The Mass Spectra of Organic Molecules. The Rearrangement of Acetylenic Ethers under Electron Impact

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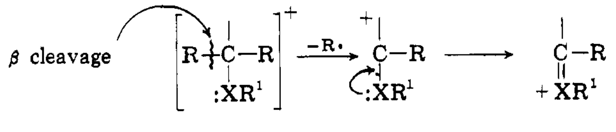
The mass spectra of a series of α-*t*-acetylenic ethers, $R^1R^2C(OR^3)C{\equiv}CH$, and several of the corresponding keto ethers, $R^1R^2C(OR^3)COCH_3$, formed by catalytic hydration of the triple bond were determined. The major fragmentation process resulting from ionization of the acetylenic ethers is a two-step rearrangement involving cleavage of the carbon–carbon bond α to the ether oxygen (cleavage of R^1 or R^2) followed by loss of R^3 as an olefin with rearrangement of a hydrogen atom. When the group R^3 is methyl, this process does not take place. Primary fragmentation in the keto ether series results in cleavage of the acyl–carbon bond followed by the loss of R^3 as an olefin molecule (when $R^3 \neq CH_3$) with rearrangement of a hydrogen atom.

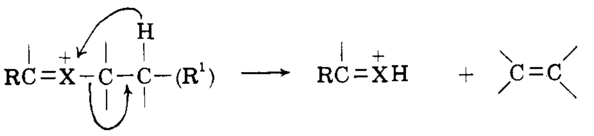
The vast majority of previous mass spectral studies have correlated the spectra of a group of compounds containing one particular functional group. However, in the study of more complex molecules containing two or more functional groups one must consider the mutual interactions of such groups for the correct interpretation of their mass spectra.[1]

Previous correlations of the mass spectra of saturated aliphatic alcohols,[2] amines,[3,4] ethers,[5] mercaptans,[6] and sulfides[6] have strong similarities, and are characterized by intense peaks associated with the cleavage of the carbon–carbon bond β to the hetero atom.[1] McLafferty attributes these spectral similarities to the electron-donating powers of this group.[7]



X = O, N, S; R¹ = H, alkyl

The ions formed by this fragmentation undergo elimination of an olefin molecule when the group R¹ contains at least two carbon atoms and has at least one hydrogen in the β-position.[2] They are frequently among the most abundant in the mass spectra of aliphatic ethers.[5] The driving force of this rearrangement is the formation of a stable trivalent oxonium ion and a neutral olefin molecule.[7–11] Such β-cleavages similarly give prominent ions in the spectra of amines,[3,4] mercaptans,[6] and sulfides.[6]

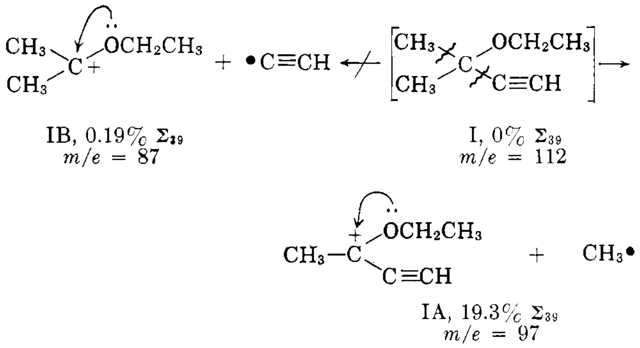


The present study of the spectra of acetylenic and keto ethers was undertaken to examine the effect of the introduction of a second functional group into the aliphatic ether system and its influence on the mass spectra of these molecules.[12]

Results

The spectra of ten substituted α-acetylenic ethers and two β-keto ethers were obtained on a CEC 21-103 mass spectrometer. All characteristic ions are tabulated in Tables I and II. The intensities of these ions are expressed in per cent of Σ_{39} (sum of the relative intensities of all peaks from mass 39 to the molecular weight).[1]

Acetylenic Ethers.—Table III indicates important cleavages and rearrangements in this series. The primary fragmentation mechanism associated with the decomposition of the acetylenic ether molecular ion results from cleavage of a substituent β to the ether oxygen.[5]



IB, 0.19% Σ_{39} *m/e* = 87

I, 0% Σ_{39} *m/e* = 112

IA, 19.3% Σ_{39} *m/e* = 97

The resultant carbonium ion (IB) is stabilized by participation of the free electron pair on oxygen,[10] by resonance interaction of the acetylenic triple bond as well as by the inductive effect of the methyl group. In the case of 3-ethoxy-3-methyl-1-butyne, this ion represents 19.3% Σ_{39}. In the nomenclature of Biemann[1] a mechanism of this type is a combination of B-type cleavage (cleavage β to a hetero atom) and type A_3 (cleavage β to a triple bond).

When R¹ and R² are different such as in the case of 3-ethoxy-3,5-dimethyl-1-hexyne (VI) there is a competition between cleavage of the isobutyl group and the methyl group. In agreement with a considerable

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[1] For a recent review of the applications of mass spectrometry to organic chemistry, see Klaus Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[2] R. A. Friedel and A. G. Sharkey, Jr., *Anal. Chem.*, **28**, 940 (1956).

[3] J. Collin, *Bull. soc. chim. Belges*, **63**, 500 (1954).

[4] J. Collin, *Bull. Soc. Roy. Sci. Leige*, **21**, 446 (1952); **23**, 377 (1954).

[5] F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

[6] E. J. Levy and W. H. Stahl, *ibid.*, **33**, 707 (1961).

[7] F. W. McLafferty, *ibid.*, **28**, 306 (1956).

[8] F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 93.

[9] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

[10] C. S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1940).

[11] L. Friedman and F. A. Long, *J. Am. Chem. Soc.*, **75**, 2832 (1953).

[12] For a study of the mass spectra of vinyl and allylic ethers, see S. Meyerson and J. D. McCollum in "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilley, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 199-215.

TABLE I

MASS SPECTRA OF ACETYLENIC ETHERS

	Compd. mol. wt.									
	I	II	III	IV	V	VI	VII	VIII	IX	X
m/e	112	126	126	112	140	154	154	168	126	140
39	6.55	6.72	6.81	5.75	5.07	5.03	5.45	4.58	6.81	6.08
41	6.49	8.70	8.17	3.82	5.66	5.39	5.13	5.73	5.17	2.55
43	8.43	8.34	9.35	8.17	9.30	11.5	7.48	10.6	4.00	4.90
51	3.09	2.58	2.62	3.54	2.14	1.70	2.01	1.54	2.02	1.70
52	1.17	1.51	0.99	1.79	1.87	0.61	1.15	0.81	1.09	0.65
53	2.54	1.62	1.77	6.03	4.14	2.41	2.84	2.38	5.26	4.60
55	0.43	0.43	0.35	1.09	1.56	1.55	1.52	1.94	2.42	6.16
57	0.08	1.03	0.09	0.30	0.61	1.12	1.14	1.50	1.65	2.04
59	0.75	0.81	1.38	1.48	0.13	0.39	0.28	0.48	0.57	0.06
63	0.59	0.47	0.51	0.85	0.46	0.39	0.50	0.38	1.14	0.92
65	1.81	1.73	1.80	1.74	0.96	0.95	1.15	0.93	2.94	1.76
67	11.1	17.9	20.6	0.78	0.78	1.48	1.03	1.07	2.64	1.98
69	23.6	21.5	23.0	0.79	29.1	21.3	1.75	15.4	0.80	0.63
77	...	0.08	...	1.24	0.81	1.28	1.33	1.08	1.29	1.03
79	...	0.11	...	2.74	2.18	0.43	2.23	1.94	1.12	1.09
81	0.05	0.60	0.07	3.34	5.98	0.52	1.14	1.43	0.70	0.79
83	0.41	0.37	0.30	36.6	5.53	0.56	38.2	0.38	1.77	23.5
91	...	...	...	...	...	0.83	1.62	1.27	0.33	0.29
95	...	0.12	0.06	0.08	...	0.34	0.54	0.58	1.61	1.78
97	19.3	0.40	0.08	5.57	0.15	18.5	0.20	21.0	37.1	0.64
111	0.02	11.3	8.37	0.08	10.7	1.75	0.28	0.09	0.27	21.7
112	...	0.91	0.68	0.03	0.86	0.49	0.05	0.60	...	1.73
125	...	0.04	0.02	...	1.06	0.12	0.94	0.32	0.05	0.08
126	...	...	...	...	0.12	...	...	0.05	0.02	...
139					0.01	1.71	1.59	0.06		...
140					...	0.22	0.18	...		...
153						0.02	0.02	1.29		
154						...	0.01	0.16		
168								...		
Σ	86.4	87.3	87.0	85.8	89.2	80.6	79.8	77.9	81.0	86.7

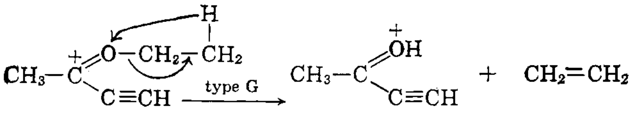
TABLE II

MASS SPECTRA OF β-KETO ETHERS

	Compd. mol. wt.	
	XI	XII
m/e	116	130
39	5.08	2.51
41	6.64	4.64
42	3.44	1.94
43	24.7	14.5
45	3.48	0.92
55	1.31	0.28
57	2.82	1.88
59	0.66	50.0
73	40.8	0.12
85	0.51	0.72
87	0.08	14.1
101	0.61	0.08
115	...	0.13
116	0.05	...
130		...
Σ	90.18	91.82

body of literature, cleavage of the isobutyl group results in the more intense ion, 18.5% Σ_{39} *vs.* 1.71% Σ_{39} for methyl cleavage.

Fragmentation of the β-substituent (A_3B cleavage) is followed by an extremely favorable rearrangement[5,12] wherein the alkoxy substituent (R_3) is lost as a neutral olefin molecule and a hydrogen atom is transferred to the hetero atom (type G). This process is illustrated below by the rearrangement of the oxonium ion IA formed by cleavage of a methyl group from the molecular ion of 3-ethoxy-3-methyl-1-butyne (I). Elimination of a molecule of ethylene yields a resonance stabilized fragment (IC) which accounts for almost 25% Σ_{39}. Evidence for the loss of ethylene in a single-step rearrangement is a metastable peak corresponding to this transition at *m/e* = 49.4. Such peaks usually appear at nonintegral masses in the mass spectrum of a molecule and often pinpoint consecutive steps in a multistep process.

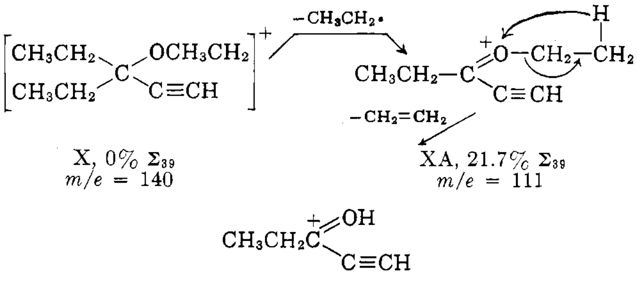


IA
m/e = 97

IC, 24.1% Σ_{39}
m/e = 69

$$(49.4)\ 97^+ \longrightarrow 69^+ + 28$$

When this rearrangement is not structurally possible[5] due to the lack of a β-substituent (when R^3 = methyl), the intensity of the ion resulting from alkyl cleavage is approximately double that in molecules where subsequent rearrangement takes place. An interesting



X, 0% Σ_{39}
m/e = 140

XA, 21.7% Σ_{39}
m/e = 111

XB, 23.5% Σ_{39}
m/e = 83

$$(62.3)\ 111^+ \longrightarrow 83^+ + 28$$

TABLE III

IMPORTANT FRAGMENTATION PROCESSES OF ACETYLENIC ETHERS

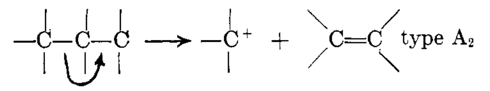
$R^1R^2C(OR^3)C{\equiv}CH$

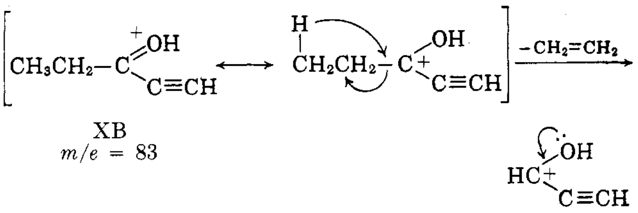
Compd.	R^1	R^2	R^3	M^{+a}	A_3B cleavages[b] R^1	A_3B cleavages[b] R^2	Type-G rearrangement	Cleavage A_2	Cleavage A_6[c]
I	Me	Me	Et	0	19.3	...	23.6	...	11.1
II	Me	Me	*n*-Pr	0	11.3	...	21.5	...	17.9
III	Me	Me	*i*-Pr	0	8.37	...	23.0	...	20.6
IV	Me	Et	Me	0.03	5.57	36.6	...	0.69	3.34
V	Me	Et	*i*-Pr	0	1.06	10.7	34.6	1.09	5.98
VI	Me	*i*-Bu	Et	0	1.71	18.5	26.9	1.55	0.47
VII	Me	*i*-AM	Me	0.01	1.59	38.2	...	1.75	0.38
VIII	Me	*i*-AM	Et	0	1.29	21.0	15.7	1.94	0.37
IX	Et	Et	Me	0.02	37.1	...	...	0.80	1.61
X	Et	Et	Et	0	21.7	...	23.5	6.16	1.78

[a] Tabulated as per cent Σ_{39}. [b] R^1 represents the per cent Σ_{39} for A_3B cleavage when R^1 is the smaller of the two R groups or the total when $R^1 = R^2$. [c] This total includes a negligible contribution from ions formed by the loss of hydrogen (H_2) from ions formed by A_3B cleavage.

comparison is 3-ethoxy- and 3-methoxy-3-ethyl-1-pentyne. The molecular ion of 3-ethoxy-3-ethyl-1-pentyne (X) fragments primarily by loss of an ethyl radical to yield the stable oxonium ion (XA) which accounts for 21.7% Σ_{39}. Subsequent rearrangement with the loss of ethylene yields a stable ion (XB) accounting for an additional 23.5% Σ_{39}. A metastable peak at m/e = 62.3 confirms this final step.

In addition, ion XB can undergo further rearrangement of the A_2 type.[1] Loss of an additional ethylene molecule from the oxonium ion XB yields the stable ion XC at m/e = 55 (6.17% Σ_{39}). The pertinent metastable peak for this transition appears at m/e = 36.6 and documents the final step in this major reaction sequence which accounts for at least 51.4% Σ_{39}.





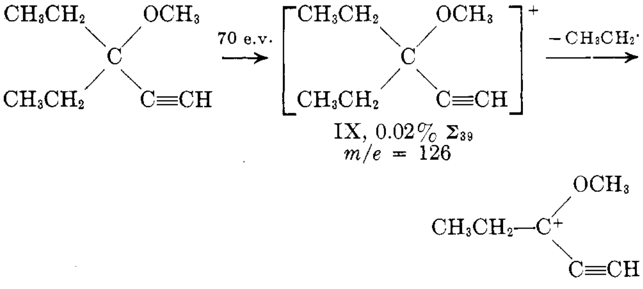
XB
m/e = 83

XC, 6.16% Σ_{39}
m/e = 55

(36.6) $83^+ \longrightarrow 55^+ + 28$

In contrast to this energetically favorable sequence illustrated above for I, VI, and X, an analogous series of fragmentations cannot take place when the alkoxy substituent (R^3, Table I) is methyl. The elimination of this pathway is reflected by the increased intensities of the molecular ion (M^+) and the $M-R$ fragment formed by alkyl cleavage.

Several of the methyl ethers examined reveal recognizable molecular ions. For example, it is found that 3-methoxy-3-ethyl-1-pentyne has a molecular ion representing 0.02% Σ_{39}. Loss of an ethyl radical from this ion yields a stable oxonium ion 70% more intense than the corresponding ion, XA, in the ethyl-type ether. This is a reflection of the loss of the more energetically favorable rearrangement pathway involving the loss of an olefin molecule. Thus, the oxonium ion IXA must seek other *less favorable* transitions for its decomposition.

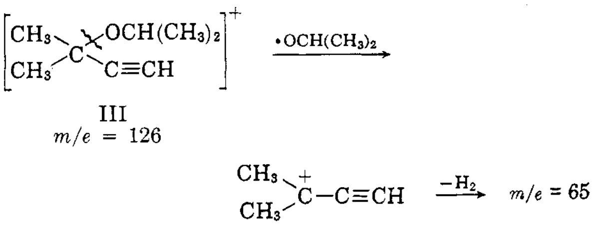


IX, 0.02% Σ_{39}
m/e = 126

IXA, 37.1% Σ_{39}
m/e = 97

The most prominent of these energetically less favorable fragmentations is cleavage of the alkoxide group ($RO{-}R^1 \rightarrow R^+ + \cdot OR^1$) yielding a tertiary carbonium ion which is reasonance stabilized by participation of the ethynyl group. Fragments of this type resulting from alkoxy cleavage have previously been found to be important in the spectra of aliphatic ethers.[5]

In the series of acetylenic ethers examined, ions formed by α-cleavage of the alkoxy group are most intense when the substituents R^1 and R^2 are methyl. The intensity of these ions decreased with increased alkyl substitution. This is a result, in part, of the fact that larger molecules contain more bonds susceptible to cleavage, and there is an increased competition between primary and secondary fragmentation processes. Thus, while the intensity of this ion in III is 20.6% Σ_{39} for the higher alkyl-substituted acetylenic ethers VI, VII, and VIII, the intensities of this type ion are only 0.47, 0.38 and 0.36% Σ_{39}.



III
m/e = 126

IIIC, 20.6% Σ_{39}
m/e = 67

IIID, 1.80% Σ_{39}
m/e = 65

(63.4) $67^+ \longrightarrow 65^+ + H_2$

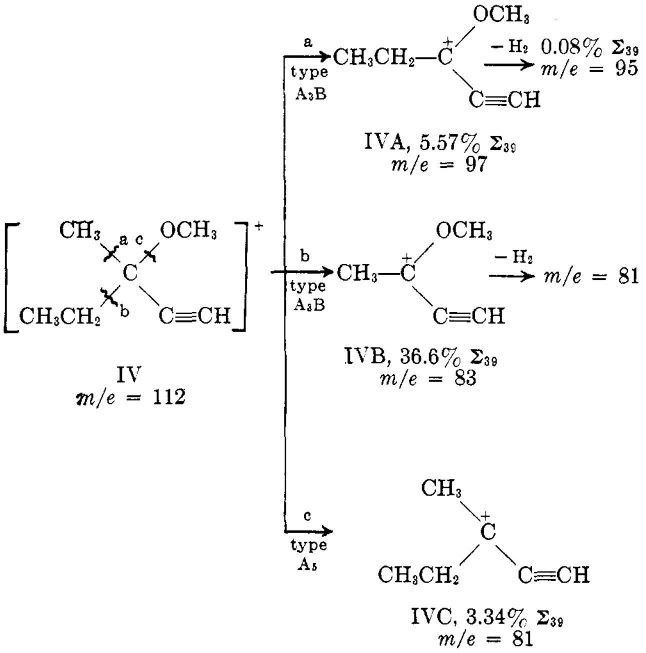
It should be pointed out, however, that ions of the same mass may also arise in part *via* another path.

TABLE IV
IMPORTANT FRAGMENTATION PROCESSES OF KETO ETHERS
$R^1R^2C(OR^3)COCH_3$

Compd.	R^1	R^2	R^3	M^{+a}	A_3B cleavage	Type BC $R^1R^2C(OR^3)^+$	Type BC $\overset{+}{C}OCH_3$	Type G
XI	Me	Me	Me	0.05	0.61	40.8	24.7	. . .
XII	Me	Me	Et	0	0.13	14.1	14.5	50.0

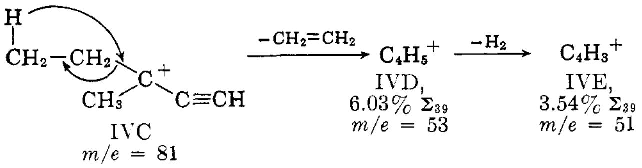
[a] Tabulated as per cent Σ_{39}.

In addition to the α-cleavage of the alkoxy group (A_5), an ion of the same mass may result in several cases from the loss of a hydrogen molecule from the oxonium ion formed by type-B cleavage. Nevertheless, it can be shown that the major mechanism for formation of this peak is alkoxy cleavage. This point may be illustrated by analyzing the spectrum of 3-methoxy-3-methyl-1-pentyne. Cleavage of the molecular ion IV can lead to two different oxonium ions *via* cleavage of either a methyl group (path a) or an ethyl group (path b), while alkoxy cleavage yields the tertiary ion IVC (path c), whereas loss of a hydrogen molecule from IVA would yield an ion two units less at m/e = 95, this ion's intensity is only 0.08% Σ_{39}. This demonstrates that the major path to the m/e = 81 ion is through type-A_5 cleavage rather than loss of a hydrogen molecule from the IVB ion.

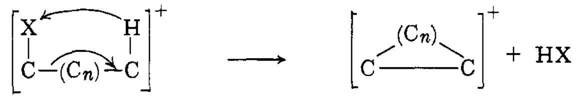


It is interesting that the ion produced by A_5 cleavage further rearranges with the loss of a hydrogen molecule resulting in one of the more characteristic peaks in the spectra of the acetylenic ethers. This transition is pinpointed by pertinent metastable peaks in all of the spectra examined.

A further rearrangement of ions produced by type-A_5 cleavage is loss of an olefin molecule illustrated below for IVC. Transfer of a hydrogen with loss of an ethylene molecule results in an unsaturated ion IVD. Further loss of a hydrogen molecule yields IVE.



Loss of a molecule of water from the oxonium ions produced by type-G rearrangement is another characteristic fragmentation in this series. Intense peaks resulting in part from this type rearrangement are prominent in the spectra of each molecule undergoing this type rearrangement. Loss of water from IC results in an ion amounting to 3.1% Σ_{39}.

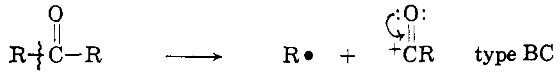


X = OH

In addition to the characteristic peaks discussed above, there are a number of intense noncharacteristic peaks resulting from a series of complex rearrangements in each spectrum. The intense peaks at m/e = 39, 40, 41, 42, and 43 are associated with acetylenic, highly unsaturated, or organic molecules in general.[13] It is interesting that except for compound X each acetylenic ether shows a noticeable M − 1 peak which in all probability arises from the loss of an α-hydrogen from the alkoxy substituent. In addition to these ions, there are a large number of lesser intensity peaks associated with low-probability fragmentation processes. Since these processes are not characteristic of the acetylenic ether molecule, they have not been investigated in detail.

Keto Ethers.—Hydration of the triple bond of the acetylenic ethers using sulfuric acid and mercuric oxide produces keto ethers in good yield. This substitution of an acyl group for an ethynyl group produces a dramatic change in the main fragmentation process in the series.

The most important fragmentation of the molecular ion in the keto ether series is the cleavage of the acyl-carbon bond (see Table IV for a tabulation of the important cleavages and rearrangements in this series). Such a fragmentation mechanism frequently yields the most intense ions in the spectra of aliphatic ketones.[14]



Cleavage of this type is followed by a most favorable rearrangement involving the loss of a neutral olefin molecule. In the case of 3-ethoxy-3-methyl-2-butanone, fragmentation by this path accounts for at least 68.6% Σ_{39}.

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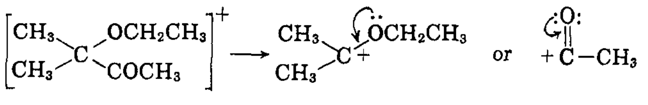
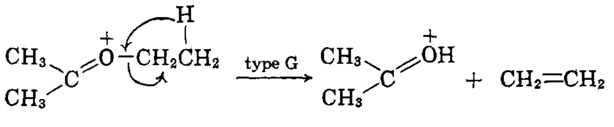
(13) F. W. McLafferty, "Mass Spectral Correlations," American Chemical Society, Washington, D. C., 1963.

(14) A. G. Sharkey, J. L. Schultz, and R. A. Friedel, *Anal. Chem.*, **28**, 934 (1956).



XII, 0% Σ_{39} $m/e = 130$ XIIA, 14.1% Σ_{39} $m/e = 87$ XIIB, 14.5% Σ_{39} $m/e = 43$



XIIA XIIC, 50.0% Σ_{39} $m/e = 59$

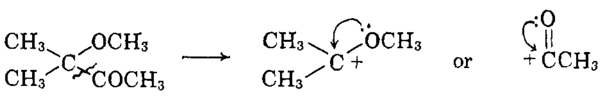
$$(40.3)\ 87^+ \longrightarrow 59^+ + 28$$

Cleavage of the acyl–carbon bond in the first step of the reaction sequence is in direct contrast to the primary cleavage of an alkyl group in the acetylenic ether series. This cleavage of the molecular ion produces a very stable ion and radical. In contrast fragmentation of the acetylenic ether molecular ion produces an alkyl radical of comparatively high energy. The facility of this rearrangement sequence is reflected in the fact that the ions produced in the decomposition of XII amount to almost 70% of Σ_{39}. It is interesting that in this series the cleavage of the acyl methyl is not an important process even though such a cleavage would be expected to result in the formation

$$R^1R^2C(OR^3)-CO\nmid CH_3 \qquad \not\longrightarrow$$

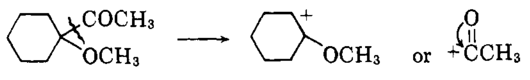
of a very stable acyl ion.[14] Once again the stabilities of the radicals and ions formed in the fragmentation are a deciding factor.

When type-G rearrangement is not structurally possible, such as in the fragmentation of 3-methoxy-3-methyl-2-butanone, the reaction sequence stops at the first step. The result is an increase in the intensity of the oxonium ion (XIA) produced by acyl–carbon cleavage by over 300% (in comparison to XIIA). As in the case of the methyl ethers in the acetylenic ether series, a molecular ion is observed, being 0.05% Σ_{39}.

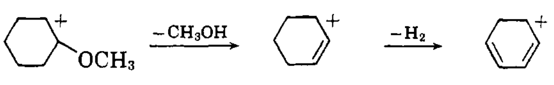


XI, 0.05% Σ_{39} $m/e = 116$ XIA, 40.8% Σ_{39} $m/e = 73$ XIB, 24.7% Σ_{39} $m/e = 43$

In contrast, 1-acetyl-1-methoxycyclohexane undergoes a two-step rearrangement not involving loss of an olefin molecule in the second step. Primary fragmentation involves the cleavage of the acyl–carbon bond followed in sequence by the loss of methanol (type-E rearrangement) and a hydrogen molecule from this ion.



XIII, 0% Σ_{39} $m/e = 156$ XIIIA, 25.4% Σ_{39} $m/e = 113$ XIIB, 9.72% Σ_{39} $m/e = 43$



XIIIA $m/e = 113$ XIIIC, 15.6% Σ_{39} $m/e = 81$ XIV, 1.41% Σ_{39} $m/e = 79$

$$(58.3)\ 113^+ \longrightarrow 81^+ + 32 \quad (77.4)\ 81^+ \longrightarrow 79^+ + 42$$

All other fragmentation processes in the keto ether series are minor in comparison with the reaction paths described above.

Experimental

All of the α-acetylenic ethers and keto ethers investigated in this work were generously donated by Professor G. F. Hennion of Notre Dame University. The assigned structures[15] have been corroborated by n.m.r. and infrared analysis.

Mass Spectra.—Spectra were obtained on a modified Consolidated 21-103c mass spectrometer operating under the following conditions: ionizing voltage, 70 v. (nominal); ion source temperature, 270°; ionizing current, 50 μa.; magnet current, 0.296 amp.; inlet system, room temperature.

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(15) G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, **26**, 2677 (1961).

Friedel–Crafts Acylation. Positional Selectivity and Reactivity of Acylating Agents

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The importance of the activity or selectivity of acylating agents in determining orientation has been demonstrated for the substrate 2,3-dimethoxytoluene. Under typical Friedel–Crafts conditions, the reaction is kinetically controlled with substitution at positions 5 and 6. When polyphosphoric acid was used as the solvent and catalyst, exclusive acetylation at position 6 was realized. It was shown, however, that acylation in polyphosphoric acid is thermodynamically controlled when steric factors become important.

In the compound, 2,3-dimethoxytoluene (I), there are two positions of high but unequal reactivity[2] and the results reported in this paper show that the or entation in acylation is determined by the activity or selectivity of the acylating agent. The concepts developed by Brown correlating *ortho*, *meta*, and *para* isomer distribution in aromatic substitutions with the activity of the electrophilic agent[3] can be used to explain the experimental data here reported.

Nitration[4] of I has been shown to give substitution at

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(2) Position 6 would be expected to be the most reactive site because of the combined effects of the *ortho* methyl and *para* methoxyl groups. The advantage of position 6 over 5 is further enhanced by steric inhibition to resonance of the 2-methoxyl group.

(3) (a) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 906; (b) J. E. Leffler and E. Grunwalk, "Rates and Equilibra of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 197.

(4) R. Majima and Y. Okazaki, *Ber.*, **49**, 1482 (1916).