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TWO-STEP EXPULSION OF ALDEHYDES AND KETONES IN THE FRAGMENTATION OF ACYCLIC α-GLYCOL DIESTERS

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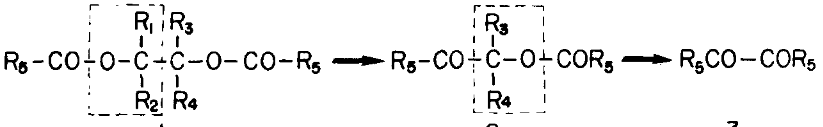
An unusual two-step loss of the middle portion of the chain has been found to occur generally upon electron impact of acyclic α-glycol diesters. Namely, the diester 1 loses the aldehyde or ketone R_1R_2CO to give 2, which further loses R_3R_4CO to yield 3; moreover, it is the carbon carrying the larger R_1/R_2 groups which is expelled first.



$$R_5\text{-CO-O-}\overset{R_1}{\underset{R_2}{C}}\text{-}\overset{R_3}{\underset{R_4}{C}}\text{-O-CO-}R_5 \longrightarrow R_5\text{-CO-}\overset{R_3}{\underset{R_4}{C}}\text{-O-COR}_5 \longrightarrow R_5CO\text{-}COR_5$$

1 2 3

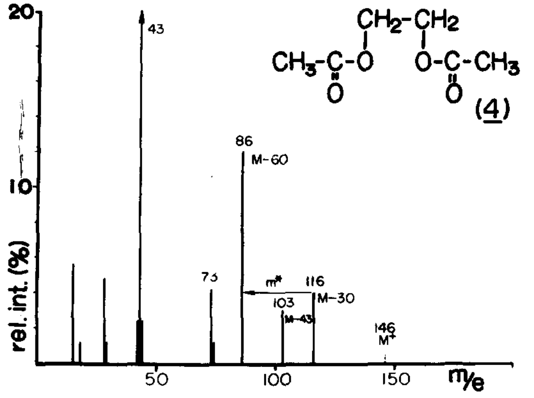


FIG. 1.
Mass Spectrum of Ethyleneglycol Diacetate (70 eV)

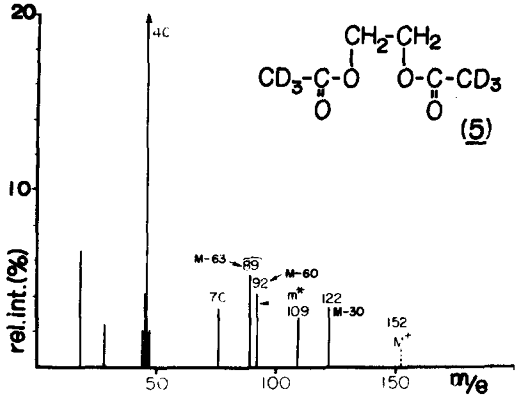


FIG. 2.
Mass Spectrum of Ethyleneglycol Ditrideuteroacetate (70 eV)

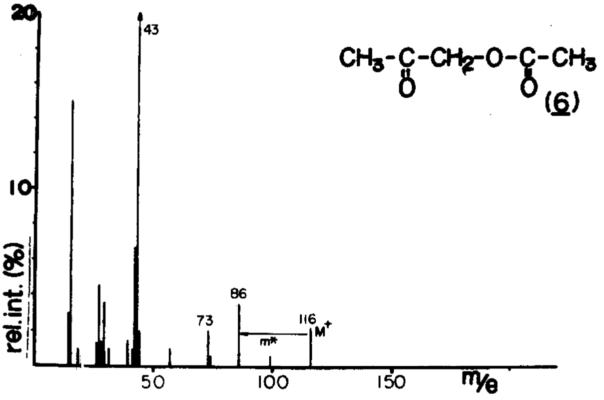


FIG. 3.
Mass Spectrum of Acetol Acetate (70 eV)

This two step expulsion has been established by measuring the mass spectra of ethylene glycol diacetate 4[1), its d_6-analog 5 and acetol acetate 6 (Figs. 1, 2, 3). Ethylene glycol diacetate 4 (M^+ at m/e 146 not observed)[1) shows peaks at m/e 116, 103, 86, 73 and 43. In the d_6-acetate 5, the m/e 116 and 103 peaks are shifted 6 m.u. higher to m/e 122 and 109, respectively, while the m/e 73 and 43 peaks are shifted 3 m.u. higher to 76 and 46, respectively; on the other hand, the m/e 86 peak in 4 is shifted to m/e 89 and 92.

The data from labeling experiments can be interpreted as depicted in Fig. 4. The loss of 30 m.u. from the molecular ion (not detected) to give rise to the m/e 116 ion is due to loss of CH_2O from the non-acetoxyl moiety containing C_1 or C_2, and not from the acetoxyl groups. The m/e 86 peak owes its genesis to the elimination of acetic acid from the molecular ion and the loss of a second CH_2O fragment from the ion with m/e 116 as demonstrated by its shift to m/e 89 and 92 in the spectrum of the d_6-analog 5; expulsion of the second CH_2O is further supported by the presence of a metastable ion at m/e 63.8. The fact that the m/e 116 ion corresponds to the acetol acetate ion 6 is substantiated by the striking similarity between the spectra of the original diester 4 and authentic acetol acetate 6 (Figs. 1 and 3).

The ion m/e 73 arises from a simple fission of the C_1-C_2 bond in 4, while the most abundant peak at m/e 43 is due to the acetylium ion originating from the acetoxyl group. Although at first sight, the m/e 103 peak might be regarded as originating from the loss of an acetyl radical from the molecular ion, this is not the case since it appears at m/e 109 in the deuterated analog. This evidence suggests that it is most probably due to the protonated acetic anhydride 7 2).

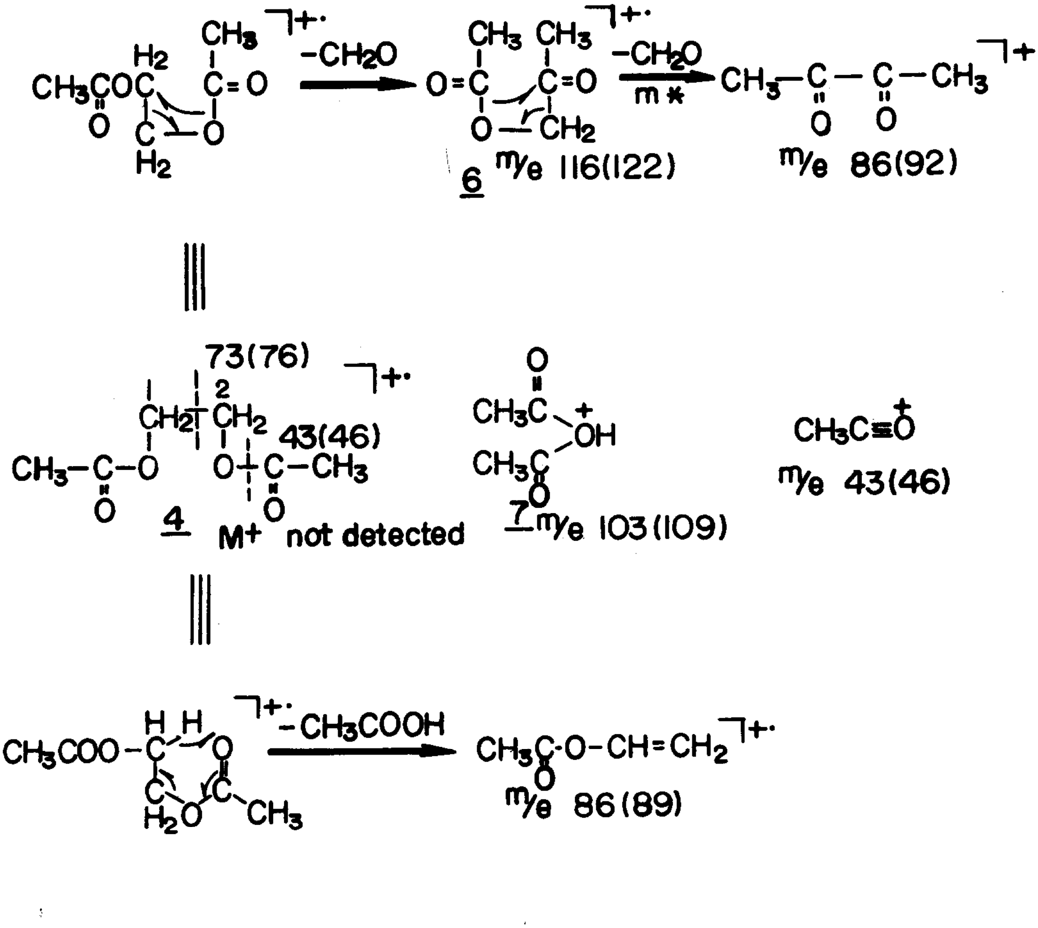


FIG. 4.

Mass Fragmentation of Ethylene glycol Diacetate (4). Parenthesized numerals indicate m/e values of the d_6-analog 5.

The consecutive expulsions of two carbonyl fragments is also clearly demonstrated in the diacetates of 1, 2-propanediol 8, 2, 3-butanediol 9, 1, 2-butanediol 10, 2-methyl-2, 3-butanediol 11 and pinacol 12. (A second expulsion is not observed in this case). It is worth noting that the larger ketone or aldehyde is eliminated first. Parenthesized numerals in Fig. 5 are peak intensities relative to the most abundant acetylium ion peak.

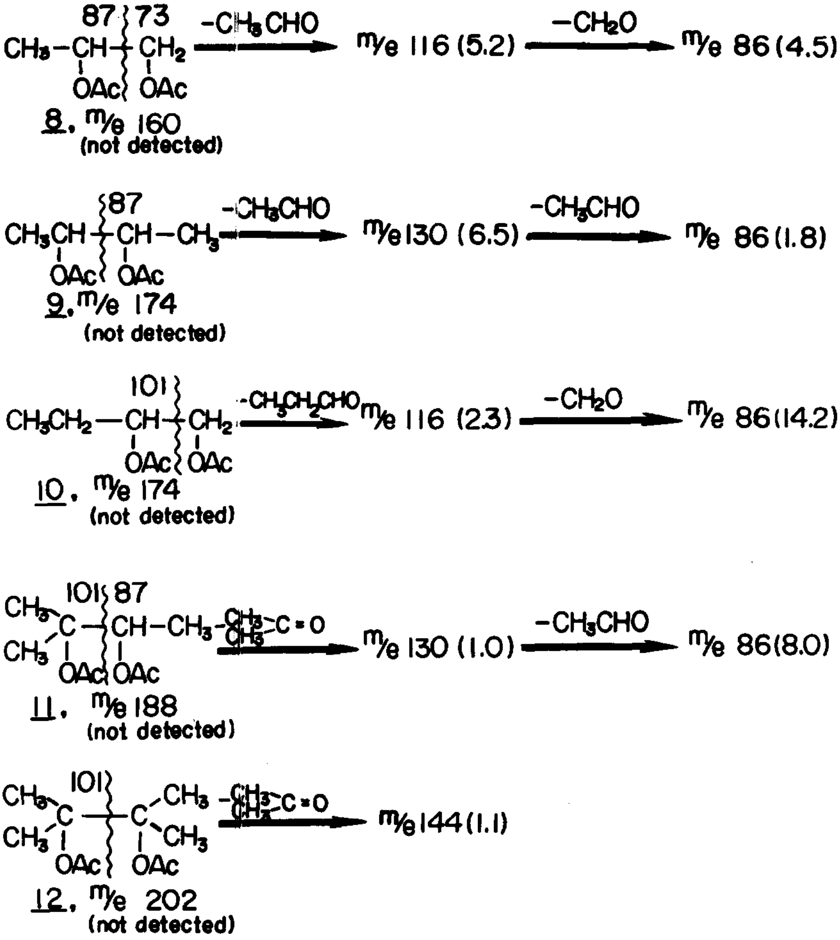


FIG. 5.

Expulsion of Carbonyl Fragments in Acyclic α-glycol Diacetates (70 eV).

The fragmentation of the higher ester shown in Table 1 also follows an exactly identical route, and here again the bulkier group is expelled first.

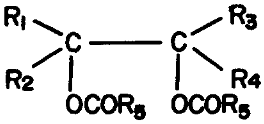
		$M-\begin{matrix}R_1\\R_2\end{matrix}{>}C=O$			$M-\begin{matrix}R_1\\R_2\end{matrix}{>}C=O-\begin{matrix}R_3\\R_4\end{matrix}{>}C=O$		
	Mol. Wt.	m/e	20 eV	70 eV	m/e	20 eV	70 eV
			rel.	int.		rel.	int.
Ethylene glycol							
dipropionate	174	144	0.5	0.4	114	3.3	2.4
di-n-butyrate	202	172	0.5	0.5	142	1.8	1.6
1, 2-Propanediol							
dipropionate	188	144	7.1	2.1	114	21.6	6.6
di-n-butyrate	216	172	4.8	3.1	142	2.9	1.8
2, 3-Butanediol							
dipropionate	202	158	12.4	3.2	114	33.8	7.2
di-n-butyrate	230	186	3.3	2.0	142	23.0	12.5
1, 2-Butanediol							
dipropionate	202	144	4.0	1.1	114	23.8	6.6
di-n-butyrate	230	172	6.3	1.2	142	11.7	5.2

TABLE 1.

Expulsion of Carbonyl Fragments in Higher Esters of α-glycols.
(Intensities are relative to base peak due to $R_5C{\equiv}O^+$).

Thus it appears that the loss of two carbonyl moieties is a general phenomenon encountered in the fragmentation of α-glycol diesters.

Acknowledgement.

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References.

1) Mass spectra were determined with a Hitachi RMU-6D instrument (Nier-Johnson type), equipped with an all-glass heated inlet system (120-140°). The ionizing voltages were 20 and 70 eV.

2) K. Biemann, D. C. DeJongh and H. K. Schnoes, J. Am. Chem. Soc., **85**, 1763 (1963).