

It should be pointed out that secondary isotope effects different in magnitude from those measured here have been reported for other reactions:  $(k_H/k_D)_{\text{sec}} = 0.65$  and  $0.66$  for ethyl vinyl ether hydrolysis,<sup>6b,9b</sup>  $0.67$  for alkyl mercuric iodide cleavage,<sup>9a</sup> and  $0.53$  for isobutene hydration.<sup>6a</sup> These effects are all based on methods which require dissection of observed data into primary and secondary isotope effects, and it may therefore be improper to compare them with values obtained here by a method which does not assume separability of primary and secondary effects. Two of the most divergent of the above values, however,  $0.65$  and  $0.53$ , were determined by a single method, analysis of rates measured in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures. It can be argued, on the other hand, that this analysis is subject to all the assumptions inherent in the theory of isotope effects in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures,<sup>7</sup> that one value ( $0.65$ ) was obtained in dilute acid ( $0.01\text{ }M$ ) whereas the other refers to moderately concentrated solutions ( $0.4\text{ }M$ ), and that the value of  $0.53$  is subject to considerable experimental error due to the difficulties inherent in measuring rates of isobutene hydration. Nevertheless, it would seem prudent to refrain for the time being from any broad generalization concerning the relationship between the magnitude of this secondary isotope effect and transition state structure.

### Experimental Section

**Materials.** 1,3,5-Trimethoxybenzene was prepared by the methylation of phloroglucinol<sup>24</sup> and was purified by alternate vacuum sublimations and recrystallizations from aqueous ethanol. 1,3-Dimethoxybenzene was purchased commercially and was purified by fractional distillation.

(24) H. Brederick, I. Henning, and W. Rau, *Ber.*, **86**, 1085 (1953).

All other materials were best quality commercial chemicals and were used without further treatment.

**Kinetic Procedure.** Runs using 1,3,5-trimethoxybenzene were conducted in glass-stoppered flasks, but the higher volatility of 1,3-dimethoxybenzene necessitated use of a special apparatus designed to prevent the substrate from escaping the reaction mixture. This consisted essentially of a leveling bulb immersed in a water bath and connected to its twin through flexible tubing. The reaction mixture was contained over mercury and under a stopper fitted with a curved capillary tube and a stopcock arranged so as to leave no air space. At suitable intervals, portions of the reaction mixture were expressed by applying pressure through the mercury, an initial amount was discarded, and an aliquot was pipetted from the remainder.

Runs with 1,3-dimethoxybenzene were conducted at  $25.0 \pm 0.02^\circ$  while those with 1,3,5-trimethoxybenzene were performed at  $24.62 \pm 0.02^\circ$ . Reaction mixtures were prepared by mixing substrate and catalyst solutions which had equilibrated with the constant-temperature bath; in the case of runs using 1,3-dimethoxybenzene, reaction mixtures were then transferred to the apparatus described above by hypodermic syringe. Samples were quenched in excess base, extracted with toluene, and the toluene extracts were washed with water a sufficient number of times (established through control experiments) to remove all nonaromatic radioactivity. (Three washings were usually sufficient.) The washed extracts were then dried over calcium chloride, and aliquots were diluted with counting solution (PPO and POPOP in toluene) and assayed by liquid scintillation counting using a Packard Model 314-EX machine. Water radioactivities were determined using Bray's counting solution.<sup>25</sup>

**Analysis for 1,3-Dimethoxybenzene.** Samples of reaction mixture were removed as described above and were added to potassium bromate-potassium bromide in a bromination flask. Dilute sulfuric acid was introduced, and the mixture was stirred thoroughly. When the color of free bromine was observed, the rapid reaction which yields 1,3-dimethoxy-4,6-dibromobenzene was complete, and potassium iodide was added. The liberated iodine was titrated with thiosulfate solution.

(25) G. A. Bray, *Anal. Biochem.*, **1**, 279 (1960).

## Stable Carbonium Ions. LXXVI.<sup>1a</sup>

### 2,2-Dimethyltetramethylene Halonium Ions and a Study of Halogen Participation in Protonated Methyl $\gamma$ -Halopropyl Ketones and 5-Halo-1-pentynes

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**Abstract:** Tertiary carbonium ions containing a halogen atom three carbon atoms removed from the positive site have been generated in antimony pentafluoride-sulfur dioxide solution and in fluorosulfuric acid-antimony pentafluoride dioxide solutions. When the halogen atom was Cl, Br, or I, the species observed in the strong acid systems were the five-membered ring 2,2-dimethyltetramethylene halonium ions. No evidence for halogen participation in protonated methyl  $\gamma$ -halopropyl ketones or 5-halo-1-pentynes was found with the exception of the protonation of 5-iodopentyne-1 which gave the 2-methylenetetramethyleneiodonium ion.

In previous investigations we have shown<sup>2</sup> that tertiary cations containing halogen on an adjacent carbon atom undergo a strong interaction with the halogen

which results in the cationic site becoming tetrahedral (the more nearly tetrahedral as the size of the halogen atom increases) and in charge dispersal to the bridged halogen atom.<sup>3</sup> We have also demonstrated that cyclic

(1) (a) Part LXXV: G. A. Olah, A. T. Ku, and A. M. White, *J. Amer. Chem. Soc.*, in press. (b) Postdoctoral Research Investigator, 1965-1967. (c) Undergraduate Research Participant, 1967-1968.

(2) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 947 (1968).

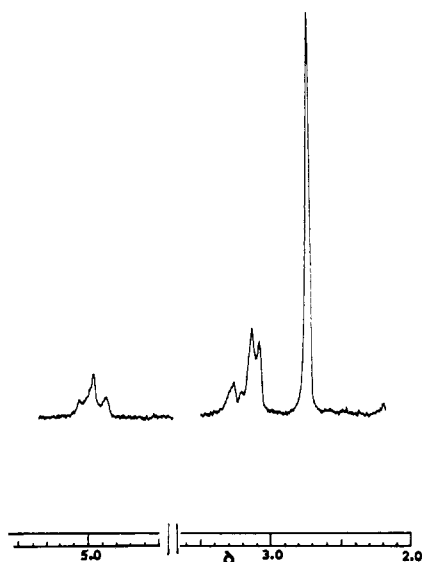
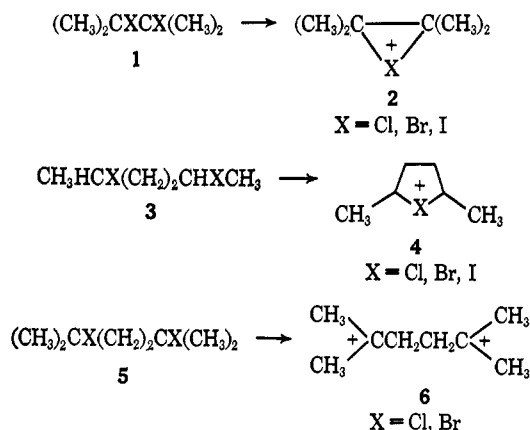


Figure 1. PMR spectrum of the 2,2-dimethyltetramethylene chloronium ion.

halonium ions are readily formed in the strong acid systems from a variety of 1,4-dihaloalkanes (and related compounds containing halogen) when the carbon atoms bearing halogen were primary or secondary.<sup>4</sup> When both carbon atoms bearing halogen were tertiary, a dicarbonium ion was produced from 1,4-dihalo-1,4-dimethylbutanes.<sup>5</sup>



In continuation of our work we felt it of interest to determine whether a tertiary ion capable of forming a five-membered ring system was stable enough to exist as an open-chain ion or would interact with the lone electron pairs on the  $\gamma$ -halogen atom to produce a halonium ion.

## Results and Discussion

Ionization of 2,5-dichloro-2-methylpentane in antimony pentafluoride-sulfur dioxide or fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solutions gave a species whose pmr spectrum consisted of four groups of resonance lines, three complex multiplets and a sharp singlet at  $\delta$  2.69 (Figure 1). This sharp singlet

(3) Charge dispersal on halogen and hybridization were inferred from the nmr data of ions reported in ref 2 and also from the spectra of other members of these series, cf. G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967).

(4) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

(5) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *ibid.*, **89**, 156 (1967).

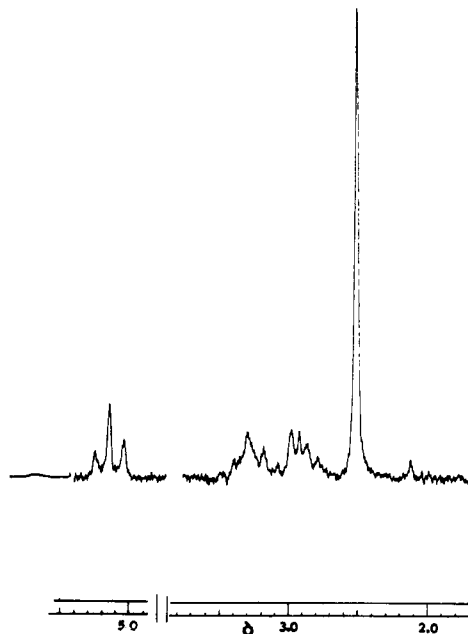
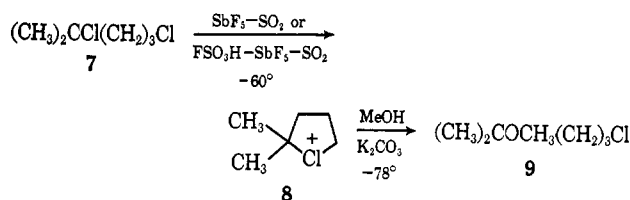
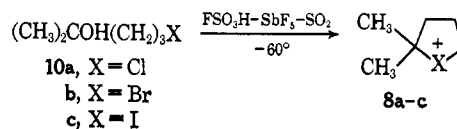


Figure 2. PMR spectrum of the 2,2-dimethyltetramethylene bromonium ion.

is a clear indication that the species present in these media is the chloronium ion **8a** for the following reasons: (1) if the ion were an open-chain tertiary ion, the methyl resonances would appear as a triplet by virtue of a long-range coupling to the methylene group through the  $\text{sp}^2$  carbon atom<sup>5</sup> and, (2) the chemical shift of the methyl groups is that expected for a chloronium ion<sup>4</sup> and different from that expected for a tertiary cation. Solvolysis of the ion in methanol at  $-78^\circ$  yielded the methyl ether **9**. Ion **8** was also readily



produced in fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solution at  $-60^\circ$  from 2-methyl-5-chloro-2-pentanol (**10**). Similarly, 2,2-dimethyltetramethylene halonium ions were obtained when the halogen atom was bromine (Figure 2) or iodine. We



initially attempted to obtain the related fluoronium ion by ionization of **11** and **12**. However, in both cases the attempts were unsuccessful and only the cyclic chloronium ion **8** or open-chain protonated hydroxycarbonium ion **13** derived from ring opening of 2,2-dimethyltetrahydrofuran (*vide infra*) was obtained. Although it is apparent from our previous work that fluoride is a better leaving group than chloride, it seems unlikely that a primary fluoride should ionize faster than a tertiary chloride atom or a tertiary hydroxyl group. We therefore suggest the following mechanism for the formation of **8** from **11** (a similar mechanism

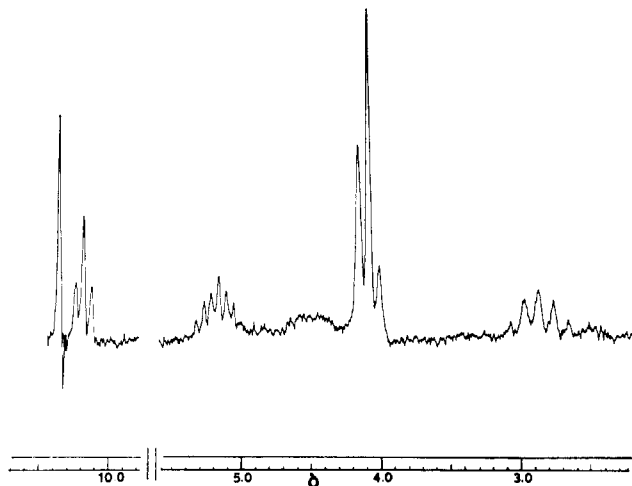
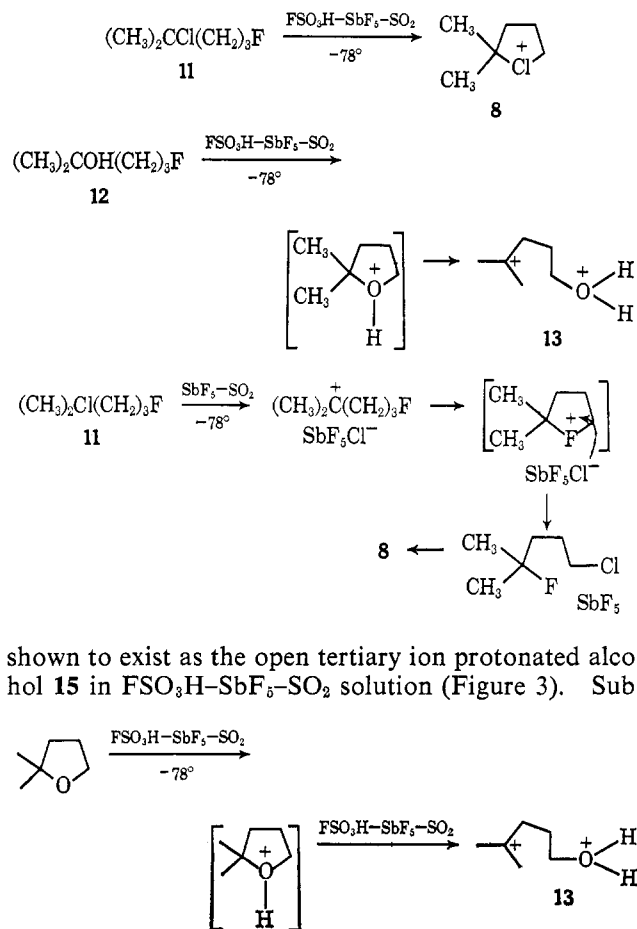


Figure 3. PMR spectrum of dimethyl- $\gamma$ -hydroxoniumpropyl cation,  $(\text{CH}_3)_2\text{C}^+(\text{CH}_2)_3\text{OH}_2^+$ .

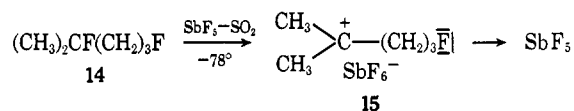
can be written for the formation of **13**).<sup>6</sup> A similar transformation producing **8b** from 4-bromo-1-fluoro-4-methylpentane occurred. 2,2-Dimethylfuran was



shown to exist as the open tertiary ion protonated alcohol **15** in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$  solution (Figure 3). Sub-

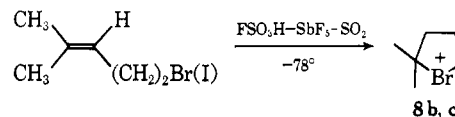
sequently we were able to prepare what is probably the fluorine-containing ion **15** by ionization of the difluoride **14**. The triplet observed for the methyl groups, as well as their chemical shift, indicates that the ion is an open-chain tertiary ion and not a fluoronium ion. The

(6) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).



lack of fluorine coupling indicates that the halogen is tightly complexed to and exchanging with antimony pentafluoride.<sup>7</sup> We were unable to locate the fluorine resonance of this ion (it must be averaged with antimony pentafluoride) and quenching the ion gave 2,5-dimethoxy-2-methylpentane.

Ions **8b** and **8c** were also prepared cleanly by protonation of the corresponding olefins. (We did not prepare pure samples of **10c** or the corresponding iodine-containing olefins (see Experimental Section).) PMR



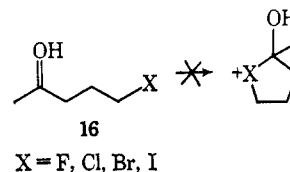
data of the observed 2,2-dimethyltetramethylene halonium ions are summarized in Table I.

Table I. PMR Chemical Shifts<sup>a</sup> of 2,2-Dimethyltetramethylene Halonium Ions

Halogen	Methyl	3-Methylene	4-Methylene	Halo-methylene
F	3.93 <sup>b</sup>	4.4 <sup>c</sup>	2.8 <sup>c</sup>	5.83 <sup>c</sup>
Cl	2.76 <sup>d</sup>	3.1 <sup>c</sup>	3.2 <sup>c</sup>	4.96 <sup>e</sup>
Br	2.53 <sup>d</sup>	2.9 <sup>c</sup>	3.2 <sup>c</sup>	5.17 <sup>e</sup>
I	2.42 <sup>d</sup>	2.7 <sup>c</sup>	3.2 <sup>c</sup>	5.13 <sup>e</sup>
O	4.11 <sup>e,f</sup>	4.6 <sup>c</sup>	2.9 <sup>c</sup>	5.16 <sup>e</sup>

<sup>a</sup> In fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solution at  $-60^\circ$ ,  $\delta$  (parts per million) from external TMS. <sup>b</sup> An open-chain ion (see text) in antimony pentafluoride-sulfur dioxide at  $-60^\circ$ ; triplet,  $J = 4.3$  Hz. <sup>c</sup> Multiplet. <sup>d</sup> Singlet. <sup>e</sup> An open-chain ion (see text); triplet,  $J = 4.2$  Hz. <sup>f</sup> Hydroxyl group appears as a two-proton triplet at  $\delta$  10.18.

As protonated ketones are expected to show contributions from the hydroxycarbonium ion forms, we extended our investigation to protonated methyl  $\gamma$ -halopropyl ketones **16** looking for evidence of halogen-carbonyl interaction.



It has been shown that the chemical shift of the proton on oxygen is a moderately sensitive probe for charge delocalization.<sup>8</sup> Thus if significant halogen participation occurred, the proton on oxygen would be expected to be more shielded as the carbonyl carbon becomes more nearly  $\text{sp}^3$  hybridized. However, no obvious trend was found between the protons on the carbonyl oxygen and  $\gamma$ -halogen substituents. We conclude that there is probably no significant interaction of the halogens with the carbonyl group (data are summarized in Table II). As Peterson<sup>9</sup> obtained chemical evidence in

(7) G. A. Olah and M. B. Comisarow (unpublished results) have observed similar behavior for methyl fluoride in this solvent.

(8) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967).

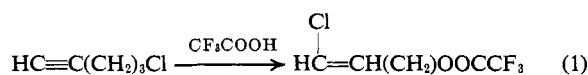
(9) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

**Table II.** Pmr Data<sup>a,b</sup> of Protonated Methyl  $\gamma$ -Halopropyl Ketones in Fluorosulfuric Acid-Antimony Pentafluoride-Sulfur Dioxide at  $-60^\circ$

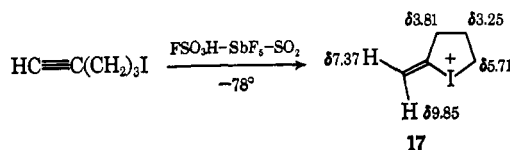
$\begin{array}{c} \text{H} \\   \\ \text{O}^+ \\    \\ \text{CH}_3\text{C}(\text{CH}_2)_3\text{X} \end{array}$					
X	CH <sub>3</sub>	C-CH <sub>2</sub>	-CH <sub>2</sub> -	-CH <sub>2</sub> X	C=OH <sup>c</sup> (%)
F	3.11	3.77	2.41	5.79	14.48 (23) 15.01 (77)
Cl	3.08	3.62	2.25	3.62	14.01 (11) 14.29 (89)
Br	3.06	3.67	2.37	3.67	14.02 (8) 14.59 (92)
I	3.07	3.65	2.59	4.33	14.59 (67) 14.77 (33)

<sup>a</sup>  $\delta$  (parts per million) from external TMS. <sup>b</sup> Center of multiplet; all absorptions have unresolved fine structure. <sup>c</sup> These exist in *syn* and *anti* forms to the extent listed. We assign the low-field resonance as *syn* to the methyl group.

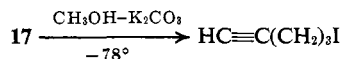
the trifluoroacetylation of 5-halo-1-pentynes for halogen participation (eq 1), we extended our studies to protonation of 5-halo-1-pentynes in order to see whether the corresponding halonium ions could be observed as a stable species in strong acid solutions. However, even the most careful addition of 5-chloro- or 5-fluoro-1-pentyne to FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub> gave uninterpretable nmr spectra. Obviously the reactions were extremely com-



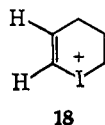
plex. 5-Iodo-1-pentyne, on the other hand, gave a clean nmr spectrum indicating the formation of ion **17** (Figure 4). We expected **17** to solvolyze to an olefinic



product characteristic of the ion. Surprisingly, solvolysis of **17** in methanol-potassium carbonate suspension at  $-78^\circ$  has a high yield of the starting acetylene, 5-iodo-1-pentyne. Although we have no definite



chemical proof for the structure of **17**, we believe the immeasurably small coupling of the olefinic protons rules out a six-membered ring halonium ion as represented by **18**. One would expect a nearly normal *cis*-



olefinic coupling in **18**. Moreover, the spectra of the ions obtained from 2,3-dibromo- and 2,3-dichloropropenes in antimony pentafluoride-sulfur dioxide solution are remarkably similar in chemical shift and multiplicity to the spectrum of **17**.<sup>10</sup> These ions should

(10) G. A. Olah and J. M. Bollinger, unpublished results.

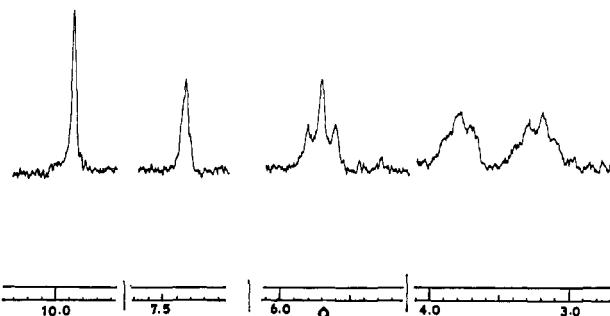


Figure 4. Pmr spectrum of protonated 5-iodo-1-pentyne.

not be expected to have any possibility for forming a system with vicinal protons.

## Experimental Section

**Materials.** 5-Chloro-2-pentanone and 2-acetyl- $\gamma$ -butyrolactone were purchased from Aldrich Chemical Co. The latter compound was used to prepare 5-bromo-<sup>11</sup> and 5-iodo-2-pentanone<sup>12</sup> by literature procedures.<sup>13</sup>

**5-Chloro-1-pentyne** was purchased from Farchan Chemicals. 5-Fluoro-1-pentyne and 5-fluoro-2-pentanone were prepared by the method of Peterson, *et al.*<sup>14</sup> 2,2-Dimethyltetrahydrofuran was prepared from  $\gamma$ -butyrolactone by the method of Henry.<sup>15</sup> 1-Chloro-4-hydroxy-4-methylpentane was prepared by the method of Suga, *et al.*,<sup>16</sup> and converted to 1,4-dichloro-4-methylpentane according to the procedure of Henry.<sup>15</sup> 5-Bromo-2-methyl-2-pentene was prepared by the method of Julia.<sup>17</sup>

**5-Iodo-1-pentyne.**<sup>18</sup> 5-Chloro-1-pentyne (100 g, 0.97 mol) in 500 ml of dry acetone was treated with 225 g (1.5 mol) of anhydrous sodium iodide at reflux for 5 hr. The reaction mixture was allowed to cool and poured into 1 l. of cold water. The organic material was taken up in 250 ml of pentane, washed five times with 100-ml portions of water, dried over sodium sulfate, and distilled. There was obtained 48.8 g of 5-iodo-1-pentyne, bp 80–85° (40 mm), and 55.0 g of 5-chloro-1-pentyne was recovered.

**1-Bromo-4-hydroxy-4-methylpentane.** To 8.3 g (0.05 mol) of 5-bromo-2-pentanone in 50 ml of dry ether was added 30 ml of 1.67 *M* methyllithium in ether (Foote Chemical Co.) maintaining the temperature near  $-40^\circ$ . After all the methyllithium was added the reaction mixture was hydrolyzed, initially at  $-40^\circ$  but with warming to  $0^\circ$ , with saturated aqueous ammonium chloride. Distillation gave 7.2 g, 75% material, bp 75–79° (9 mm), which was the desired alcohol. This alcohol (6 g) was shaken with 50 ml of ice-cold concentrated aqueous hydrochloric acid. The resulting organic material was taken up in 50 ml of pentane, washed with dilute sodium bicarbonate solution, dried, and distilled. There was obtained 5.3 g (80%) of 1-bromo-4-chloro-4-methylpentane, bp 64–67° (8 mm).<sup>19</sup>

**4-Hydroxy-1-iodo-4-methylpentane.** An identical procedure as described for chloro compounds was used. From 10.6 g (0.05 mol) of 5-iodo-2-pentanone there was obtained 9.0 g of an oil, bp 60–75° (7 mm), which rapidly darkened even at  $0^\circ$ . An nmr spectrum of this material showed that it was a mixture of the desired alcohol, 5-iodo-2-methyl-2-pentene<sup>17</sup> and 5-iodo-2-methyl-1-pentene.

(11) A. Verley, *Bull. Soc. Chim. Fr.*, 3717, 192 (1867).

(12) A. Lipp, *Ber.*, 22, 1206 (1889).

(13) W. R. Boon, U. S. Patent 2,370,392 (1945) and British Patent 558,286 (1943); *Chem. Abstr.*, 39, 40903 (1945).

(14) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, 89, 5902 (1967).

(15) L. Henry, *C. R. Acad. Sci. Paris*, 143, 1224 (1906).

(16) K. Suga, S. Watanabe, and J. Okohi, *Bull. Chem. Soc. Jap.*, 39, 1335 (1966).

(17) M. Julia, S. Julia, and R. Guegan, *Bull. Soc. Chim. Fr.*, 1, 1072 (1966).

(18) E. G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

(19) L. U. Bugrova and I. P. Tsukervanik, *Zh. Org. Khim.*, 1, 714 (1965), report bp 90–92° (30 mm) for the isomeric compound 4-bromo-1-chloro-4-methylpentane.

**5-Fluoro-2-hydroxy-2-methylpentane.**<sup>20</sup> An identical procedure as described for the chloro compound was used. From 10.4 g (0.1 mol) of 5-fluoro-2-pentanone<sup>21</sup> there was obtained 6.8 g (57%) of the desired compound, bp 62–64° (60 mm); fluorine spectrum:  $\phi + 216.6$  (m). Three grams (0.025 mol) of alcohol was shaken with 25 ml of ice-cold aqueous concentrated hydrochloric acid for 15 min. The organic material was taken up in pentane, washed with dilute sodium bicarbonate solution, dried, and distilled. There was obtained 2.6 g (74%) of the desired compound, bp 58–61° (45 mm); fluorine spectrum:  $\phi + 218.8$  (m).

**2,4-Difluoro-2-methylpentane.** 5-Fluoro-2-hydroxy-2-methylpentane (6 g, 0.05 mol) was shaken with 50 ml of ice-cold concentrated aqueous hydrobromic acid for 15 min. The organic material was taken up in pentane, washed with cold dilute sodium bicarbonate, dried, and distilled. There was obtained 8.1 g (87%) of an oil, bp 49–52° (28 mm), whose nmr spectrum was consistent with that expected for 5-bromo-2-fluoro-2-methylpentane; fluorine spectrum:  $\phi + 218.9$  (m). This material (0.044 mol) was treated with

25.4 g (0.2 mol) of argentous fluoride (Harshaw) in 50 ml of dry acetonitrile at room temperature for 2 hr. The reaction mixture was filtered and poured into 150 ml of cold water and extracted with 50 ml of pentane. The pentane extract was washed twice with 25-ml portions of water, dried, and distilled through a 6-in. micro-column packed with glass helices. There was obtained 3.4 g of material, bp 30–32° (20 mm); fluorine spectrum:  $\phi + 218.7$  (m) and  $+138.9$  (m).

**Preparation of Ions and Nmr Studies.** Solutions of ions in antimony pentafluoride-sulfur dioxide solution were prepared as described previously.<sup>2,3</sup> Solutions of ions in fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solution were prepared by adding ca. 0.15 g of precursor dropwise with vigorous stirring to 1 ml of 1:1 *M* antimony pentafluoride in fluorosulfuric acid diluted with 1 ml of sulfur dioxide at  $-78^\circ$ .

Nmr spectra were obtained on a Varian A-56-60A nmr spectrometer with variable-temperature probe. Chemical shifts are referred to external TMS. Methanolysis was performed as described previously.<sup>2,3</sup>

**Acknowledgment.** Support of the work by grants of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

(20) Fluorine spectra (56.4 MHz) were recorded at room temperature in  $\text{CCl}_4$  with  $\text{CFCl}_3$  as internal standard. Abbreviations used: t, triplet; m, multiplet.

(21) Fluorine spectrum:  $\phi + 219.7$  (t)  $J_{\text{H-F}} = 47.6$  Hz; (t)  $J_{\text{H-F}} = 25.4$  Hz.

## Mass Spectrometry in Structural and Stereochemical Problems. CLXV.<sup>1</sup> A Study of Skeletal Rearrangements in $^{13}\text{C}$ -Labeled Aromatic Amines<sup>2</sup>

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**Abstract:** The mass spectra of  $1\text{-}^{13}\text{C}$ -aniline,  $1\text{-}^{13}\text{C}$ -acetanilide,  $1\text{-}^{13}\text{C}$ -sulfanilamide, and  $1\text{-}^{13}\text{C}$ -*p*-nitroaniline were examined. The fragmentations  $\text{C}_6\text{H}_7\text{N}^+ \rightarrow \text{C}_5\text{H}_6^+ + \text{HCN}$  and  $\text{C}_6\text{H}_8\text{N}^+ \rightarrow \text{C}_5\text{H}_7^+ + \text{HCN}$  were studied to determine the extent of any skeletal rearrangement of the  $\text{C}_6\text{H}_7\text{N}$  and  $\text{C}_6\text{H}_8\text{N}$  species. Careful intensity measurements under high resolution were required to separate various isobaric components of the same nominal mass. Analysis of the results reveals that for the reactions involving loss of HCN, the odd-electron species  $\text{C}_6\text{H}_7\text{N}^+$  is rearranged only to a small extent, whereas the even-electron species  $\text{C}_6\text{H}_8\text{N}^+$  is rearranged to a considerable extent. The rearrangement is discussed in terms of ring-expanded azepinium ions. For *p*-nitroaniline, the fragment  $\text{C}_5\text{H}_6\text{N}^+$  formed by successive loss of  $\text{NO}^\cdot$  and CO from the molecular ion contains only five-sixths of the label, suggesting that the structure of the ion  $\text{C}_6\text{H}_6\text{NO}^+$  from which the CO is expelled has the label uniformly randomized.

We describe here further experiments to provide more definitive information on the structure of some fragment ions in the mass spectrometer. They are based on the potential analogy between the fragmentation of toluene and the aromatic amines. The extensive labeling experiments of Meyerson and coworkers on toluene are most readily explained by a tropylium structure for the  $\text{M}-1$  ion.<sup>3</sup> Rinehart's group recently established with doubly  $^{13}\text{C}$ -labeled toluene that the methyl carbon is inserted randomly between the ring carbons.<sup>4</sup> Similar ring expansions have been

postulated, but rarely proven, in many other systems. The fragmentation of several  $^{13}\text{C}$ -labeled nitrogen heterocycles demands skeletal rearrangement, and ring expansion provides the most obvious rationalization.<sup>5</sup> We recently reported, in a preliminary communication, semiquantitative results of experiments to test the possibility of rearrangement, presumably to azepinium structures, of ions in the mass spectra of  $1\text{-}^{13}\text{C}$ -labeled aniline, acetanilide, and sulfanilamide.<sup>6</sup> Independently, Rinehart and coworkers have also published similar, more accurate results on the mass spectral fragmentation of aniline- $1\text{-}^{13}\text{C}$ .<sup>7</sup> Full details of our work, which now include a study of  $1\text{-}^{13}\text{C}$ -*p*-nitroaniline, are presented below. Our present results are more accurate for experimental reasons than those of the preliminary

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(3) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

(4) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Am. Chem. Soc.*, **90**, 2938 (1968).

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(7) K. L. Rinehart, Jr., A. C. Buchholz, and G. E. Van Lear, *J. Am. Chem. Soc.*, **90**, 1073 (1968).