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Carbonium Ion Rearrangements. III.<sup>1</sup> The Question of Primary Carbonium Ions

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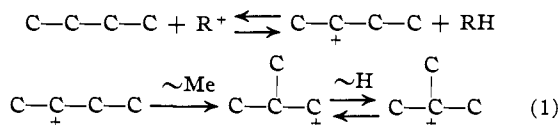
All liquid phase reactions of paraffins, olefins, alkyl halides and related compounds in which intermediate primary carbonium ions have been suggested to arise from rearrangements of secondary and tertiary ones may also be explained in terms of bimolecular reactions not involving primary carbonium ions. The effect of time, temperature and concentration of aluminum chloride, methylbutenes, hydrogen chloride and water on the reaction of *t*-amyl chloride with aluminum chloride was studied. At higher temperatures and aluminum chloride concentrations the disproportionation of *t*-amyl chloride increases, a fact which is in accord with the expected increase in the occurrence of bimolecular reactions. It was found that the reaction stops after about 5 min. at 0°, the most likely reason being the deactivation of the catalyst by polymer being formed. The data support the previous suggestion that during the life-span of carbonium ions many reactions occur simultaneously. The nature of the fission step of carbonium ions is briefly examined.

## Introduction

The discovery by Bartlett, Condon and Schneider<sup>2</sup> of the rapid hydrogen-halogen exchange between isoparaffins and alkyl halides under the influence of Lewis acids, and the concepts developed therein, represent the basis upon which are founded the modern mechanistic interpretations of many carbonium ion reactions. By utilizing their concepts one can explain the formation of any product during liquid phase reactions of paraffins, olefins, alkyl halides and related compounds under carbonium ion conditions. The number of reaction sequences, however, able to rationalize a given product is relatively large, and it is difficult to single out a particular sequence as the correct or even dominant one. Furthermore, the fact that during the life-span of such carbonium ions many reactions occur simultaneously renders elucidation of this problem more difficult.<sup>3</sup>

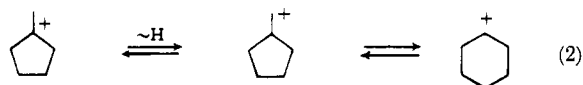
We decided to study the problem in terms of understanding the nature of the carbonium ions involved and the relative importance of individual rearrangement steps. The intermediacy of non-classical carbonium ions<sup>4</sup> and protonated cyclopropanes<sup>1a,5</sup> to any appreciable extent in reactions of acyclic compounds has been discounted. Two questions pertinent to the problem, however, have not been answered satisfactorily. These questions are the significance in acyclic systems of Wagner-Meerwein shifts of orders higher than one-two, and the rearrangement of tertiary and secondary carbonium ions to primary ones. We shall discuss in this paper the second question.

Primary carbonium ions, formed from the more stable secondary and tertiary ones, have been proposed often as reaction intermediates in liquid phase isomerization reactions. The following are typical examples: (a) Isomerization of straight chain hydro-

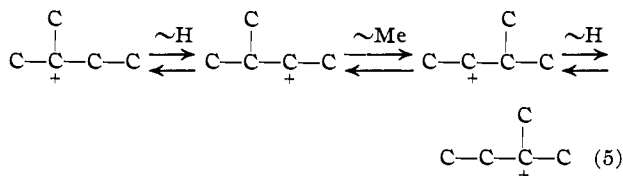
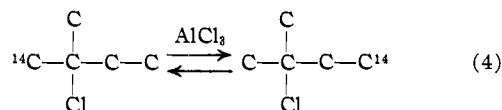
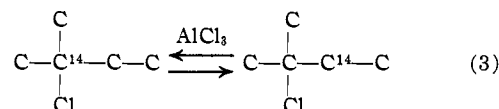


carbons to branched chain hydrocarbons (1). (b) Isomerization and position-isotope rearrangement of cyclic hydrocarbons.<sup>6</sup> The isomerization of methylcyclo-

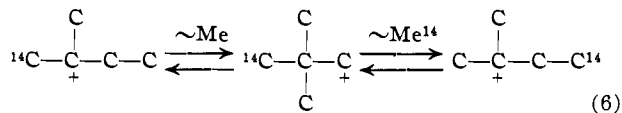
pentane to cyclohexane, cycloheptane to methylcyclohexane and the 31% C<sup>14</sup>-ring distribution during the reaction of methyl-C<sup>14</sup>-cyclohexane with aluminum bromide, hydrogen bromide and 2-bromobutane are explained by intramolecular rearrangements involving primary carbonium ions (2). (c) Isotope-position rear-



rangement of the *t*-amyl system. It was demonstrated<sup>7</sup> that 3 does not proceed twice as fast as 4,



as anticipated if 5 were the only path of isotopic equilibration. The data necessitated the interpretation that 87% of the rearrangement occurs *via* 5 and 13% *via* 6



Although the above mechanisms explain the observed results, calculations indicating that tertiary carbonium ions are 33 kcal./mole and secondary carbonium ions 22 kcal./mole more stable than primary ones<sup>8</sup> suggest that alternate mechanisms not involving primary carbonium ions should be considered.

One can rationalize the results of the above and related reactions on the basis of bimolecular reactions without intervention of primary carbonium ions (7).

H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4055 (1950); H. Pines and V. N. Ipatieff, *ibid.*, **67**, 1631 (1945); H. Pines and R. W. Myerholtz, *ibid.*, **77**, 5392 (1955).

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

(8) A. G. Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, Eng., 1946, p. 15.

(1) For previous papers in the series see: (a) G. J. Karabatsos and J. D. Graham, *J. Am. Chem. Soc.*, **82**, 5250 (1960); (b) G. J. Karabatsos, F. M. Vane and S. Meyerson, *ibid.*, **83**, 4297 (1961).

(2) P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

(3) P. D. Bartlett and G. J. Karabatsos, unpublished results.

(4) J. D. Roberts and J. A. Yancy, *J. Am. Chem. Soc.*, **77**, 5558 (1955); J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955); S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

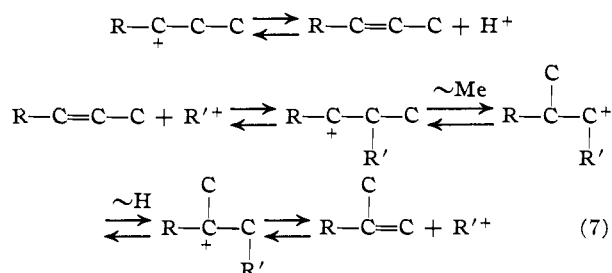
(5) The absence of protonated cyclopropanes under basic conditions has been demonstrated; P. S. Skell, I. Starer and A. P. Krapcho, *ibid.*, **82**, 5257 (1960); W. A. Sanderson and H. S. Mosher, *ibid.*, **83**, 5033 (1961).

(6) H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948);

TABLE I  
THE REACTION OF *t*-AMYL CHLORIDE WITH ALUMINUM CHLORIDE AT 0°. EFFECT OF REACTION TIME<sup>a</sup>

	Time							
	5 sec. <sup>b</sup>	5 sec.	30 sec.	3.5 min.	5 min.	7 min.	15 min.	25 min.
<i>t</i> -Amyl chloride/AlCl <sub>3</sub> (mole)	28	28	28	28	28	82	28	28
Recovery (volatile fraction), %	87	91	86	78	72	71	72	63
% (w./w.) compn. of recovd. prod.								
Isobutane	+	+	+	0.2	0.4	0.6	0.3	0.2
Isopentane	0.3	0.7	1.1	1.9	2.7	2.9	2.4	2.0
<i>t</i> -Butyl chloride	1.2	2.4	3.9	15.0	16.7	20.2	18.5	21.8
2-Methylpentane	+	+	+	0.4	0.6	0.6	0.6	0.6
3-Methylpentane	+	+	+	0.2	0.2	0.3	0.3	0.2
<i>t</i> -Amyl chloride	93.7	90.7	83.0	71.5	68.2	62.8	65.5	62.1
3-Chloro-2-methylbutane	4.0	5.5	10.2	5.6	5.7	5.4	5.2	4.8
2-Chloro-2-methylpentane	0.3	0.5	1.1	3.4	4.2	4.8	4.5	5.2
3-Chloro-3-methylpentane	0.1	0.2	0.7	1.7	1.5	2.2	2.7	2.4

<sup>a</sup> All reactions were quenched with *N,N*-dimethylaniline. <sup>b</sup> The reaction temperature was -37°.



The above considerations led us to undertake a general study of various carbonium ion reactions with the objective of assessing the relative contributions of unimolecular or intramolecular reactions and bimolecular or intermolecular reactions to carbonium ion rearrangements. This paper discusses mainly the quantitative and qualitative effects of temperature, time and concentration on the reaction of *t*-amyl chloride with aluminum chloride.

### Results

Tables I-III summarize the effects of time, temperature and aluminum chloride concentration on the reaction of *t*-amyl chloride with aluminum chloride. Product analysis was by vapor phase chromatography and by comparison of the individual components with samples of known compounds. The product consists of a volatile fraction, whose analysis is given in the tables, and a brown polymeric residue. The ratio volatile fraction/residue and the percentage of *t*-amyl chloride in the volatile fraction decrease with increase in time, temperature and aluminum chloride concentration.

The qualitative composition of the product is practically unaffected by reaction time, temperature and aluminum chloride concentration. We regard this fact as further support for the suggestion<sup>8</sup> that carbonium ions during their life-span undergo many reactions of comparable rapidity. It is evident from the data (Table I) that reaction stops after about five minutes. In an effort to understand what causes the reaction to stop, various experiments were carried out. Olefins (methylbutenes) were added to the *t*-amyl chloride to the extent of 1.8-22% and the mixtures were treated with aluminum chloride. The results were identical with those obtained in the absence of olefins. Saturation of the *t*-amyl chloride with hydrogen chloride, water, or exposure of the aluminum chloride to the atmosphere for ten minutes had no effect on the reaction either. The possibility that the aluminum chloride may be deactivated by the polymer was also examined. The reaction of the brown residue—presumably polymer and aluminum chloride—with *t*-amyl chloride resulted in quantitative recovery of the *t*-amyl chloride.

TABLE II  
THE REACTION OF *t*-AMYL CHLORIDE WITH ALUMINUM CHLORIDE FOR 1.5 MIN. EFFECT OF TEMPERATURE

	Temperature, °C.				
	-61	-35	0	22	50
<i>t</i> -Amyl chloride/AlCl <sub>3</sub> (mole)	28	28	28	28	28
Recovery (volatile fraction), %	89	88	72	72	66
% (w./w.) compn. of recovd. prod.					
Isobutane	-	+	0.4	0.9	0.6
Isopentane	0.3	0.4	2.7	3.5	2.8
<i>t</i> -Butyl chloride	1.3	1.4	16.7	17.2	18.1
2-Methylpentane	-	-	0.6	0.6	0.8
3-Methylpentane	-	-	0.2	0.3	0.2
<i>t</i> -Amyl chloride	93.7	91.8	68.2	63.7	61.7
3-Chloro-2-methylbutane	4.7	5.7	5.7	7.0	8.3
2-Chloro-2-methylpentane	+	0.4	4.2	4.7	4.0
3-Chloro-3-methylpentane	+	0.2	1.5	2.3	3.5

TABLE III  
THE REACTION OF *t*-AMYL CHLORIDE WITH ALUMINUM CHLORIDE AT 0° FOR 1.5 MIN. EFFECT OF CONCENTRATION

	<i>t</i> -Amyl chloride/AlCl <sub>3</sub> (mole)				
	190	43	33	26	15
Recovery (volatile fraction), %	97	94	97	76	59
% (w./w.) compn. of recovd. prod.					
Isobutane	+	+	0.2	0.9	2.7
Isopentane	0.3	0.6	1.7	5.0	6.4
<i>t</i> -Butyl chloride	0.3	2.6	10.7	19.1	30.8
2-Methylpentane	-	-	+	0.5	1.5
3-Methylpentane	-	-	+	0.4	0.5
<i>t</i> -Amyl chloride	97.7	90.2	77.7	64.1	47.4
3-Chloro-2-methylbutane	1.7	5.9	5.8	5.0	3.1
2-Chloro-2-methylpentane	+	0.5	1.9	3.7	5.8
3-Chloro-3-methylpentane	+	0.2	1.9	1.3	1.6

This finding suggests that the polymer is involved in the deactivation of the catalyst.<sup>9</sup>

The yield of hexyl chlorides is much lower than that of *t*-butyl chloride while equimolar amounts of the two are expected. This observation was made previously<sup>10</sup> and the suggestion was advanced that the methylpentenes formed polymerize faster than isobutene. The data of Table IV are in accord with this view and clearly demonstrate, especially the last column, the more rapid disappearance of methylpentyl chloride over *t*-butyl chloride. It is interesting to note that the hexyl chloride formed from the reaction of *t*-butyl chloride is mainly 2-chloro-2,3-dimethylbutane with traces of methylpentyl chlorides, while the reverse is true in the reaction of *t*-amyl chloride.

(9) B. L. Evering, "Advances in Catalysis and Related Subjects," Academic Press, Inc., New York, N. Y., 1954, Vol. VI, pp. 209-211.

(10) F. E. Condon, Ph.D. Thesis, Harvard University, 1944.

TABLE IV  
THE REACTIONS OF *t*-BUTYL CHLORIDE AND METHYLPENTYL CHLORIDES WITH ALUMINUM CHLORIDE<sup>a</sup> AT 0°

Reacting halide Reaction time, min.	C <sub>4</sub> CCl		(CC) <sub>2</sub> CC Cl		C <sub>5</sub> CCl + C <sub>5</sub> CCCC Cl		C <sub>5</sub> CCl + C <sub>5</sub> CCC + C <sub>5</sub> CCCC Cl	
	0	5	0	5	0	5	0	5
% (w./w.) compn. of recovd. prod.								
Isobutane	—	2.0	—	0.04	—	1.0	—	1.7
Isopentane	—	0.2	—	0.09	—	0.2	—	2.7
<i>t</i> -Butyl chloride	100	87.4	—	2.3	43	45.7	18	30.0
2-Methylpentane	—	+	—	1.6	—	1.9	—	0.8
3-Methylpentane	—	+	—	1.3	—	0.7	—	0.4
<i>t</i> -Amyl chloride	—	4.5	—	4.4	—	7.7	67	47.1
3-Chloro-2-methylbutane	—	0.5	—	0.4	—	0.7	—	4.2
2-Chloro-2,3-dimethylbutane	—	5.4 <sup>c</sup>	—	—	—	<sup>b</sup>	—	<sup>b</sup>
2-Chloro-2-methylpentane	—	+	—	40.3	57	25.1	15	9.2
3-Chloro-3-methylpentane	—	+	100	40.3	—	15.6	—	4.2
Recovery (volatile product), %		73		75		62		78

<sup>a</sup> The mole ratio alkyl halide/aluminum chloride was about 28. <sup>b</sup> The presence of small amounts of 2-chloro-2,3-dimethylbutane cannot be excluded. <sup>c</sup> The presence of small amounts of isoöctane cannot be excluded.

TABLE V  
THE REACTIONS OF PROPYL + *t*-AMYL CHLORIDES, AND BUTYL + *t*-AMYL CHLORIDES WITH ALUMINUM CHLORIDE<sup>a</sup> AT 22°

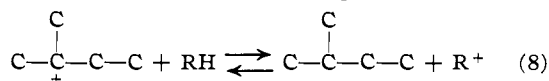
Reacting halide Reaction time, min.	CCC + C <sub>5</sub> CCCC Cl		CCCCl + C <sub>5</sub> CCC Cl		CCCC + C <sub>5</sub> CCC Cl		CCCCCl + C <sub>5</sub> CCC Cl	
	0	5	0	5	0	5	0	5
Selected products, % (w./w.)								
2-Chloropropane	14.4	21.7	..	1.0	..	..	..	..
1-Chloropropane	..	..	12.0	20	..	..	..	..
2-Chlorobutane	..	..	..	..	12.2	25.6	..	1.5
1-Chlorobutane	..	..	..	..	..	..	10.5	25.4
<i>t</i> -Amyl chloride	85.6	22.4	88.0	23.5	87.8	22.2	89.5	23.2

<sup>a</sup> The mole ratio alkyl halides/aluminum chloride was about 10.

The absence of isopropyl chloride and 2-chlorobutane from all recovered products is noteworthy, because it implies that the isopropyl and the 2-butyl cations are not formed during fission of carbonium ions. This absence, however, is not sufficient evidence against the formation of these cations, for the following reasons: (a) These chlorides might be formed and subsequently destroyed under the reaction conditions. (b) The cations might be formed and preferentially undergo reactions other than formation of the chlorides, e.g., attack on olefins. The data (Table V) show that, had any *isopropyl* or *2-butyl* cation been formed in the reactions of *t*-butyl, *t*-amyl or methylpentyl chlorides with aluminum chloride, it would have been detected as isopropyl chloride or 2-chlorobutane.

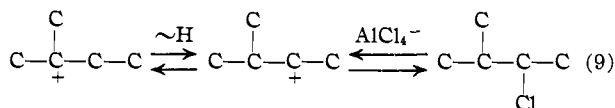
Discussion

The formation of isobutane, isopentane and methylpentanes, although not anticipated, is not entirely surprising. A hydride transfer reaction, e.g., 8, is undoubtedly responsible for their formation. The hydride source is most likely a polyolefin which is

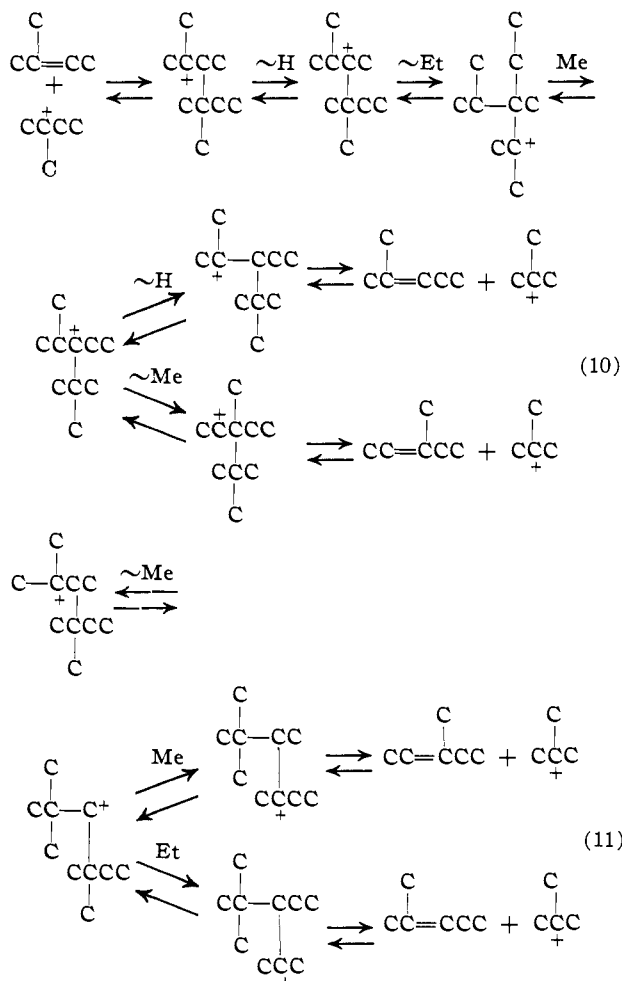


eventually converted into polymer.

The simplest path leading to 3-chloro-2-methylbutane is 9.



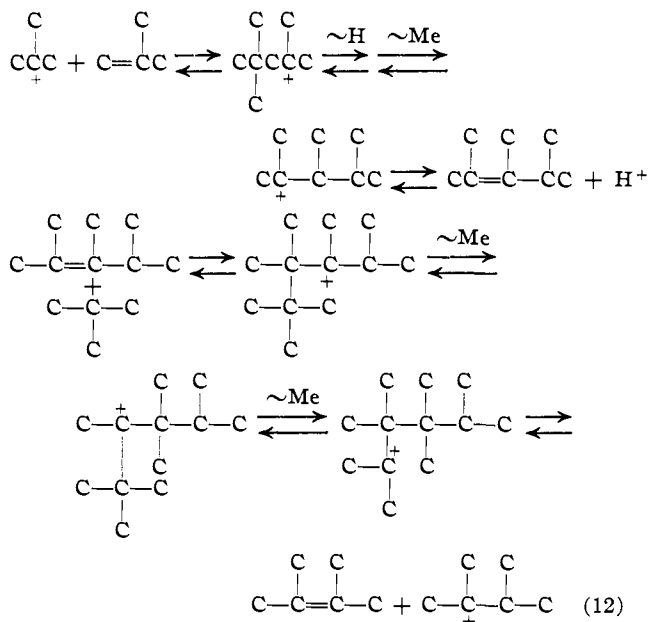
The disproportionation of *t*-amyl chloride to *t*-butyl chloride and hexyl chlorides is viewed as occurring mainly *via* 10 and 11, two commonly written reaction paths.<sup>3,10,11b</sup> The absence of 2-chloro-2,3-dimethyl-



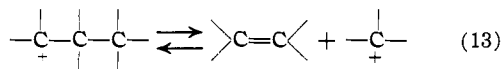
butane is noteworthy since it demonstrates once again the slow interconversion of the methylpentyl and the 2,3-dimethylbutyl systems.<sup>8,11</sup>

The data support the idea that the *t*-amyl cation undergoes both unimolecular and bimolecular reactions. Low temperatures should favor 9 over 10 and 11, because of the greater stability of the *t*-amyl cation-tetrachloroaluminate complex at lower temperatures; the data (Table II) support this prediction. Higher aluminum chloride concentrations on the other hand should increase the disproportionation of *t*-amyl chloride, a fact which is demonstrated by the data of Table III.

It is significant that the hexyl chloride obtained from the reaction of *t*-butyl chloride with aluminum chloride is mainly 2-chloro-2,3-dimethylbutane and not methylpentyl chlorides. Any reasonable reaction sequence postulated requires three butyl units and leads to the 2,3-dimethylbutyl system, *i.e.*, 12.



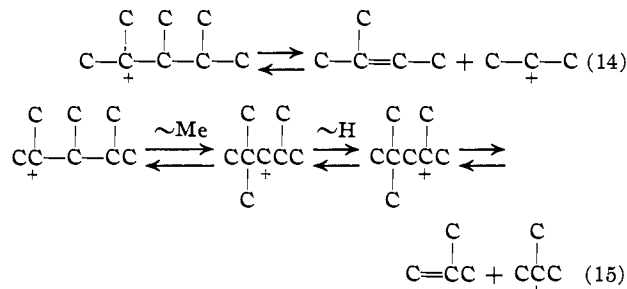
Finally, we wish to indicate the pertinence of the data of Table V to the fission step of carbonium ions, *e.g.*, 13, and specifically to the question of whether



the carbonium ions formed are secondary or tertiary.

(11) (a) D. A. McCaulay, *J. Am. Chem. Soc.*, **81**, 6437 (1959); (b) A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5013, 5017 (1951).

If fission steps leading to secondary carbonium ions were to be excluded, the number of reaction paths leading to the formation of a product would be decreased appreciably. The data indicate that, at least under the experimental conditions of this work, the carbonium ions formed in the fission step are tertiary. Apparently fission of a carbonium ion to an olefin and a *secondary* carbonium ion is more expensive energetically than rearrangement to another carbonium ion which can undergo fission to an olefin and a *tertiary* carbonium ion; *e.g.*, 15 is favored over 14. The general-



ity of the above statements in terms of substrate, catalyst and reaction conditions must be further tested.<sup>12</sup>

### Experimental

**The Reactions of *t*-Amyl Chloride with Aluminum Chloride.**—In a 50-ml. round-bottom flask equipped with a side-arm inlet and a small column connected to a vacuum system was placed 1.75 g. of *t*-amyl chloride. The flask was placed in an ice-water-bath. To the magnetically stirred *t*-amyl chloride was added 0.078 g. of anhydrous aluminum chloride (Baker and Adamson, reagent grade). At the end of 5 min., 73  $\mu$ l. of *N,N*-dimethylaniline was injected into the light brown solution and immediately all of the liquid was collected under vacuum at liquid nitrogen temperatures. The amount collected was 1.26 g. or 72% yield. The above procedure was followed for all reactions with variations in time, temperature and relative concentration of reagents. In many instances no *N,N*-dimethylaniline was added; the results (yield and product composition) remained unchanged.

**Product Analysis.**—Small amounts (0.5–1.5  $\mu$ l.) of the collected product were injected into a Perkin-Elmer vapor fractometer model 154. The columns used were 5–30% Silicone Oil on Celite and the column temperatures were about 80°. Identification of the individual components was achieved by comparison of their retention times with those of authentic samples. Quantitative determination of the components in the mixture was carried out by integration of the appropriate areas under the signals and direct correlation of the area weight to component weight. It was found that the error involved (standard deviation) did not exceed  $\pm 10\%$ .

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(12) Under more drastic conditions formation of secondary carbonium ions in the fission step apparently occurs, see ref. 11a.