catalysis. This suggestion is also further supported by the "bubbled air" cupric acetate–acetic acid experiment. Clearly, however, the interpretation of a given reaction, particularly the temperature dependence, in such circumstances as postulated would be a very complicated affair, as oxidation reactions occur at several steps in the proposed mechanism. Therefore one can only conclude that the above is a reasonable explanation of the observations for the case of the reactions in the presence of metallic salts.

The decreased yield of porphyrin in the presence of metallic salts of these acidic condensations carried out in a relatively oxidizing atmosphere indicates that there are essential differences in the mechanism of these reactions and those previously observed to show an increase of yield in the presence of metallic cations under other conditions. For example, such cation-increased yields were observed either in relatively high temperature melts,[8,11] basic media,[8,10] relatively reducing atmospheres under pyrolytic conditions,[6,7] or in the presence of free-radical generators.[12] The continued and extended physical chemical and kinetic investigations of these reactions will prove both interesting and informative.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

Mass Spectrometry in Carbohydrate Chemistry. Diethyl Dithioacetal and Dithioketal Peracetates

BY DON C. DEJONGH

RECEIVED MARCH 5, 1964

The mass spectra of various monosaccharide diethyl dithioacetal peracetates and of D-fructose diethyl dithioketal pentaacetate are discussed. A detailed interpretation of the fragmentation processes which these molecules undergo is presented; it is supported by the mass spectra of analogous peracetates prepared with acetic anhydride-d_6. The molecular weight can readily be obtained from the molecular ion peak. It is possible to relate the characteristics of the mass spectra to the position of deoxy groups in these molecules and to distinguish between aldoses and ketoses.

Introduction

The potential importance of mass spectrometry as a technique for structure determination in the carbohydrate field has recently been demonstrated. The mass spectra of the peracetates of hexoses and pentoses[1] and their partially O-methylated derivatives,[2] of the O-isopropylidene derivatives of hexoses and pentoses,[3] and of various carbohydrate methyl ethers[4,5] have been interpreted in terms of molecular weight, ring size, variation in the type and degree of substitution, ketose or aldose structure, and stereochemistry. The structure of a newly isolated di-O-isopropylidene derivative of D-galactose was determined by applying this technique.[3]

Dithioacetal derivatives are very useful for the characterization of monosaccharides because of their stability and ease of preparation. They also are useful intermediates for the preparation of acylic derivatives of sugars. The peracetates of these compounds, which usually are crystalline, are sufficiently volatile and thermally stable to be introduced directly into a conventional inlet system of the mass spectrometer.

Since the diethyl dithioacetal peracetates are monosaccharide derivatives in the acyclic structure, their mass spectra need not be interpreted in terms of ring size and exhibit only minor intensity differences with a change in stereochemistry. Structural differences which express themselves in the size of substituents and of the entire molecule and in the position of the carbonyl group lead to significant variation in their mass spectra; this is borne out in the following discussion by a comparison of the mass spectra of the corresponding diethyl dithioacetal peracetate derivatives of hexoses, pentoses, deoxyhexoses, and of a diethyl dithioketal hexose pentaacetate.

The mass spectra of typical representatives of these derivatives are presented and interpreted. The fragmentation schemes proposed have been substantiated by the mass spectra of deuterated analogs, obtained by acetylation with anhydride-d_6. Perhaps the most valuable aspect of these mass spectra is the presence of a sizable molecular ion peak which allows direct determination of the molecular weight. In all the mass spectra of carbohydrate derivatives published previously, the molecular weight must be determined from a fragment peak resulting from the loss of a substituent on a carbon atom of the pyranose or furanose ring[1,2,4,5] or from the loss of a methyl group from an O-isopropylidene ring.[3]

The mass spectra of D-arabinose diethyl dithioacetal tetraacetate (I, Fig. 1) and its d_{12}-analog (II, Fig. 2) will be discussed in detail to elucidate the fragmentation processes characteristic of this class of compound. This shall be followed by a discussion of the influence of adding a $-CH_2OCOCH_3$ group to form a ketohexose or an aldohexose and of adding a CH_2- group to form a 2- and a 6-deoxyaldohexose.

D-Arabinose Diethyl Dithioacetal Tetraacetate (I, Fig. 1).—The peak at m/e 424(436)[6] corresponds to the molecular weight of this compound. Elimination of a molecule of acetic acid[1] from the molecular ion forms fragment 364(373). The peak at m/e 363(375) arises from the fission of a carbon–sulfur bond in the molecu-

(1) K. Biemann, D. C. DeJongh, and H. K. Schnoes, *J. Am. Chem. Soc.*, **85**, 1763 (1963).
(2) D. C. DeJongh and K. Biemann, *ibid.*, **85**, 2289 (1963).
(3) D. C. DeJongh and K. Biemann, *ibid.*, **86**, 67 (1964).
(4) N. K. Kochetkov, N. S. Wulfson, O. S. Chizhov, and B. M. Zolotarev, *Tetrahedron*, **19**, 2209 (1963).
(5) K. Heyns and H. Scharmann, *Ann.*, **667**, 183 (1963).

(6) Throughout this article, the m/e assignments are followed by parentheses containing the location of the peak in the mass spectrum of the deuterated analog, when known.

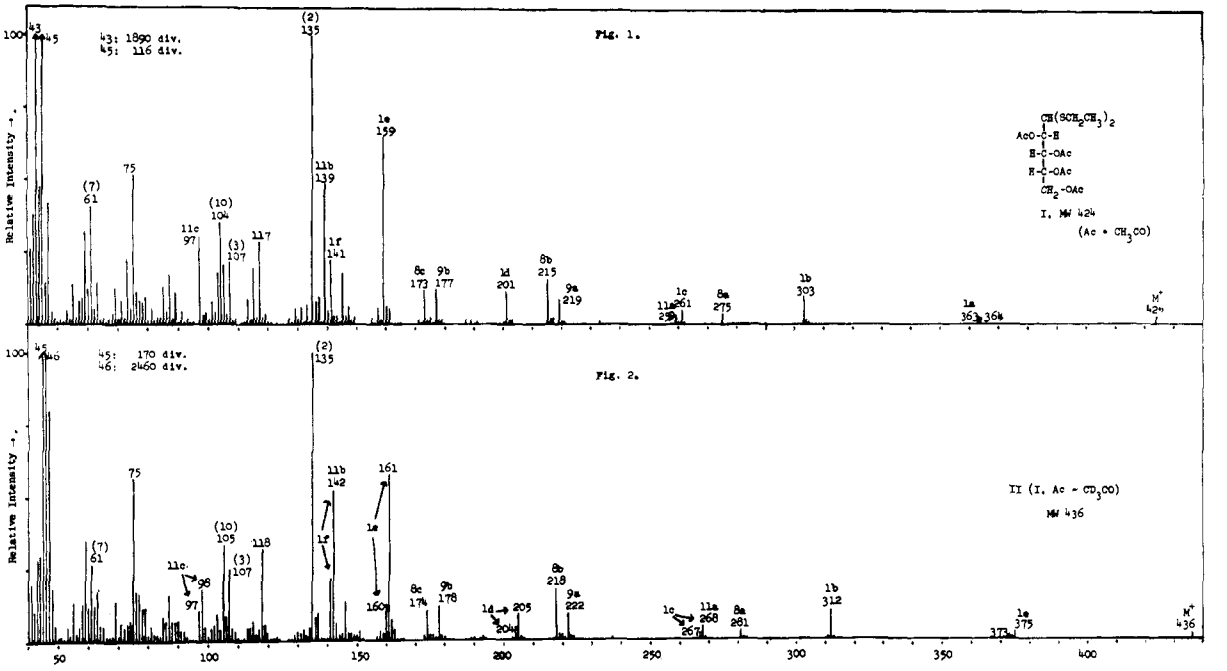


Fig. 1.—Mass spectrum of D-arabinose diethyl dithioacetal tetraacetate (I).
Fig. 2.—Mass spectrum of D-arabinose diethyl dithioacetal tetraacetate-d_{12} (II).

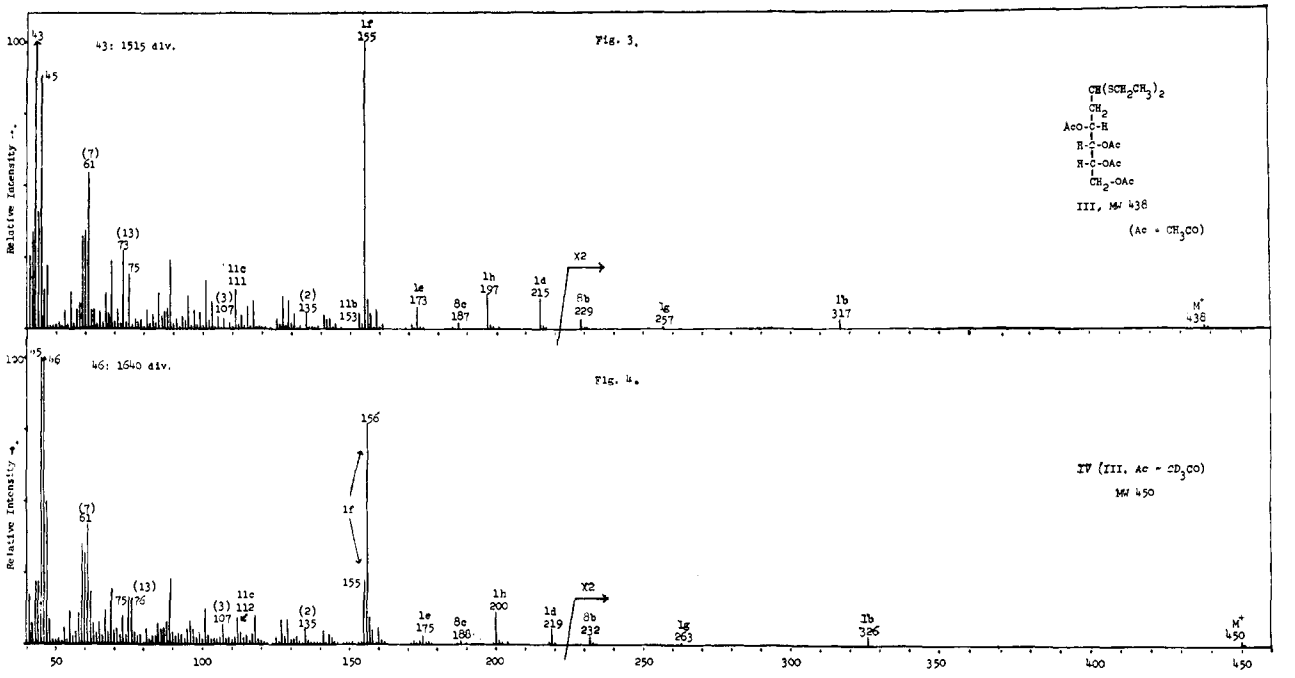
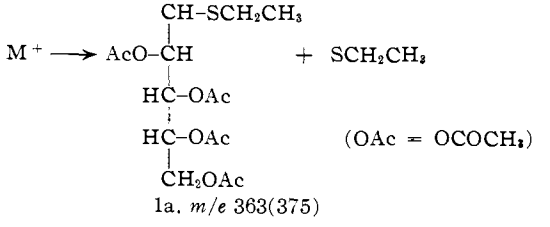


Fig. 3.—Mass spectrum of 2-deoxy-D-glucose diethyl dithioacetal tetraacetate (III).
Fig. 4.—Mass spectrum of 2-deoxy-D-glucose diethyl dithioacetal tetraacetate-d_{12} (IV).

lar ion, leading to fragment 1a containing the four acetoxyl groups and to a thioethoxyl radical.



1a, *m/e* 363(375)

This is analogous to the carbon–oxygen bond cleavage found in the mass spectra of diethyl acetals[7] and the carbon–sulfur bond cleavage characteristic of thioethers.[8,9] Fragment 1b at *m/e* 303(312) forms by explusion of a molecule of acetic acid from fragment 1a or of a thioethoxyl radical from the fragment at *m/e* 364 (373). Loss of acetic acid [60(63) m.u.], ketene [42 (44) m.u.], and acetic anhydride [102(108) m.u.] is a very important mode of fragmentation of peracetyl derivatives of carbohydrates[1,2]; fragments 1c-f at *m/e* 261(267,268), 201(204,205), 159(160,161), and 141

(7) R. A. Friedel and A. G. Sharkey, *Anal. Chem.*, **28**, 940 (1956).
(8) E. J. Levy and W. A. Stahl, *ibid.*, **33**, 707 (1961).
(9) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 1648 (1962).

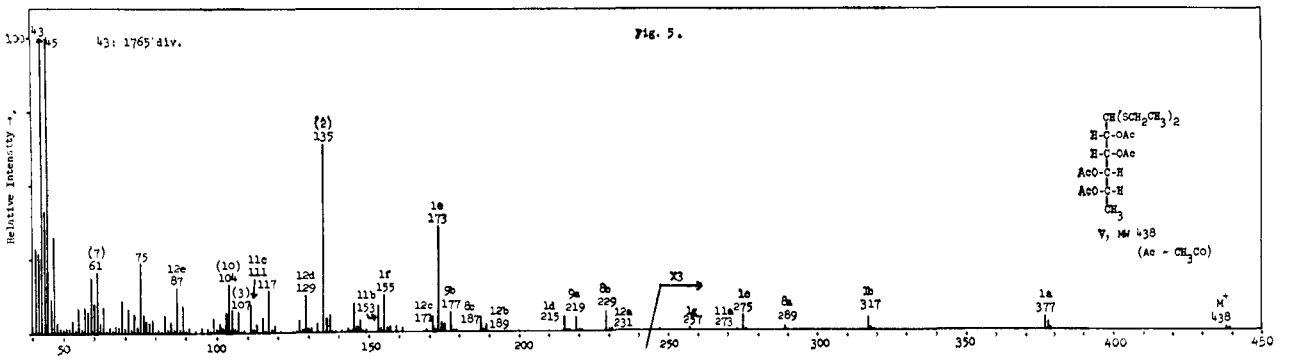


Fig. 5.—Mass spectrum of 6-deoxy-L-mannose diethyl dithioacetal tetraacetate (V).

(141,142), arise from the elimination of combinations of these stable molecules. The most intense peak in the mass spectra of these diethyl dithioacetal and dithioketal peracetates is at *m/e* 43(46), corresponding to the acetyl ion CH_3CO^+. Many of the fragmentations proposed throughout this discussion are corrobrated by metastable peaks in the mass spectra shown in Fig. 1–5 (see Table I).

TABLE I

METASTABLE PEAKS IN FIG. 1–7

Fig.	Fragmentation	Calcd.	Found
1	424 → 363	310.8	311, broad
	424 → 364	312.6	
	275 → 215	168.1	168.5
	201 → 159	125.8	126.1
	135 → 107	84.8	84.9
	139 → 97	67.7	67.8
2	436 → 375	322.5	321, broad
	436 → 373	319.1	
	281 → 218	169.1	169.5
	205 → 161	126.4	126.5
	135 → 107	84.8	84.9
	142 → 98	67.6	67.6
3	257 → 197	151.0	151.3
	215 → 155	111.7	111.9
	197 → 155	122.1	122.4
4	263 → 200	152.1	152.4
	219 → 156	111.1	111.3
	200 → 156	121.7	122.1
5	438 → 379	328.0	Broad, 324–329
	438 → 378	326.2	
	438 → 377	324.5	
	289 → 229	181.5	182.0
	215 → 173	139.2	139.5
6			None
7			None

In the diethyl dithioacetal portion of the molecule, two carbon–carbon bond cleavages next to a sulfur atom are possible. Fission of the carbon–carbon bond of the thioethoxyl groups is not important, but fission of the C-1–C-2 bond of the arabinose forms fragment 2 at *m/e* 135(135). Stabilization of the charge by two

$$CH_3CH_2S—\overset{+}{C}H—SCH_2CH_3$$

2, *m/e* 135(135)

neighboring sulfur atoms accounts for the preference for the latter fission. Fragment 2 is abundant in the mass spectra of all the diethyl dithioacetal peracetates studied with the exception of the derivative of 2-deoxy-D-glucose (III, Fig. 3); the corresponding radical formed from compound III by C-1–C-2 cleavage is primary and is not stabilized by a neighboring heteroatom. The corresponding peak from ethylene dithioacetal peracetates is found at *m/e* 105(105).[10] Fragment 3 at *m/e* 107(107) results from ethylene expulsion from fragment 2 with hydrogen migration

$$CH_2—CH_2—\overset{+}{S}=CH—S—CH_2CH_3 \xrightarrow{-CH_2=CH_2} CH_3CH_2S—CH=\overset{+}{S}H$$

2, *m/e* 135(135) 3, *m/e* 107(107)

A metastable peak at *m/e* 84.9 (calcd. 84.8) substantiates this mechanism. Olefin elimination is a common decomposition of thioethers.[8]

Fragment 4 at *m/e* 75 also appears to be related to fragment 2. In those mass spectra where *m/e* 135 is small or absent, *e.g.* Fig. 3 and 7 and in the mass spectra of ethylene dithioacetal peracetates,[10] peak 75 is also small. The following mechanism tentatively can be proposed for fragment 4

$$CH_3CH—S—\overset{+}{C}H—SCH_2CH_3 \longrightarrow CH_2—\overset{+}{S}CH_2CH_3 + CH_3CH=S$$

2, *m/e* 135(135) 4, *m/e* 75(75) 5

An elimination of this type does not appear favorable for thioethers,[8,9] there being no α-sulfur atom remaining to stabilize the charge. A basic study of simple diethyl dithioacetals is underway to elucidate their characteristic fragmentation patterns.

A thioaldehydo ion (6) can account for the major fragment at *m/e* 45(45). Fragment 7 at *m/e* 61(61) is a thioethoxyl ion rather than protonated acetic acid[1] since it does not shift in the deuterated analog.

$^+CH=S$ $CH_3CH_2S^+$

6, *m/e* 45(45) 7, *m/e* 61(61)

The peak at *m/e* 275(281) is part of another series of peaks differing by 60(63) and 42(44) m.u. It results from the over-all loss of two molecules of acetic acidand an ethyl radical. A highly stabilized five-membered

(10) D. C. DeJongh, in press.

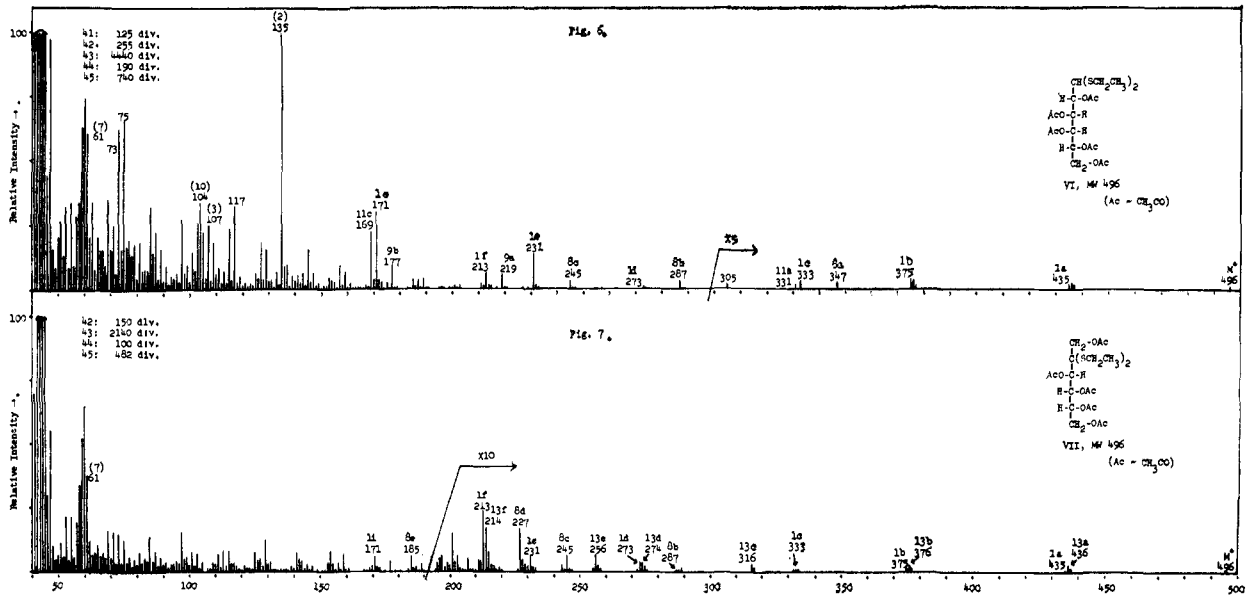
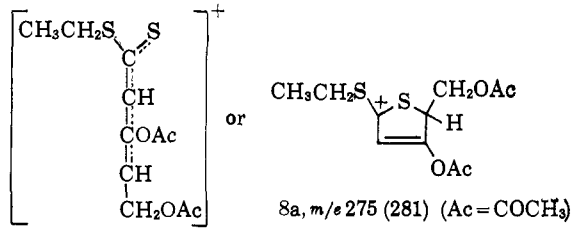


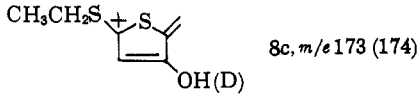
Fig. 6.—Mass spectrum of D-galactose diethyl dithioacetal pentaacetate (VI).
Fig. 7.—Mass spectrum of D-fructose diethyl dithioketal pentaacetate (VII).

ring can be drawn for this fragment.



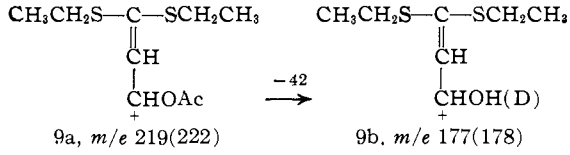
8a, *m/e* 275 (281) (Ac = $COCH_3$)

Fragment 8b is found 60(63) m.u. lower at *m/e* 215 (218) and fragment 8c another 42 m.u. lower at *m/e* 173(174).



8c, *m/e* 173 (174)

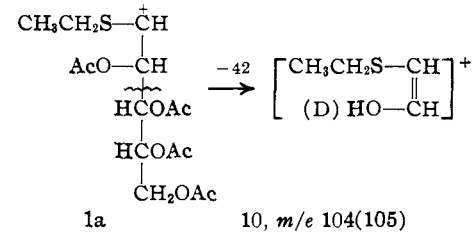
Elimination of a molecule of acetic acid from the C-1–C-2 bond of the molecular ion, followed by C-2–C-3 bond fission, leads to fragment 9a found at *m/e* 219(222) in Fig. 1. Fragment 9b results from ketene expulsion; perhaps the peak at *m/e* 117(118) is formed



9a, *m/e* 219(222) 9b, *m/e* 177(178)

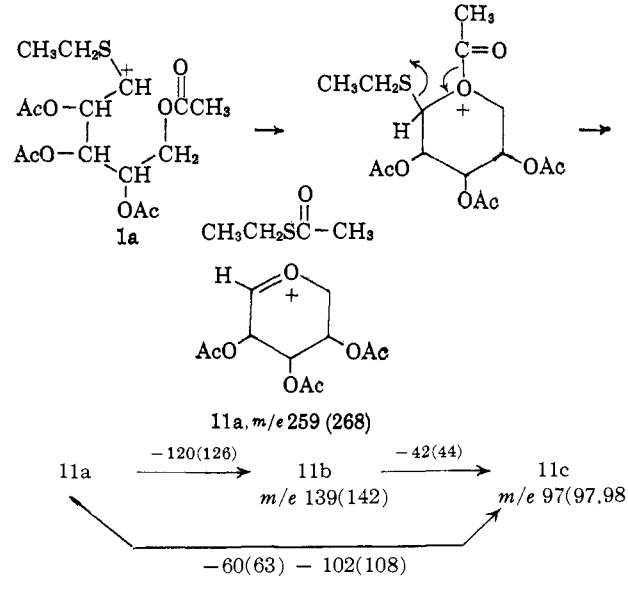
by thioacetaldehyde (5) elimination from fragment 9b. Series 9 is not found in the mass spectra of the fructose and 2-deoxyglucose derivatives, Fig. 3 and 7, respectively, indicating its formation is sensitive to changes at C-1 and C-2 of the carbohydrate. It is found in Fig. 5 and 6 at *m/e* 219, showing that C-5 is not included in these fragments.

Apparently fragment 10 at *m/e* 104(105) also contains C-2 since it is found in Fig. 1, 5, and 6 but is absent from Fig. 3 and 7; a stable olefin containing C-1 and C-2 of the monosaccharide accounts for this fragment.



1a 10, *m/e* 104(105)

The peaks at *m/e* 259 and 261 in Fig. 1 are found at *m/e* 267 and 268 in the deuterated analog, Fig. 2. A close examination of series 1, as mentioned above, indicates that peak 261 should be found split between 267 and 268 because of both acetic anhydride [102(108) m.u.] and acetic acid plus ketene [102(107) m.u.] elimination from fragment 1b. Fragment 11a, at *m/e* 259, is shifted to *m/e* 268, retaining three acetoxyl groups; this is substantiated by the presence of peaks 120(126) and 162(170) m.u. lower from the loss of 2 and 3 acetoxyl groups from fragment 11a. The following scheme is postulated for this series.

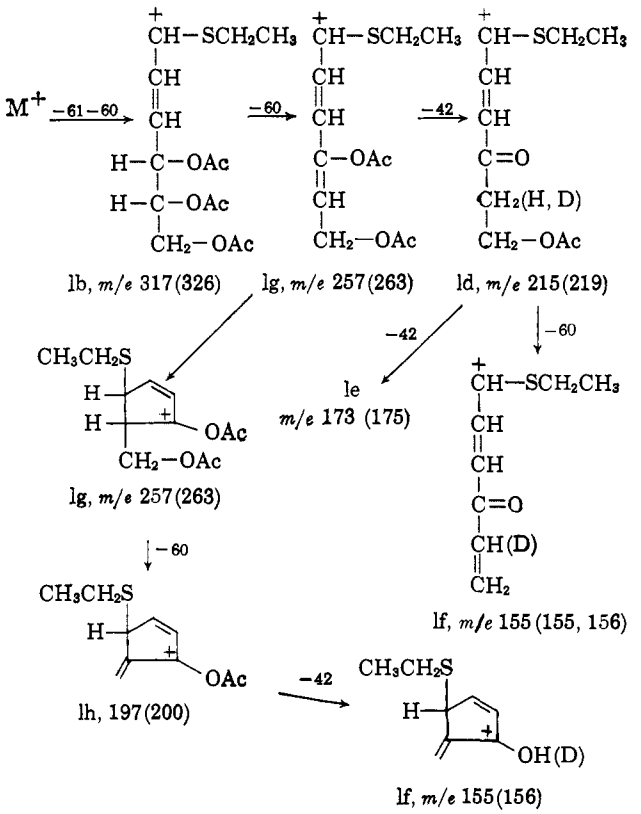


11a, *m/e* 259 (268)

11a —(−120(126))→ 11b, *m/e* 139(142) —(−42(44))→ 11c, *m/e* 97(97,98)

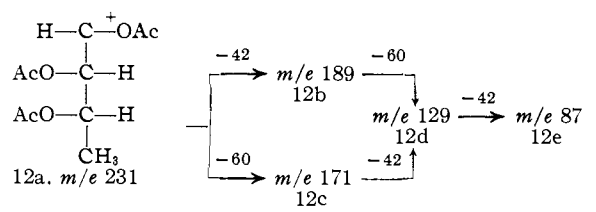
11a —(−60(63) − 102(108))→ 11c

Deoxyhexose Diethyl Dithioacetal Tetraacetates.—The molecular weight of 2-deoxy-D-glucose diethyl dithioacetal tetraacetate (III, Fig. 3), its d_{12}-analog (IV, Fig. 4), and 6-deoxy-L-mannose diethyl dithioacetal tetraacetate (V, Fig. 5) can be directly determined from the molecular ion and are found 14 m.u. higher than the molecular weight of the pentose derivative. Also present in these mass spectra are "M + 1" peaks resulting from ion-molecule collision.[11] Series 1 is a prominent fragmentation path for both the 2-deoxy and the 6-deoxy derivatives. In fact, the most intense peak in the mass spectrum of 2-deoxy-D-glucose diethyl dithioacetal tetraacetate, with the exception of *m/e* 43(46), is fragment 1f. The following scheme shows two pathways leading to fragment 1f; most of the steps are substantiated by metastable peaks (see Table I).



Fragments characteristic of series 8 and 11 are found 14 m.u. higher than in Fig. 1 for both deoxy compounds, but they are quite small for compound III.

The major difference between the mass spectra of the 2- and 6-deoxy derivatives lies in the intensity of fragment 2 at *m/e* 135, as discussed above. Also, fragments of series 9 are absent in the mass spectrum of 2-deoxy isomer III. Figure 5 exhibits a series of peaks arising from cleavage of the C-2–C-3 bond of the 6-deoxyhexose.



(11) For a summary see K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 55.

Cleavage of the C-5–C-6 bond of the 2-deoxyhexose (or of a fragment ion) produces a fragment at *m/e* 73 (76) which has structure 13 (see Fig. 3 and 4).

$^{+}CH_2OCOCH_3$ 13

The mass spectrum of 6-deoxy-L-galactose diethyl dithioacetal tetraacetate is identical with the mass spectrum of 6-deoxy-L-mannose diethyl dithioacetal tetraacetate (Fig. 5) except for some minor intensity differences. This makes it difficult to gain insight into the stereochemistry of such molecules.

Hexose Diethyl Dithioacetal and Dithioketal Pentaacetates.—The pentaacetates of D-galactose diethyl dithioacetal and of D-fructose diethyl dithioketal, Fig. 6 and 7, respectively, differ only by an interchange of substituents at C-1 and C-2 of the hexose, yet their mass spectra differ extensively. The ketal carbon atom is more highly substituted than the acetal carbon atom which accounts for the absence of fragment 2 at *m/e* 135 in Fig. 7. The mass spectrum of aldohexose derivative VI resembles that of pentose derivative I with series 1, 8, and 11 and the molecular weight being found 72 m.u. higher due to the AcOCH substituent added to C-5; series 9 and fragments 2, 3, 4, 7, and 10 are found at the same *m/e* value for both the aldopentose and the aldohexose.

Series 1 is a major fragmentation path of ketohexose derivative VII. It is preceded by series 13 which results from losses of 60 and 42 m.u. from the molecular ion and various members of the series. Series 9 and 11 and fragments 2, 3, 4, and 10 are not prominent in the mass spectrum of compound VII. Peaks at *m/e* 287, 245, 227, and 185 most likely are fragments of series 8.

Discussion

The data obtained from the mass spectra of these diethyl dithioacetal and dithioketal peracetate derivatives will be useful for the characterization of a sugar and may be useful in the structure determination of a newly-discovered sugar. The mass spectra can be interpreted in terms of stabilization of positive charge by the sulfur atoms which direct fragmentation in a predictable manner. The peracetates of aldohexose, aldopentose, and 6-deoxyhexose diethyl dithioacetals can be differentiated from their 2-deoxy and their ketose isomers by the intense peak for the former group at *m/e* 135(135), arising from C-1–C-2 cleavage with charge retention on C-1, and from each other by their molecular weights (H *vs.* CH_3 *vs.* CH_2OCOCH_3). The 2-deoxy and ketose derivatives can be differentiated from each other by their molecular weights. Stereochemical differences have little influence on the fragmentation.

Experimental

Mass Spectra.—The spectra were determined with a CEC 21-103C mass spectrometer, equipped with a heated stainless steel inlet system operated at 170°; ionizing potential 70 e.v., ionizing current 50 μa., temperature of the ion source 250°. The sample (~0.5–1.0 mg.) was sublimed from a glass tube into the reservoir (3 l.).[12]

Diethyl Dithioacetals.—D-Arabinose diethyl dithioacetal, m.p. 124.5–125.5° (lit.[13] m.p. 125.0–125.5°), D-galactose diethyl dithioacetal, m.p. 138.5–139.5° (lit.[14] m.p. 140–142°), 2-deoxy-

(12) Reference 11, p. 28.

(13) H. Zinner, *Chem. Ber.*, **84**, 780 (1951).

(14) M. L. Wolfrom, *J. Am. Chem. Soc.*, **52**, 2464 (1930).

D-glucose diethyl dithioacetal, m.p. 137.0° (lit.[15] m.p. 134.0°), 6-deoxy-L-mannose diethyl dithioacetal, m.p. 134.5–136° (lit.[13] m.p. 136.5–137°), and 6-deoxy-L-galactose diethyl dithioacetal, m.p. 165.5° (lit.[16] m.p. 167–168.5°), were prepared from 0.5–1.0 g. of monosaccharide according to the procedure of Zinner.[13]

Acetylation of the Diethyl Dithioacetals.—D-Arabinose diethyl dithioacetal tetraacetate (I), m.p. 78–79° (lit.[17] m.p. 79–80°), D-galactose diethyl dithioacetal pentaacetate (VI), m.p. 77.5–78.5° (lit.[14] m.p. 77–78°), 2-deoxy-D-glucose diethyl dithioacetal tetraacetate (III), m.p. 76.5–77.0° (lit.[15] m.p. 77°), 6-deoxy-L-mannose diethyl dithioacetal tetraacetate (V), m.p. 59.5–60.0° (lit.[18] m.p. 60–62°), and 6-deoxy-L-galactose diethyl dithioacetal tetraacetate, m.p. 96.5–97.5° (lit.[19] m.p. 99–100°), were prepared from 0.1–0.6 g. of the diethyl dithioacetal by acetylating with acetic anhydride and pyridine at room temperature.

(15) J. L. Barclay, A. J. Cleaver, A. B. Foster, and W. G. Overend, *J. Chem. Soc.*, 789 (1956).
(16) E. Votoček and V. Veselý, *Z. Zuckerind. Böhmen.*, **40**, 207 (1916).
(17) M. L. Wolfrom and M. R. Newlin, *J. Am. Chem. Soc.*, **52**, 3619 (1930).
(18) E. L. Patterson, R. Milstrey, and E. L. R. Stokstad, *ibid.*, **78**, 5868 (1956).
(19) M. L. Wolfrom and J. A. Orsino, *ibid.*, **56**, 985 (1934).

D-Arabinose Diethyl Dithioacetal Tetraacetate-d_{12} (II).—One-tenth gram of D-arabinose diethyl dithioacetal was dissolved by heating in 0.40 ml. of deuterium oxide. After the deuterium oxide was removed in a vacuum desiccator, the residue was acetylated with 0.20 ml. of acetic anhydride-d_6 and 0.10 ml. of dry pyridine; m.p. 78–79°.

2-Deoxy-D-glucose Diethyl Dithioacetal Tetraacetate-d_{12} (IV).—The procedure described for compound II was followed; m.p. 76.5–77.5°.

D-Fructose Diethyl Dithioketal Pentaacetate (VII).—*keto*-D-Fructose pentaacetate was prepared according to the procedure of Cramer and Pacsu[20]; m.p. 69.0–69.5° (lit.[21] m.p. 70°). The diethyl dithioketal pentaacetate was prepared[21] from the pentaacetate, m.p. 80–81° (lit.[21] m.p. 83°).

Acknowledgment.—The author wishes to thank Professor K. Biemann for allowing him to use the mass spectrometer in his laboratories. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(20) F. B. Cramer and E. Pacsu, *ibid.*, **54**, 1697 (1932).
(21) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 880 (1934)

COMMUNICATIONS TO THE EDITOR

Mechanism of Electrochemical Reduction of Alkyl Bromides

Sir:

Although both ionic and free-radical mechanisms have been proposed for the electrochemical reduction of alkyl bromides at a mercury cathode,[1] the orientation of the carbon–bromine bond during the reduction has been discussed primarily in terms of the ionic mechanism. Regardless of whether carbon–bromine bond fission and electron uptake occur simultaneously or consecutively, it has been assumed that the bromine is as far as possible from the electrode surface and the carbon is as close as possible to the electrode surface so as to permit electron transfer directly to the carbon. While this spatial arrangement is an eminently reasonable one in view of the polarity of the carbon–bromine bond, the supporting evidence is sufficiently indirect[1,2] that it seemed desirable to test this feature of the mechanism more directly by investigating the reducibility of bridgehead halogen compounds, whose cage structures would make it impossible for the rear of the carbon–bromine bond to approach a mercury cathode.

Accordingly, half-wave potentials of a number of alkyl bromides have been determined (Table I) under experimental conditions similar to those of Lambert and Kobayashi.[2] Our use of a silver–silver bromide anode as well as more concentrated solutions of alkyl bromides and tetraethylammonium bromide led to values which are 0.45–0.50 v. more positive than those reported by Lambert and Kobayashi, but otherwise in excellent agreement.

(1) (a) P. J. Elving, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 99 (1953); (b) P. J. Elving and B. Pullman, *Advan. Chem. Phys.*, **1**, 1 (1960).
(2) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960)

The observed reduction of 1-bromobicyclo[2.2.2]-octane and 1-bromobicyclo[2.2.1]heptane could not have taken place by any mechanism which involved back-side attack on carbon, and such a process is therefore excluded in the case of these compounds. While reductive attack on carbon from the bromine side is conceivable, a more attractive alternative would be a displacement on bromine to give an alkyl free radical and a bromide ion, the latter located immediately next to the mercury surface. This process would require the transfer of electrons *through* the bromine atom *from* the cathode *to* the carbon atom, a direction opposite to that encountered in the SN2 displacement reaction; the intermediate would be very similar to the "bridged activated complex" proposed by Taube[3] for the reduction of certain metal halide complex ions.

Similar arguments apply to the reduction of 1-bromotriptycene, which also cannot occur by direct back-side attack on carbon. Furthermore, an indirect back-side attack on carbon, in which electrons are relayed through a benzene ring to the carbon atom of the carbon–bromine bond, seems highly improbable, since it could hardly be expected to take place more readily than a direct reductive attack on an aliphatic carbon–bromine bond. The only reasonable possibility seems to be reduction from the bromine side of the bond, the strained free radical formed at the bridgehead carbon atom being stabilized to a considerable extent by the three benzene rings. Although the effect of the rings is large enough to make bromotriptycene more easily reducible than the acyclic alkyl bromides, it is nevertheless much smaller than that encountered in benzyl bromide (Table I), which has a single ring free to assume the optimum

(3) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 24 (1959).