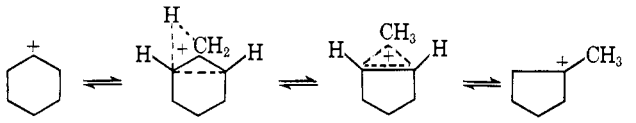
a protonated cyclopropane intermediate, merits consideration.



Experimental Section

All compounds with the exception of 1-chloromethylcyclopentane and 1-methylcyclopentyl methyl ether were commercially available. 1-Chloro-1-methylcyclopentane was prepared by the procedure of Merrwein and Mühlendyk.[14] 1-Methylcyclopentyl methyl ether was prepared according to the method of Lutz, *et al.*[12]

Nmr Spectra. The nmr spectra were obtained on a Varian Associates Model A56-60A spectrometer equipped with a variable-temperature probe. All spectra were run at −60°. The chemical shifts are recorded in parts per million relative to external TMS.

Preparation of Solutions of 1-Methylcyclopentyl Cation. a. From Halides. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Portions (2 ml) of this solution were cooled to −78°, causing some antimony pentafluoride to crystallize from solution. To this suspension was added with stirring approximately 0.2 g of the appropriate 1-methylcyclopentyl or cyclohexyl halide. Slight warming was required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were around 10%.

b. From Alcohols. The precursor alcohol (1-methyl-1-cyclopentanol or cyclohexanol) in SO_2 was cooled to −60° and added to a vigorously stirred 1:1 molar mixture of FSO_3H and SbF_5 at −60°. Generally an excess of SO_2 was used to prepare the solution which was then concentrated by pumping off SO_2 to give an approximately 8–10% concentration of the carbonium ion solution.

c. From Cycloalkanes. The cycloalkane (1-methylcyclopentane, cyclohexane) and a tenfold (weight) excess of acid (1:1 FSO_3–SbF_5) were vigorously stirred at room temperature until they formed a homogeneous colorless mixture.

d. From Cycloalkenes (1-Methylcyclopentene and Cyclohexene). A cold (−60°) solution of the cycloalkene in SO_2 was added slowly with stirring to a cold solution of HF–SbF_5 and FSO_3H–SbF_5 in SO_2. Excess SO_2 was pumped off in order to obtain a ~10% solution of the methylcyclopentyl cation.

Quenching the methylcyclopentyl cation in a suspension of methanol and potassium carbonate at −78° gave an 81% yield of 1-methylcyclopentene according to comparison with authentic samples.

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

(14) H. Meerwein and M. Mühlendyk, *Ann.*, 405, 171 (1964).

Stable Carbonium Ions. XXXVIII.[1] Alkenyloxocarbonium Ions

George A. Olah and Melvin B. Comisarow[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received December 21, 1966*

Abstract: An investigation of the alkenoyl fluoride–antimony pentafluoride complexes has been carried out. Acryloyl-, methacryloyl-, crotonoyl-, tigloyl-, β,β-dimethylacryloyl-, and cinnamoyl fluoride all form complexes with antimony pentafluoride, which based on infrared and nmr investigations are alkenyloxocarbonium ions.

No investigation of the complex formation of alkenoyl halides with Lewis acid halides has been reported in the literature. Deno, Pittman, and Wisotsky[3] investigated the behavior of crotonic, 2-methylcrotonic (tiglic), 3-methylcrotonic, and 2,4-hexadienoic (sorbic) acid in sulfuric acid and oleum. It was suggested, based on nmr studies, that an equilibrium exists between the oxocarbonium ions and protonated acids.

$$RCOOH_2^+ \rightleftharpoons RCO^+ + H_2O$$

In continuation of our previous work[4] on oxocarbonium ions it was of interest to attempt the preparation of alkenyloxocarbonium ion complexes ($RC^+{=}O$, R = unsaturated).

(1) Part XXXVII: G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Am. Chem. Soc.*, 89, 1268 (1967).

(2) National Science Foundation Predoctoral Research Investigator, 1965–1967.

(3) N. C. Deno, C. U. Pittman, Jr., and J. Wisotsky, *J. Am. Chem. Soc.*, 86, 4370 (1964).

(4) (a) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *ibid.*, 84, 2733 (1962); (b) G. A. Olah, *Rev. Chim., Acad. Rep. Populaire Roumaine*, 7, 1139 (1962); (c) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, 85, 1328 (1963); (d) G. A. Olah and M. B. Comisarow, *ibid.*, 88, 3313, 4442 (1966).

Results and Discussion

Stable alkenyloxocarbonium ion complexes were obtained by treating alkenoyl fluorides with antimony pentafluoride ("fluoride method" of oxocarbonium ion formation[4]).

$$RR'C{=}CR''COF + SbF_5 \rightleftharpoons RR'C{=}CR''C^+O\ SbF_6^-$$

The necessary alkenoyl fluorides were prepared from the corresponding acyl chlorides and anhydrous hydrogen fluoride except for acryloyl fluoride, methacryloyl fluoride, and crotonoyl fluoride, which were prepared from the corresponding acids and benzoyl fluoride. Yields were generally better than 90%. Table I summarizes the boiling points of the alkenoyl fluorides. Their purity, based on nmr and infrared spectra, was better than 98%.

The alkenoyloxocarbonium ion complexes were prepared by mixing cold 1,1,2-trifluorotrichloroethane (Freon 113) solutions of the corresponding alkenoyl fluorides with Freon 113 solutions of antimony pentafluoride. The complexes separate as liquids at room temperature except for the cinnamoyl complex which crystallizes (mp 75°). They are all brown in color except for the cinnamoyl complex which is bright red.

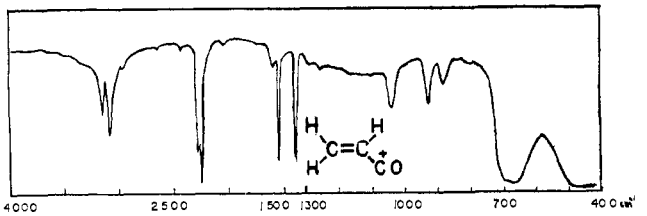


Figure 1.

When stored in the absence of moisture the complexes appear to be stable indefinitely.

Table I. Alkenoyl Fluorides

Fluoride	Bp, °C (mm)
Acryloyl	34[a]
Methacryloyl	56–57[b]
Crotonoyl	80–82[c]
Tigloyl	63–64 (180)
β,β-Dimethylacryloyl	66 (188)
Cinnamoyl	108 (12)[d]

[a] Lit.[6b] 34.5°. [b] B. W. Howk and R. A. Jacobson [U. S. Patent 2,330,000; *Chem. Abstr.*, **42**, 4794 (1948)] report 56.5–58°. [c] F. Seel and J. Langer [*Ber.*, **91**, 2553 (1958)] report 81–82° (745 mm). [d] Lit.[c] 108° (12 mm).

Infrared Investigations. The liquid complexes were examined as neat films between Irtran-2 plates using the necessary techniques for exclusion of moisture.[4d] The solid cinnamoyl complex was examined as a Fluorolube mull.

The infrared investigations show that all of the complexes are exclusively oxocarbonium ions ($RC^+{=}O$) as evidenced by the absence of carbonyl absorption and the presence of an absorption band (around 2240 cm^{-1}) characteristic of oxocarbonium ions.[4] The infrared absorption data are summarized in Table II.

Table II. Infrared Absorption of Alkenoyl Fluoride–Antimony Pentafluoride Complexes (cm^{-1})

	Acyl fluoride		Oxocarbonium ion	
	ν_{CO}	$\nu_{C=C}$	$\nu^+_{C=O}$	$\nu_{C=C}$
Acryloyl	1825	1635	2250	1555
Methacryloyl	1815	1645	2240	1590
Crotonoyl	1815	1655	2240	1580
Tigloyl	1800	1650	2230	1580
β,β-Dimethylacryloyl	1800	1645	2220	1555
Cinnamoyl	1805	1640	2210	1550

The $C^+{=}O$ stretching frequency is generally close to 2240 cm^{-1}, which is lower than the $C^+{=}O$ stretching frequency found in saturated alkyloxocarbonium ions[4] and close to the stretching frequency of the phenyloxocarbonium ion (2212 cm^{-1}). This is undoubtedly due to conjugation with the adjacent double bond. As was found previously for other oxocarbonium ions[4d] the absence of carbonyl absorption bands is dependent on the purity of the complexes. Addition of water to the complexes diminishes the intensity of the 2240-cm^{-1} absorption and causes a concomitant appearance of bands at 1600 cm^{-1}. The spectrum of the acryloyl complex is shown in Figure 1 as representative of the infrared spectra of the alkenyloxocarbonium ions.

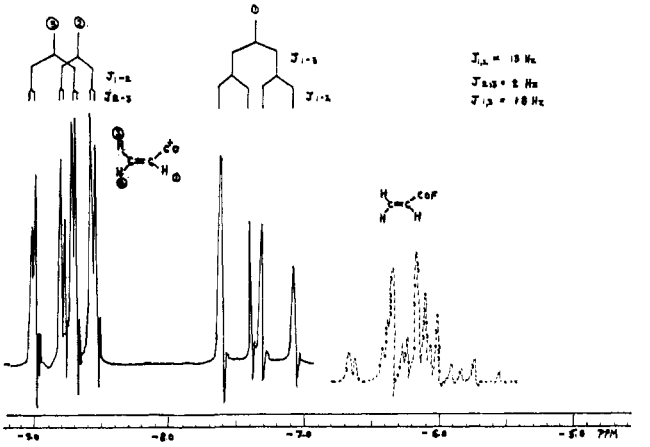


Figure 2.

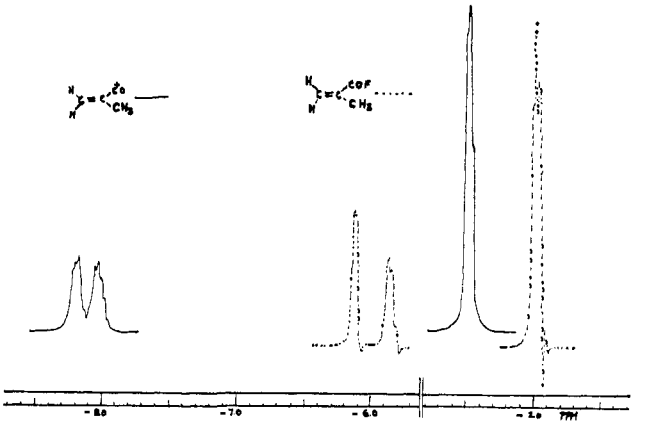
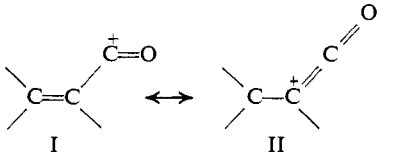


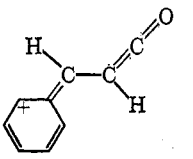
Figure 3.

Nmr Investigations. The pmr spectra of the alkenyloxocarbonium hexafluoroantimonate complexes and the starting acyl fluorides as solution in SO_2 at −40 to −60° are shown in Figures 2–7. First-order techniques were used for the analysis of all of the spectra except that of acryloyl fluoride.[5] The data are summarized in Table III. They clearly indicate the oxocarbonium ion nature of the investigated complexes. The deshielding ($\Delta\delta$ values) of the methyl protons β to the $C^+{=}O$ group is greater than that of the α-methyl protons, indicating substantial contributions from the resonance forms I and II. Comparison of $\Delta\delta$ values



I II

indicates that the proton *cis* to the $C^+{=}O$ group in the cinnamoyl complex is deshielded less than the same proton in the other complexes indicating a further strong contribution from resonance form III.



III

(5) (a) The authors wish to thank Professor Axel Bothner-By for communication of the analysis of the acryoylfluoride spectrum prior to publication. (b) D. F. Koster, *J. Am. Chem. Soc.*, **88**, 5062 (1966).

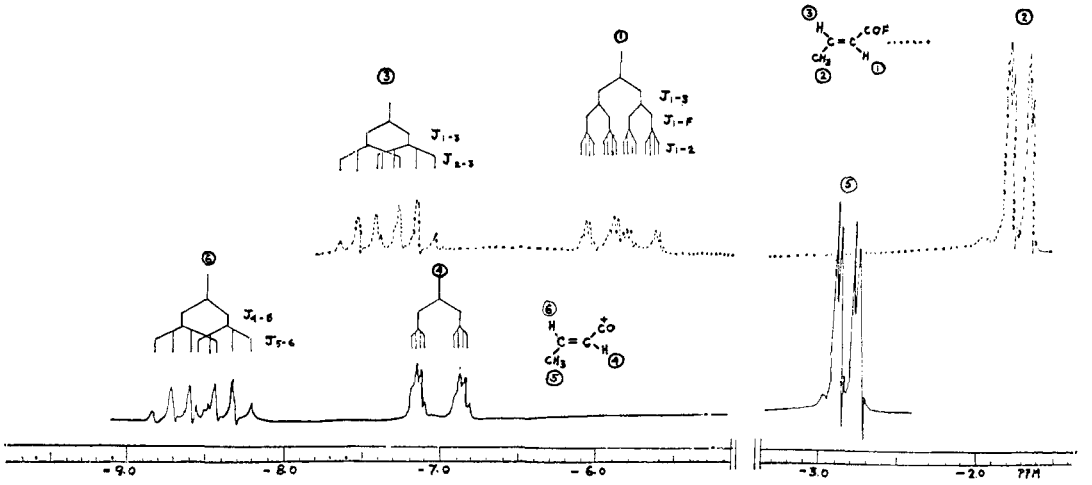


Figure 4.

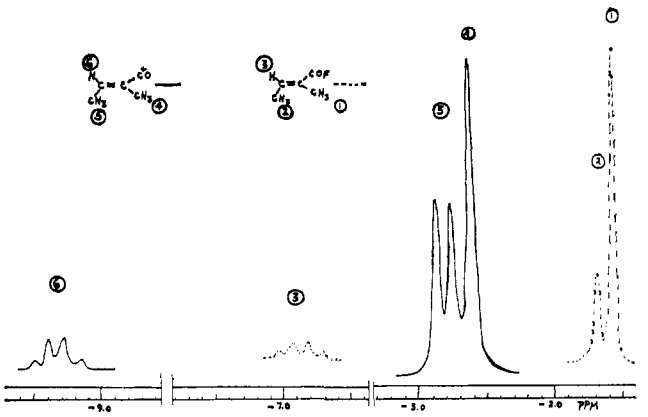


Figure 5.

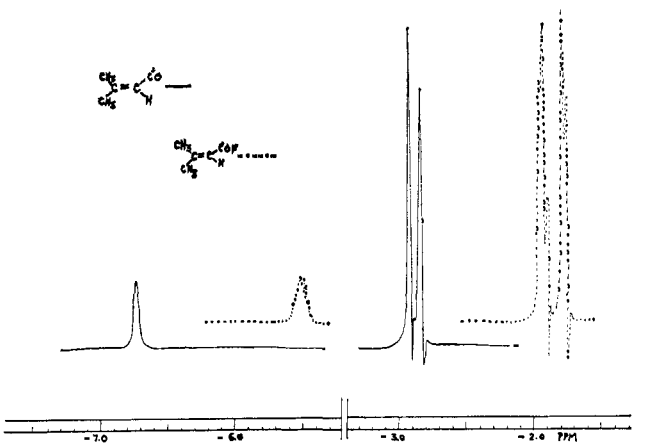


Figure 6.

Addition of small amounts of water to the nmr samples results in the appearance of new resonances at higher field than the oxocarbonium ion peaks but at lower field than the starting acyl fluorides peaks. These can be assigned to the donor:acceptor complexes.[4d,6]

The alkenyloxocarbonium hexafluoroantimonate complexes could also be examined as neat liquids at

(6) NOTE ADDED IN PROOF. The protonation of alkenoic acids in FSO_2H–SbF_5 solution and their dehydration to alkenyloxocarbonium ions is being investigated with Dr. M. Calin and will be reported. This work indicates that the donor–acceptor complex $RC(F)=O\text{-}SbF_5$ is most likely the O-protonated acid $RCO_2H_2^+$.

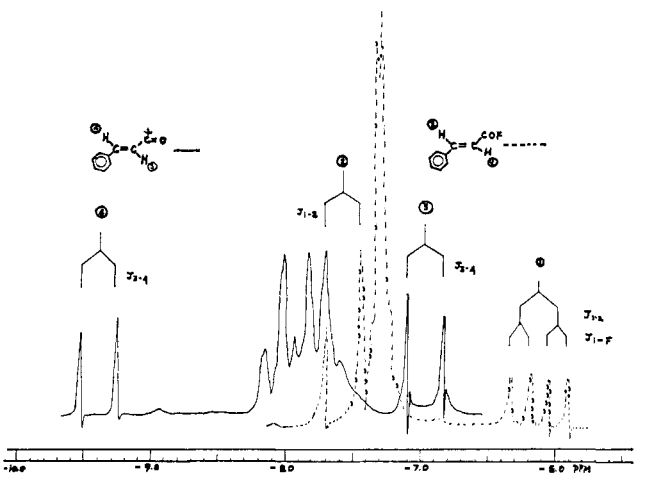


Figure 7.

Table III. Nuclear Magnetic Proton Resonance Shifts of Alkenyloxocarbonium Ions

$$\beta_{cis}\beta_{trans}>C=C<\overset{+}{CO}\ \alpha$$

		δ, ppm		
		Fluoride in SO_2	Oxocarbonium In SO_2	Oxocarbonium Neat
Acryloyl	α	−5.88[a]	−7.33	−7.70
	β-*cis*	−6.26[a]	−8.85	−9.22
	β-*trans*	−5.79[a]	−8.60	−9.05
Methacryloyl	α-CH_3	−1.16	−2.73	−3.12
	β-*cis*	−6.13	−8.45	−8.70
	β-*trans*	−5.89	−8.17	−8.53
Crotonyl	α	−5.65	−7.00	−7.31
	β-*cis*	−7.12	−9.50	−9.88
	β-*trans*-CH_3	−1.61	−2.83	−3.35
Tigloyl	α-CH_3	−1.55	−2.62	−3.04
	β-*cis*	−6.88	−9.33	−9.60
	trans-CH_3	−1.61	−2.82	−3.32
β,β-Dimethyl-acryloyl	α	−5.50	−6.72	−7.05
	cis-CH_3	−1.93	−2.92	−3.42
	trans-CH_3	−1.78	−2.83	−3.33
Cinnamoyl	α	−6.11	−6.96	...
	β-*cis*	−7.57	−9.40	...
	Ring H	−7.27	≈7.90	...

[a] These values were obtained from ref 5b by adding 0.1 from the chemical shifts in $CFCl_3$; +0.1 ppm is a typical solvent shift from $CFCl_3$ (internal TMS) to SO_2 (external TMS): Olah and Comisarow, unpublished data.

room temperature (with the exception of the cinnamoyl complex) and their spectra were very similar to the solution spectra except for the solvent shift. The resolution of the neat spectra was slightly lower due to the higher viscosity of the neat complexes as compared with their SO_2 solutions.

The F^{19} spectra of the complexes shows no C–F resonances, only antimony–fluorine peaks at around ϕ +100 (parts per million from external $CFCl_3$).

Experimental Section

Acryloyl, methacryloyl, and crotonoyl fluorides were prepared from the acids and benzoyl fluoride using the published procedure for cyclopropanecarbonyl fluoride.[4d] Tigloyl, β,β-dimethylacryloyl, and cinnamoyl fluorides were prepared from the corresponding chlorides and anhydrous hydrogen fluoride using the published procedure for preparing cyclobutanecarbonyl fluoride.[4d]

The preparation of the alkenyloxocarbonium ion complexes from alkenoyl fluorides and antimony pentafluoride in 1,1,2-trifluorotrichloroethane solution was carried out according to methods previously described to prepare other types of oxocarbonium complexes.[4a–d]

The techniques of infrared and nmr studies were also analogous to those described previously. Infrared spectra were obtained on a Beckman Model IR 10 spectrophotometer and a PE 337 spectrophotometer. Nmr spectra were obtained on Varian Associates Model HA-60-IL and A56-60A spectrometers equipped with variable-temperature probes. All chemical shifts are relative to external TMS (H^1) or CCl_3F (F^{19}) as references (capillary tubes).

Acknowledgment. Generous support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

Carbodiimide–Sulfoxide Reactions. VI.[1] Syntheses of 2′- and 3′-Ketouridines

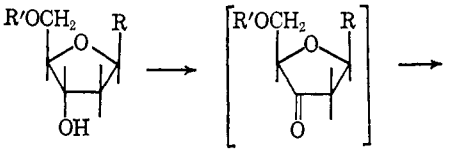
A. F. Cook[2] and J. G. Moffatt

Contribution No. 46 from the Institute of Molecular Biology, Syntex Research, Palo Alto, California. *Received January 23, 1967*

Abstract: Oxidation of 2′,5′-di-O-trityluridine by the dimethyl sulfoxide–dicyclohexylcarbodiimide method gave crystalline 2′,5′-di-O-trityl-3′-ketouridine in good yield. Treatment with hydrogen chloride in chloroform then gave free 3′-ketouridine. In a similar way oxidation of 3′,5′-di-O-trityluridine gave 3′,5′-di-O-trityl-2′-ketouridine which was detritylated to free 2′-ketouridine. These oxidations could also be performed using dimethyl sulfoxide together with acetic anhydride or phosphorus pentoxide. The uridine ketones were very labile toward alkali, being cleaved to uracil. Borohydride reduction of the free or tritylated 2′-ketone led predominantly to the formation of products with the arabinose configuration while similar reduction of the 3′-ketones gave mixures of the corresponding xylosides and ribosides in a ratio of 2:1. Attempts to alkylate the ditrityl 3′-ketone with Grignard reagents, methyllithium, or diazomethane have not as yet been successful. Nuclear magnetic resonance spectra data are presented for the various compounds.

An extremely mild, yet efficient, oxidation of alcohols through their reaction with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) has been developed in this laboratory.[3] Since the oxidation proceeds at room temperature, and under essentially neutral conditions (*e.g.*, using pyridinium trifluoroacetate as the proton source), it has found considerable application when dealing with sensitive compounds.[4] A particular merit lies in the oxidation of primary alcohols exclusively to the aldehyde stage,[3] and this property has permitted the oxidation of the 5′-hydroxyl group of protected nucleosides to give the corresponding nucleoside 5′-aldehydes.[3a,5]

Our earlier observations[3b] showed that the reaction of deoxynucleosides, such as thymidine, substituted at the 5′ position by phosphate, acetyl, or *p*-nitrobenzoyl groups (**1**, R = thymine, R′ = PO_3H_2, Ac, *p*-nitrobenzoyl) with DMSO and DCC in the presence of anhydrous orthophosphoric acid led to the rapid and complete cleavage of the N-glycosidic bond with release of thymine. Such a degradation undoubtedly proceeds *via* oxidation to the 5′-substituted 3′-ketonucleoside **2** which then undergoes β elimination of the heterocyclic base. The elimination step was apparently extremely rapid and no sign of the intermediate ketones **2** could be detected chromatographically. Similar results have been encountered by others during attempted oxidation of the 3′-hydroxyl group of protected deoxynucleosides with manganese dioxide,[6] chromium trioxide in pyridine,[7] or platinum and oxygen under forcing conditions.[8]



1 **2**

R + sugar fragments

(1) For part V see M. G. Burdon and J. G. Moffatt, submitted for publication.

(2) Syntex Postdoctoral Fellow, 1964–1966.

(3) (a) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); (b) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661 (1965); (c) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 3670 (1965).

(4) See, *e.g.*, (a) J. D. Albright and L. Goldman, *J. Org. Chem.*, **30**, 1107 (1965); (b) B. R. Baker and D. H. Buss, *ibid.*, **30**, 2304 (1965); (c) A. G. Brook and J. B. Pierce, *ibid.*, **30**, 2566 (1965).

(5) A detailed account of these studies is in preparation by G. H. Jones and J. G. Moffatt.

(6) A. S. Jones, R. T. Walker, and A. R. Williamson, *J. Chem. Soc.*, 6033 (1963).

(7) A. S. Jones, A. R. Williamson, and M. Winkley, *Carbohydrate Res.*, **1**, 187 (1965).

(8) Personal communication from Dr. G. M. Tener of the University of British Columbia.