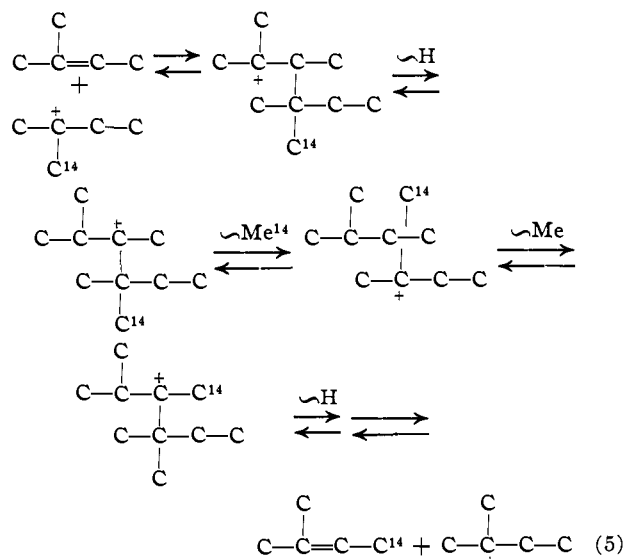
equilibration. Bimolecular reaction 5 explains the results also. If both *t*-amyl units taking part in 5 are labeled, the net effect is shown in 6. Thus, identification of dilabeled species in the recovered *t*-amyl chloride would support the occurrence of 5 or its equivalent.

Although identifying 5 is relatively simple, assessing the relative contributions of 4 and 5 to C-1, C-4 equilibration is less so. The contribution of 5 to the overall rearrangement can be assessed from the amount of dilabeled *t*-amyl chloride formed in relation to the extent of C-1, C-4 equilibration. This information, in turn, can lead to an estimate of the contribution of 4. First, however, other sources of dilabeled species, such as 7, must be considered. Paths 5 and 7 differ in that the latter effects not only C-1, C-4 equilibration, but also C-2, C-3; the net effect on isotope-position equilibration is the same as that of 3. The fact that 7, unlike 5, leads to dilabeled species from the C-2 labeled *t*-amyl chloride also—the net effect is shown in 8—makes possible evaluation of its contribution. Because

(1) Research and Development Department, American Oil Co., Whiting, Ind.

(2) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 729 (1963).

(3) J. D. Roberts, R. E. McMahon and J. S. Hine, *ibid.*, **72**, 4237 (1950).

$$C-\overset{\text{C}}{\underset{+}{C}}=C-C \rightleftharpoons C-\overset{\text{C}}{\underset{+}{C}}-C-C \underset{\sim H}{\rightleftharpoons}$$

$$\overset{+}{C}-C-C-C \qquad C-\overset{\text{C}}{\underset{\text{C}^{14}}{C}}-C-C$$

$$C-\overset{\text{C}}{\underset{\text{C}^{14}}{C}}-\overset{+}{C}-C \underset{\sim Me^{14}}{\rightleftharpoons} C-\overset{\text{C}}{\underset{\text{C}}{C}}-\overset{\text{C}^{14}}{\underset{}{C}}-C \underset{\sim Me}{\rightleftharpoons} C-\overset{\text{C}}{\underset{+}{C}}-C-C$$

$$C-\overset{\text{C}}{\underset{\text{C}}{C}}-\overset{+}{C}-C^{14} \underset{\sim H}{\rightleftharpoons} \rightleftharpoons C-\overset{\text{C}}{\underset{\text{C}}{C}}-C-C$$

$$C-\overset{\text{C}}{\underset{}{C}}=C-C^{14} + C-\overset{\text{C}}{\underset{+}{C}}-C-C \quad (5)$$

$$^{14}C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C + {}^{14}C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C \xrightleftharpoons{\text{AlCl}_3}$$

$$^{14}C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C^{14} + C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C \quad (6)$$

$$^{13}C-\overset{+}{\underset{}{C}}-\overset{\text{C}}{\underset{}{C}}-C \underset{\sim Et}{\rightleftharpoons} {}^{13}C-\overset{\text{C}}{\underset{}{C}}-\overset{\text{C}}{\underset{}{C}}-C-C \underset{\sim i\text{-}Pr}{\rightleftharpoons}$$

$$^{+}\overset{}{C}-C-C \underset{\sim Me}{\rightleftharpoons} C-\overset{\text{C}}{\underset{}{C}}-C-C \underset{\sim H}{\rightleftharpoons} \rightleftharpoons$$

$$^{13}C-\overset{\text{C}}{\underset{}{C}}=C-C^{13} + C-\overset{\text{C}}{\underset{+}{C}}-C-C \quad (7)$$

$$C-\overset{\text{C}}{\underset{\text{Cl}}{C^{13}}}-C-C + C-\overset{\text{C}}{\underset{\text{Cl}}{C^{13}}}-C-C \xrightleftharpoons{\text{AlCl}_3}$$

$$C-\overset{\text{C}}{\underset{\text{Cl}}{C^{13}}}-C^{13}-C + C-\overset{\text{C}}{\underset{\text{Cl}}{C}}-C-C \quad (8)$$

in the third step of 7 either labeled or unlabeled methyl can migrate with equal probability, the amount of

dilabeled species formed from $t$-amyl chloride-1-$C^{13}$ via 7 would be one-half the amount of dilabeled species formed from $t$-amyl chloride-2-$C^{13}$.

The soundness and completeness of the above arguments require further scrutiny, especially with respect to the question of whether the bimolecular reactions examined up to this point are the only ones contributing to rearrangement and/or dilabeled species (see Conclusions).

### Results

Both $t$-amyl chloride-1-$C^{13}$ and $t$-amyl chloride-2-$C^{13}$ were treated with aluminum chloride at 0° for five minutes, and the products were collected and quantitatively analyzed as before.[2] Table I summarizes the composition of the volatile fraction.

TABLE I

THE REACTIONS OF $C^{13}$-LABELED $t$-AMYL CHLORIDES WITH ALUMINUM CHLORIDE AT 0° FOR 5 MIN.

|  | Reacting halide | |
|  | 1-$C^{13}$ | 2-$C^{13}$ |
|---|---|---|
| Wt. of $t$-amyl chloride, g. | 1.0 | 1.0 |
| Wt. of aluminum chloride, g. | 0.047 | 0.047 |
| Recovery (volatile fraction), % | 52 | 52 |
| % (w./w.) compn. of recovd. prod. | | |
| Isobutane | Trace | Trace |
| Isopentane | 0.9 | 1.2 |
| $t$-Butyl chloride | 21.6 | 21.0 |
| 2-Methylpentane | 0.4 | 0.2 |
| 3-Methylpentane | 0.2 | 0.1 |
| $t$-Amyl chloride | 62.4 | 66.6 |
| 3-Chloro-2-methylbutane | 4.1 | 3.6 |
| 2-Chloro-2-methylpentane | 7.4 | 5.3 |
| 3-Chloro-3-methylpentane | 2.0 | 1.5 |

**Isotopic Analysis of the $t$-Amyl Chlorides.**—It was important to know that the starting $C^{13}$-labeled chlorides had the label only at the designated carbon atoms. For this reason both the alcohols from which the chlorides were prepared and the chlorides were analyzed by mass spectrometry and proton n.m.r.

The mass spectrum of a labeled compound can, at least in principle, furnish information on both the distribution of molecules containing various numbers of labels—that is, an isotopic analysis—and the location of labels in the molecules.

The isotopic analysis is usually calculated from intensities of parent ions[4]; these are vanishingly small in the spectra of both $t$-amyl chloride and $t$-amyl alcohol. The chloride spectrum contains a satisfactory alternative, the $C_5H_{11}^+$ ion; but even this is subject to interference, in the spectra of labeled species, from $C_5H_{10}^+$ and $C_5H_9^+$. The interference could not be eliminated by reducing the ionizing voltage, because $C_5H_{10}^+$ has a lower appearance potential than $C_5H_{11}^+$.[5] At the same time, $C_5H_{10}^+$ intensity is too low at ionizing voltages below the appearance potential of $C_5H_{11}^+$ to permit using it as a basis for an isotopic analysis. A satisfactory analysis was derived from the 70-volt spectrum by assuming that $C_5H_{11}^+$, $C_5H_{10}^+$ and $C_5H_9^+$ are all produced with the same isotopic distribution. In the spectrum of $t$-amyl alcohol the intensities of these ions are far lower than in that of the chloride; moreover, the peaks due to them may also include contributions from oxygen-containing ions. Isotopic analysis of the labeled alcohols, therefore, was made by attributing the peak at mass 59—unlabeled $C_3H_7O^+$—solely to the un-

(4) D. P. Stevenson and C. D. Wagner, J. Am. Chem. Soc., **72**, 5612 (1950).

(5) This observation is inconsistent with the inference drawn by F. W. McLafferty, Anal. Chem., **34**, 2 (1962), from relative abundance of fragment ions that loss of Cl may be energetically favored over loss of HCl in ionic decomposition of secondary and tertiary alkyl chlorides under electron impact.

labeled species and that at 60 to the labeled species. Good agreement of the analysis so arrived at with that

|  | 1-$C^{13}$ | 2-$C^{13}$ |
|---|---|---|
| Alcohol, % labeled | 43.0 | 57.6 |
| Chloride, % labeled | 43.0 | 57.7 |

of the chlorides supports and justifies the procedure.

The mass spectrum of a labeled molecule can be used to locate the label only if the relevant decomposition paths are known and if the various parts of the molecule do not lose identity before decomposition.[6] Spectra of the 1- and 2-$C^{13}$-labeled species define clearly certain primary decomposition steps and show that no rearrangement precedes these steps. Table II shows partial spectra of $t$-amyl chloride unlabeled, 1-$C^{13}$ and 2-$C^{13}$, corrected for contributions of unlabeled material in the labeled chlorides and of ions containing heavy isotopes in natural abundance; Table III shows the corresponding data for the $t$-amyl alcohols. Table IV shows derived label-retention values[6] in $C_4H_8X^+$ and

TABLE II

PARTIAL SPECTRA OF $t$-AMYL CHLORIDES

| Mass | Ion[a] | Relative intensity | | |
|  |  | Unlabeled | 1-$C^{13}$ | 2-$C^{13}$ |
|---|---|---|---|---|
| 69 | $C_5H_9^+$ | 2.9 | 0.0 | 0.0 |
| 70 | $C_5H_{10}^+$ | 16.5 | 2.5 | 2.6 |
| 71 | $C_5H_{11}^+$ | 100.0 | 16.3 | 16.2 |
| 72 | ... | 0.0 | 100.0 | 100.0 |
| 75 | $C_3H_4Cl^+$ | 1.2 | 0.5 | 0.0 |
| 76 | $C_3H_5Cl^+$ | 54.8 | 1.2 | 1.5 |
| 77 | $C_3H_6Cl^+$ | 92.6 | 57.8 | 59.3 |
| 78 | ... | 0.1 | 92.3 | 98.2 |
| 89 | $C_4H_6Cl^+$ | 0.4 | 0.1 | 0.0 |
| 90 | $C_4H_7Cl^+$ | 1.4 | 0.8 | 0.2 |
| 91 | $C_4H_8Cl^+$ | 15.8 | 8.0 | 1.6 |
| 92 | ... | 0.1 | 8.1 | 16.4 |
| 105 | $C_5H_{10}Cl^+$ | 0.1 | 0.1 | 0.0 |
| 106 | $C_5H_{11}Cl^+$ (parent) | 0.1 | .1 | .1 |
| 107 | ... | ... | .2 | .1 |

[a] Unlabeled ions only are listed.

TABLE III

PARTIAL SPECTRA OF $t$-AMYL ALCOHOLS

| Mass | Ion[a] | Relative intensity | | |
|  |  | Unlabeled | 1-$C^{13}$ | 2-$C^{13}$ |
|---|---|---|---|---|
| 59 | $C_3H_7O^+$ | 100.0 | [b] | [b] |
| 60 | ... | 0.0 | 100.0 | 100.0 |
| 69 | $C_5H_9^+$ | 0.7 | 0.0 | 0.0 |
| 70 | $C_5H_{10}^+$ | 1.6 | 0.5 | 0.5 |
| 71 | $C_5H_{11}^+$ | 6.0 | 1.1 | 1.0 |
| 72 | ... | 0.2 | 7.0 | 5.3 |
| 73 | $C_4H_9O^+$ | 56.2 | 26.9 | 0.0 |
| 74 | ... | 0.0 | 27.9 | 57.2 |
| 87 | $C_5H_{11}O^+$ | 0.1 | 0.0 | 0.0 |
| 88 | $C_5H_{12}O^+$ (parent) | .0 | .0 | .1 |
| 89 | ... | .0 | .0 | .0 |

[a] Unlabeled ions only are listed.    [b] Assumed zero.

TABLE IV

LABEL RETENTION IN SELECTED IONS

|  | $t$-Amyl chloride | | $t$-Amyl alcohol | |
|  | 1-$C^{13}$, % | 2-$C^{13}$, % | 1-$C^{13}$, % | 2-$C^{13}$, % |
|---|---|---|---|---|
| $C_4H_8X^+$ | 51 | 100 | 51 | 100 |
| $C_3H_6X^+$ | 99 | 100 | 100 | 100 |

$C_3H_6X^+$, formed by respective loss of $CH_3$ and $C_2H_5$ from the parent ions. In the chlorides, these values were calculated on the assumption that $C_4H_8Cl^+$, $C_4H_7Cl^+$, and $C_4H_6Cl^+$ all have the same retention,

(6) H. M. Grubb and S. Meyerson, in "The Mass Spectrometry of Organic Ions," F. W. McLafferty, ed., Academic Press, Inc., New York, N. Y., in press.

TABLE V

ISOTOPIC COMPOSITION OF t-AMYL CHLORIDES FROM MASS-SPECTRAL ANALYSIS[a]

| Reaction time | $C_5H_{11}^+$ | Label, % | $C_5H_{11}^+$ | $C_4H_8Cl^{+b}$ | $C_3H_6Cl^{+b}$ | Label, % | 1,1′ | 2 | 3 and 4 |
|---|---|---|---|---|---|---|---|---|---|
| | — 0 — | | — | — 5 min. — | — | | | Label distribution in position, % | |
| t-Amyl chloride-1-C13 | | 43.0 | | | | 42.5 | 65.4 | 0 | 34.6 |
| Unlabeled (% molecules) | 57.0 | | 61.0 | 31 | 30.0 | | | | |
| Monolabeled | 43.0 | | 35.5 | 66 | 68.2 | | | | |
| Dilabeled | 0.0 | | 3.5 | 3 | 1.8 | | | | |
| t-Amyl chloride-2-C13 | | 57.7 | | | | 57.4 | 0 | 49.2 | 50.8 |
| Unlabeled | 42.3 | | 46.9 | 0.0 | 47.8 | | | | |
| Monolabeled | 57.7 | | 48.8 | 94 | 52.2 | | | | |
| Dilabeled | 0.0 | | 4.3 | 6 | 0.0 | | | | |

[a] The label % denotes the number of labeled atoms per 100 molecules. [b] The isotopic composition was computed on the basis of labeled molecules only (contribution of unlabeled t-amyl chloride removed).
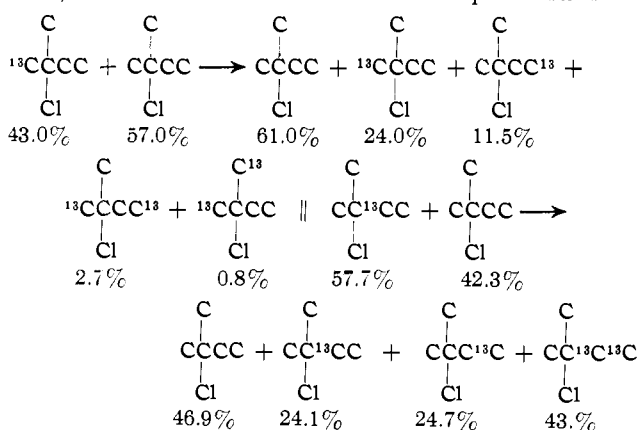
and that $C_3H_6Cl^+$, $C_3H_5Cl^+$ and $C_3H_4Cl^+$ all have the same retention.

In the alcohols, interference from other ions is evidently very small and was neglected; thus, respective intensities at masses 73 and 74 were attributed to unlabeled and labeled $C_4H_8OH^+$, and those at 59 and 60 to unlabeled and labeled $C_3H_6OH^+$. Evidently, $C_4H_8X^+$ and $C_3H_6X^+$ in the spectra of both the chloride and the alcohol are formed solely by loss of the original $CH_3$ and $C_2H_5$ groups on the tertiary carbon atom.[7] The data gave assurance that the starting chlorides contained only the desired isotopic species, and the method of purification and analysis was acceptable.

The pertinent mass-spectral results on the t-amyl chlorides recovered from the reactions with aluminum chloride are given in Table V. The data do not distinguish directly between C-3 and C-4, and these positions are therefore grouped together under % label distribution. Because identification of individual isotopic species is pertinent to our arguments, distinction between C-3 and C-4 is necessary. The fact that no label is found in C-2 from the reaction of the 1-C13 chloride is strong evidence that no label is present in C-3, but all of it (34.6%) is in C-4. Analogously, the finding that no label is in C-1 from the reaction of the 2-C13 chloride implies that no label is in C-4, but all of it (50.8%) is in C-3. Corroborative evidence is afforded by proton n.m.r. The spectrum of t-amyl chloride recovered from the reaction of the 1-C13 chloride shows C13 satellites for the gem-dimethyl protons (8.47 τ) and the methyl protons (8.97τ) of the ethyl group ($J_{C^{13}H}$ in both cases is about 130 c.p.s.). No excess label was detected in C-3.

## Discussion

On the basis of the mass-spectral and proton n.m.r. data, one can summarize the isotopic results as

$$^{13}C\overset{\underset{Cl}{C}}{C}CC + C\overset{\underset{Cl}{C}}{C}CC \longrightarrow C\overset{\underset{Cl}{C}}{C}CC + ^{13}C\overset{\underset{Cl}{C}}{C}CC + C\overset{\underset{Cl}{C}}{C}CC^{13} +$$

43.0%      57.0%      61.0%      24.0%      11.5%

$$^{13}C\overset{\underset{Cl}{C}}{C}CC^{13} + ^{13}C\overset{\underset{Cl}{C^{13}}}{C}CC \parallel C\overset{\underset{Cl}{C^{13}}}{C}CC + C\overset{\underset{Cl}{C}}{C}CC \longrightarrow$$

2.7%      0.8%      57.7%      42.3%

$$C\overset{\underset{Cl}{C}}{C}CC + C\overset{\underset{Cl}{C^{13}}}{C}CC + C\overset{\underset{Cl}{C}}{C}C^{13}C + C\overset{\underset{Cl}{C^{13}}}{C}C^{13}C$$
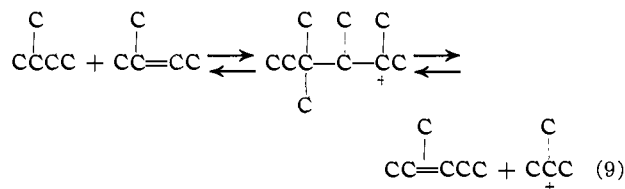
46.9%      24.1%      24.7%      43.%

The proposed mechanisms demand that the formation of every dilabeled molecule be accompanied by the

(7) Compare P. N. Rylander and S. Meyerson, J. Am. Chem. Soc., 77, 6683 (1955); and F. W. McLafferty, cited in footnote 5.

formation of an unlabeled molecule and the destruction of two monolabeled molecules. The data are in good accord with this contention. The data imply that C-1, C-4 and C-2, C-3 equilibration has been reached, and the small deviations observed are probably within experimental error. Because formation of the hexyl chlorides is best explained by invoking some of the intermediates involved in 5 and 7, knowledge of their isotopic composition could be useful. Attempts to separate these chlorides by v.p.c. from small amounts of $C_{10}$ and/or $C_9$-hydrocarbons failed, and these hydrocarbons interfere in the mass-spectral analysis. In addition, the hexyl chlorides decomposed into hexenes and hydrogen chloride to some extent upon standing and the mass spectra were complicated further. The n.m.r. spectrum of the hexyl chlorides from the reaction of t-amyl chloride-1-C13 shows that all the label is in the methyl groups and none (less than 5%) in the non-methyl carbons.

**Some Calculated Distribution of Label in the Products.**—The degree to which either all carbon atoms in the sample or specific groups of atoms equilibrated is determined by the rearrangements undergone by the carbonium ions. Some light can therefore be thrown on the rearrangements by comparing experimental results with calculated values of label distribution.

According to the proposed mechanisms a $C_{10}$-carbonium ion, as shown in 9, is the intermediate involved in

$$C\overset{\underset{}{C}}{C}CC + C\overset{\underset{}{C}}{C}=CC \rightleftarrows C\overset{\underset{C}{C}}{C}C-\overset{\underset{}{C}}{C}-\overset{\underset{+}{C}}{C}C \rightleftarrows$$

$$C\overset{\underset{}{C}}{C}=CCC + C\overset{\underset{+}{C}}{C}C \quad (9)$$

the formation of both dilabeled t-amyl chloride and hexyl and t-butyl chlorides. Formation of these products requires rearrangements of the carbonium ion before disproportionation; these rearrangements can result either in complete or partial equilibration of the carbon atoms. The experimental results exclude equilibration of the six methyl carbon atoms with the four carbon atoms inside the chain; thus, the only equilibrations possible are those among the six methyl carbon atoms, or those among the four non-methyl carbon atoms.

Two separate calculations of label distribution were carried out. The first, process A, is based on the assumption that the six methyl carbon atoms, or the four non-methyl carbon atoms, of the $C_{10}$ unit attain statistical distribution prior to disproportionation into either two $C_5$ units or a $C_6$ and a $C_4$ unit; these smaller units recombine at random, and the process is repeated until all methyl carbon atoms or all non-methyl carbon atoms in the same are statistically distributed in the various molecules. The second, process B, is based on the assumption that after the original statistical distri-

TABLE VI

SOME CALCULATED VALUES OF ISOTOPIC COMPOSITION[a] OF RECOVERED t-AMYL CHLORIDES FROM THE REACTIONS OF 1-C[13] AND 2-C[13] LABELED t-AMYL CHLORIDES WITH ALUMINUM CHLORIDE

| | 1-C[13] | | | | | 2-C[13] | | | | |
| | % $C_0$ | % $C_1$ | % $C_2$ | % $C_3$ | Over-all label, % | % $C_0$ | % $C_1$ | % $C_2$ | % $C_3$ | Over-all label, % |
|---|---|---|---|---|---|---|---|---|---|---|
| Process A (calcd.)[b] | 62.9 | 31.6 | 5.3 | 0.3 | 43.1 | 50.6 | 41.1 | 8.3 | 0.0 | 57.7 |
| Process B (calcd.) | 60.7 | 35.6 | 3.7 | .0 | 43.0 | 47.9 | 46.6 | 5.55 | .0 | 57.7 |
| Experimental | 61.0 | 35.5 | 3.5 | .0 | 42.5 | 46.9 | 48.8 | 4.3 | .0 | 57.7 |

[a] The $C_0$, $C_1$, $C_2$ and $C_3$ represent unlabeled, monolabeled, dilabeled and trilabeled molecules, respectively. [b] For distinction between process A and B see text.

bution the $C_{10}$ unit disproportionates as above, but the reaction stops there (no recombination of the new units occurs).

The results, summarized in Table VI, exclude process A. Comparison with the data on the recovered t-amyl chlorides suggests that in these experiments each molecule of t-amyl chloride has undergone on the average about one bimolecular reaction during which the methyl carbon atoms of the $C_{10}$ unit have been statistically distributed, while the four non-methyl carbon atoms have not.

## Conclusions

Several conclusions can be drawn from this work that appear pertinent not only to the t-amyl cation, but to the general problem of the behavior of carbonium ions undergoing fast and reversible reactions and rearrangements: (1) Bimolecular reactions play an important role in the isotope-position rearrangements of the t-amyl cation. In mechanistic interpretations of disproportionation reactions of alkyl units the importance of bimolecular reactions has been recognized for some time. They are equally important in nominally simple isomerizations also.

(2) Protonated cyclopropanes, such as the one shown in 10, do not intervene as intermediates. Had such

(10)
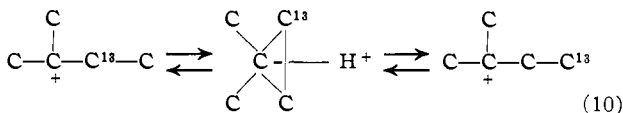
intermediates been involved, equilibration between methyl and non-methyl carbon atoms would have occurred.

(3) All the evidence agrees with the suggestion[2] that during the fission step only tertiary carbonium ions are formed. Reaction sequences such as 11 are excluded because the hexyl chlorides obtained from the reaction of t-amyl chloride-1-C[13] have practically all the

(11)
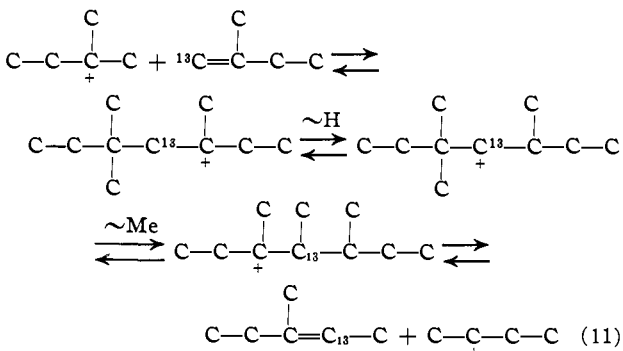
label in the methyl groups and none in C-2, C-3 or C-4. These results imply that the reactions of 2-methyl-1-butene and 3-methyl-1-butene with carbonium ions do not contribute appreciably to formation of hexyl chlorides; such reactions would inevitably lead to incorporation of originally methyl label into C-2, C-3 or C-4. Most likely $C_{10}$-carbonium ions such as those shown in 11 are eventually converted into polymer.

(4) Behavior of the t-amyl cation under the experimental conditions used can be described in terms of three competitive reactions: (a) reversible formation of olefin by proton loss, (b) unimolecular rearrangements according to (3), and (c) reversible bimolecular reactions with olefin. The data are in accord with I as the first important intermediate in c, undergoing
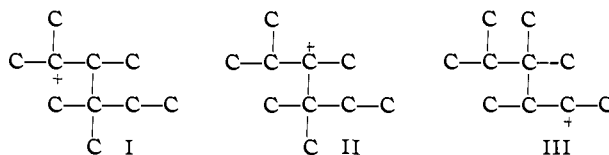
fast and reversible rearrangements to other $C_{10}$-carbonium ions which, in turn, undergo similar rearrangements. During these rearrangements the six methyl carbon atoms attain statistical distribution faster than the four carbon atoms inside the chain. The faster equilibration of the methyl carbon atoms can be seen by inspection of I, II and III or any of the other $C_{10}$-carbonium ions; methyl groups can be equilibrated without effect on the other carbon atoms. On the other hand, rearrangements by which the four carbon atoms inside the chain can be equilibrated effect simultaneous equilibration of methyl groups. The data do not allow an exact evaluation of the relative rates of methyl vs. non-methyl equilibration because the methyl groups have already attained statistical distribution. A lower limit of 1.2 of methyl over non-methyl equilibration can be set, although the true value may be higher. Disproportionation of the $C_{10}$-carbonium ions into either two $C_5$ units or a $C_6$ and a $C_4$ unit follows these rearrangements; reactions 5, 7, 12, 13, 14, 15 as well as those given for the formation of hexyl chlorides are typical examples.[8]

(5) The question of the relative contributions of bimolecular and unimolecular reactions to the over-all isotope-position rearrangement in the t-amyl system cannot be answered with any degree of accuracy, not only because complete isotope-position equilibration has been achieved under the experimental conditions, but also for the following reason: The only way by which the contributions of bimolecular reactions can be assessed accurately is to measure the amount of dilabeled species formed vs. the extent of C-1, C-4 and C-2, C-3 equilibration. However, many bimolecular reactions lead to isotope-position rearrangement but not dilabeled species, e.g., 12, 13, 14, 15 and others.

Reactions 13, 14 and 15, like 5, effect isotope equilibration in a way which is identical with that of 4; unlike 5, they do not lead to dilabeled species and, consequently, their contributions cannot be estimated. Hence, an accurate estimate of 4 cannot be made until the relative rates of 1 and 2 are measured under conditions where bimolecular reactions do not occur.

(8) Undoubtedly some of the $C_{10}$-carbonium ions or their olefins add to other carbon units and are eventually converted to polymer. In describing the behavior of the system we have not mentioned secondary reactions between $C_3$ and $C_4$ or $C_5$ and $C_6$ carbon units. Although some of these reactions undoubtedly occur to some extent, they neither detract from nor add anything significant to the arguments regarding the t-amyl cation.

$$^{13}C-\overset{C}{\underset{\underset{C}{\overset{|}{{}_{13}C}}-C-C}{\overset{|}{\underset{|}{C}}}-C \xrightarrow{\sim Me} \;\; ^{13}C-\overset{\overset{C}{|}}{\underset{\underset{13C}{\overset{|}{|}}-C-C}{C}}-C \longrightarrow$$

$$^{13}C-C=\overset{C}{\underset{|}{C}}-C + {}^{13}C-\overset{C}{\underset{\underset{C}{|}}{\overset{|}{C}}}-C-C \quad (12)$$

$$^{13}C\overset{+}{C}CC \;/\; {}_{13}CCCC \xrightarrow{\sim Me} {}^{13}C\overset{C}{\underset{\underset{C}{|}}{C}}-C^{+} \;/\; {}_{13}CCCC \xrightarrow{\sim Me^{13}} C\overset{+}{C}CC^{13} \;/\; {}_{13}CCCC \rightleftharpoons$$

$$C\overset{C}{\underset{|}{C}}=CC^{13} + {}^{13}C\overset{+}{C}CC \quad (13)$$

$$^{13}C\overset{+}{C}\overset{C}{\underset{|}{C}} \;/\; {}_{13}CCCC \xrightarrow{\sim Me^{13}} CC\overset{C^{13}}{\underset{+}{C}}C \;/\; {}_{13}CCCC \xrightarrow{\sim Me} C-\overset{C}{\underset{\underset{C}{|}}{C}}-\overset{+}{\underset{|}{C}}-C^{13} \;/\; {}^{13}C-\overset{C}{\underset{\underset{C}{|}}{C}}-C-C \xrightarrow{\sim H}$$

$$\rightleftharpoons C-\overset{C}{\underset{|}{C}}=C-C^{13} + {}^{13}C-\overset{C}{\underset{\underset{C}{|}}{C}}-C-C \quad (14)$$

## Experimental

**Synthesis of $C^{13}$-Labeled $t$-Amyl Alcohols.**—2-Methyl-2-butanol-2-$C^{13}$ was prepared by the usual Grignard reaction involving magnesium (0.456 mole), methyl iodide (0.456 mole) and methyl propionate-carbonyl-$C^{13}$ (0.114 mole). The yield, based on the methyl propionate, was 80%. 2-Methyl-2-butanol-1-$C^{13}$ was synthesized from the Grignard reaction of magnesium (0.150 mole), methyl iodide-$C^{13}$ (0.134 mole) and butanone (0.144 mole). The yield, based on the methyl iodide, was 66%. Both alcohols were purified by use of a Beckman Megachrom.

$$^{13}C\overset{C}{\underset{|}{C}}CC \;/\; {}_{13}CCCC \xrightarrow{\sim Me} {}^{13}C\overset{C}{\underset{|}{C}}-CC \;/\; {}_{13}CCCC \xrightarrow{\sim H} {}^{13}C\overset{C}{\underset{\underset{+}{|}}{C}}-CC \;/\; {}_{13}CCCC \xrightarrow{\sim Me^{13}}$$

$$^{13}C\overset{C}{\underset{\underset{+CCC}{|}}{C}}-\overset{C}{\underset{|}{C}}C \;/\; {}_{13}CC\overset{C}{\underset{|}{C}}-\overset{C}{\underset{+}{C}}C \;/\; CCCC^{13} \xrightarrow{\sim H} \xrightarrow{\sim Me}$$

$$^{13}C\overset{+}{C}\overset{C}{\underset{|}{C}}-C \;/\; \overset{C}{\underset{|}{CCCC^{13}}} \xrightarrow{\sim H} {}^{13}C\overset{C}{\underset{|}{C}}=CC + C\overset{C}{\underset{+}{C}}CC^{13} \quad (15)$$

**Synthesis of $C^{13}$-Labeled $t$-Amyl Chlorides.**—The chlorides were prepared by the same method as used by Roberts and his co-workers.[3] The following is a typical experiment. 2-Methyl-2-butanol-2-$C^{13}$ (0.071 mole) and concentrated hydrochloric acid (0.222 mole) were heated together and the fraction boiling at 65–82° was collected and purified. The yield of 2-chloro-2-methylbutane (0.069 mole) was 97%. Both chlorides were purified by use of a Beckman Megachrom.

**Reactions of the Labeled $t$-Amyl Chlorides with Aluminum Chloride.**—The labeled $t$-amyl chlorides were treated with aluminum chloride as described previously.[2] Both the $t$-amyl chlorides and the hexyl chlorides were separated from the reaction mixture with the aid of a Beckman Megachrom.

**Isotopic analysis of the alkyl chlorides and alcohols** was done with a Consolidated model 21-103C mass spectrometer. The n.m.r. spectra were taken with a model V4300-2 Varian Associates high resolution n.m.r. spectrometer at 60 Mc.

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# Effects of Metallic Compounds in Oxidation Systems. I. Ferric Chloride as an Inhibitor

BY GEORGE S. HAMMOND, LEE R. MAHONEY AND U. S. NANDI

Ferric chloride is a good inhibitor of the ABN-initiated oxidation of cumene and tetralin in chlorobenzene solution but does not inhibit the oxidation of cyclohexene. A mechanism is proposed to account for the results. Phenols are believed to be produced by rearrangement of cumyl and tetralyl hydroperoxides in the presence of ferric chloride, and chains are broken by reaction of peroxy radicals with ferric phenoxides.

Liquid-phase oxidation of hydrocarbons is well known to be affected by salts of heavy metals.[1-6] At least one of the effects of such additives is acceleration of initiation by hydroperoxides that are commonly formed by the oxidative process.[1,5,6,7] Direct evidence for radical-producing oxidation–reduction reactions between hydroperoxides and metal ions is provided by studies of hydroperoxide decomposition rates[8,9] and by the use of metal ion–hydroperoxide recipes as initiators for vinyl polymerization reactions.

On the other hand, inhibition of oxidation by salts of metals capable of undergoing one-electron oxidation–reduction transformations has been reported. Denisov and Emanuel[5,10] have shown that solutions originally containing cobaltous or manganous stearates show residual inhibitory action after they have ceased to function as initiators. They indicate that inhibition is associated with the existence of the metal ions mainly in their lower oxidation states in the absence of substantial amounts of hydroperoxide. Inhibition of hydrocarbon oxidation by copper stearate has also been reported[11] and induction periods, which can be eliminated by addition of hydroperoxide, in oxidations catalyzed by manganous and cobaltous salts have been reported.[12] Furthermore, Bamford, $et\ al.$,[13] have shown

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