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SMALL RING COMPOUNDS-III.[1a)]
A STUDY ON [4.3.2]-, [5.3.2]-, AND [4.4.1]PROPELLANONE ACETALS

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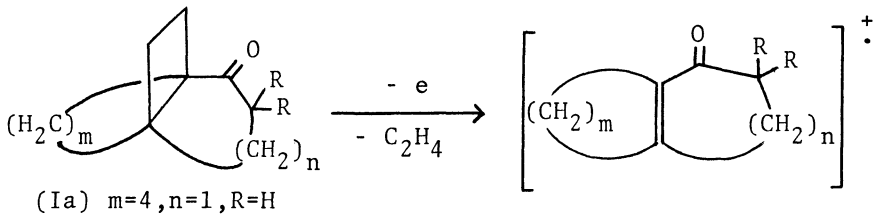
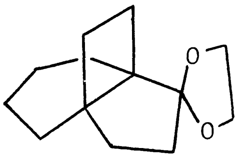
The particular mass spectral behavior of [4.3.2]propellan-7-one and [5.3.2]propellan-2-one ethylene acetals, and 11,11-dimethoxy and diethoxy[4.4.1]propellanes is discussed.

We previously reported[1a)] that [4.3.2]propellan-7-one (Ia) and [5.3.2]propellan-2-one (II), containing a cyclobutane ring, exhibited characteristic mass spectral behavior because of the large strain arising from three dimensionally fused rigid ring system, i.e., "spatial compression" exclusively gave rise to the cleavage of the cyclobutane ring to form enone cations.[1b,c)] We wish now to discuss the particular mass spectral behavior of propellanone acetals (IIIa)-(VI).

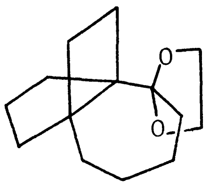
The acetals[2)] (IIIa) and (IV) were synthesized by acetalization of the corresponding propellanones (Ia) and (II) with ethylene glycol in benzene in the presence of trace amounts of *p*-toluenesulfonic acid. The acetals (V)[3)] and (VI) were synthesized by treatment of (VII) with silver nitrate in methanol and ethanol, respectively.



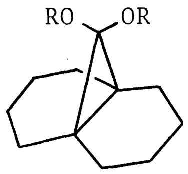
(Ia) m=4,n=1,R=H
(Ib) m=4,n=1,R=D
(II) m=3,n=3,R=H



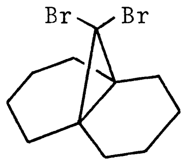
(IIIa)



(IV)



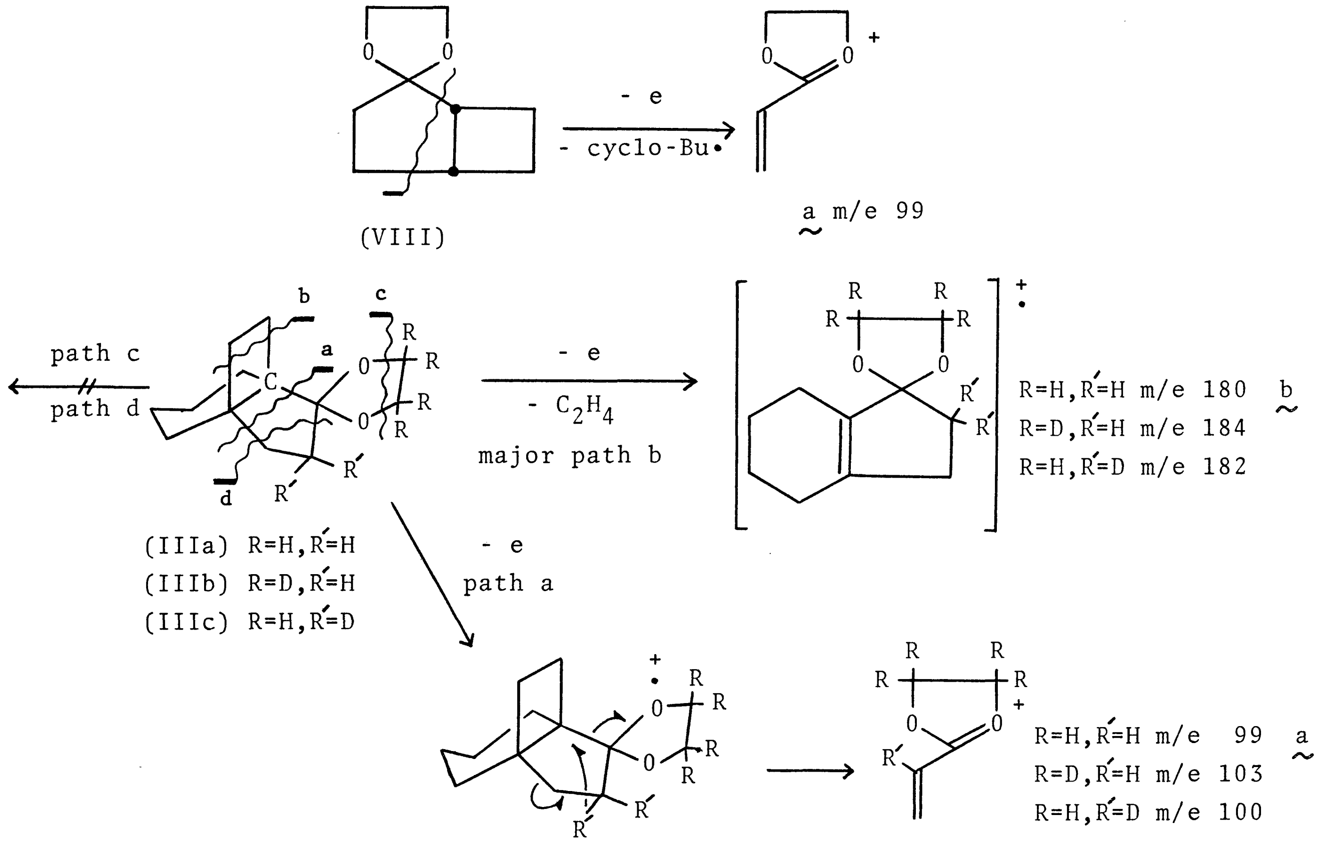
(V) R=Me
(VI) R=Et



(VII)

The energy of the electron beam is generally maintained at 70 eV, but such a large input of energy may be unfavorable to make a search for primary bond fission of strained small ring compounds. We obtained, therefore, the mass spectra at 14 eV (Table 1). First, we examined the spectrum of *cis*-bicyclo[3.2.0]heptan-2-one ethylene acetal (VIII), containing a cyclobutane and a cyclopentanone ethylene acetal segments, which constituted the skeleton of the propellanone acetal (IIIa). In the case of the bicyclic system (VIII), the strained cyclobutane ring was not cleaved at all, but preferential α-cleavage occurred to generate a common ion of m/e 99 a.4)

In contrast with (VIII), the propellanone ethylene acetal (IIIa) generated a predominant fragment of m/e 180 b , corresponding to loss of ethylene from the cyclobutane ring, besides the ion a . Since there might have been the possibility of ethylene loss from the ethylene acetal bridge (path c) or α,β-position with respect to the acetal group (path d), we examined the spectra of deuterium labelled acetals (IIIb) and (IIIc)5) to obtain more exact evidence for cyclobutane cleavage. The acetals (IIIb) and (IIIc) generated an ion of m/e 184 and an ion of m/e 182, respectively. However, an ion, corresponding to loss of deuterated ethylene (C_2D_4 or $C_2H_2D_2$), was not observed. Consequently, it may be concluded that the propellanone acetal (IIIa) fragments by cyclobutane cleavage to generate the bicyclic ion b (path b), in preference to competitive α-cleavage to generate the ion a (path a)(Scheme 1). The characteristic mass spectral behavior of (IIIa), as well as that of (Ia),1a) may be caused by "spatial compression".

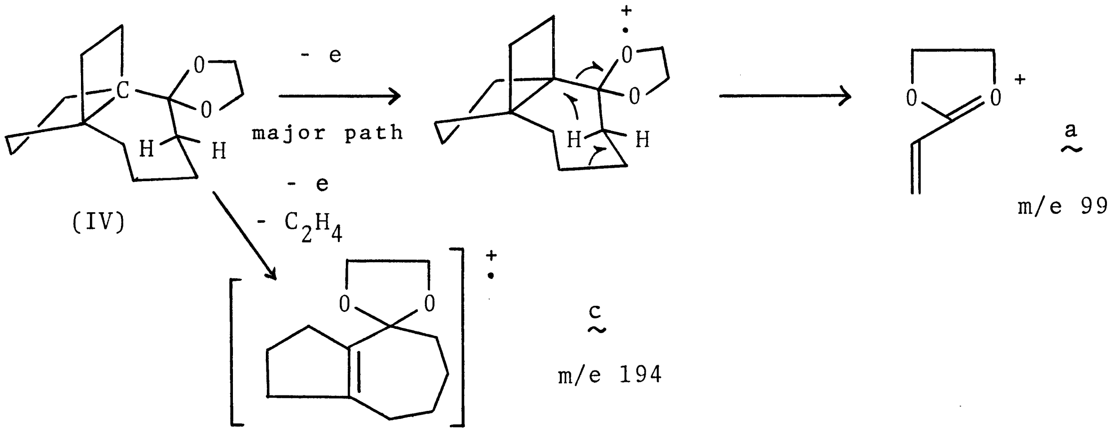


Scheme 1

Table 1 Mass spectra of *cis*-bicyclo[3.2.0]heptan-2-one ethylene acetal (VIII), propellanone ethylene acetals (IIIa), (IIIb), (IIIc), and (IV) at 14 eV.

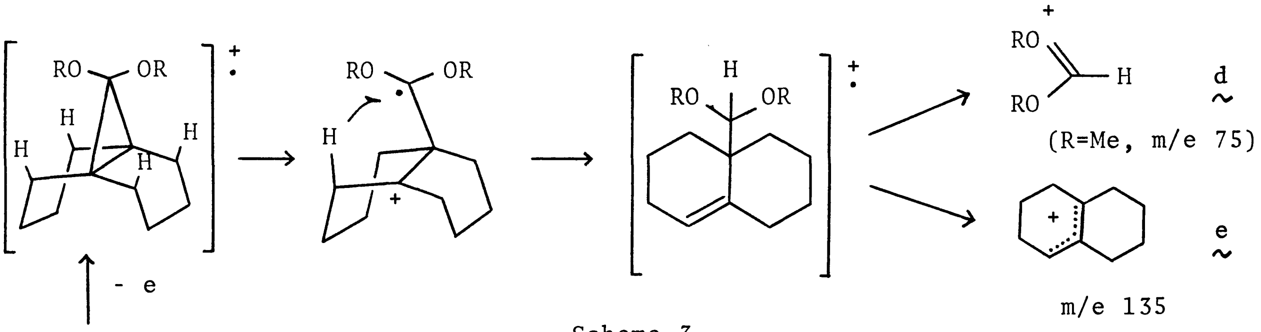
Ethylene acetals	m/e(I% rel.)
(VIII)	154(100,M^+) 99(62)
(IIIa)	208(100,M^+) 180(60) 99(52)
(IIIb)	212(100,M^+) 184(58) 103(40)
(IIIc)	210(100,M^+) 182(47) 100(<45)
(IV)	222(21,M^+) 194(10) 99(100)

On the other hand, the propellanone ethylene acetal (IV) underwent α-cleavage to form the ion a rather than cyclobutane cleavage to form an ion c . From the molecular model consideration⁶⁾ for (IV) and (IIIa), it is suggested that the distance between a bridgehead carbon and α-hydrogens adjacent to the acetal group of (IV) is considerably shorter (about 2.5 Å) than that of (IIIa) (about 2.8 Å). The former situation is so favorable to hydrogen transfer that α-bond fission may be promoted (Scheme 2).



Scheme 2

In connection with above study, we examined the spectra of 11,11-dialkoxy[4.4.1]-propellanes (V) and (VI). It may be considered that degradation of the above compounds gives species generated by hydrogen transfer rather than dioxycarbene species⁷⁾ because of existence of four proximate α-hydrogens adjacent to cyclopropane ring of (V) and (VI). As expected, both (V) and (VI) exhibited the peaks of m/e 75 and/or m/e 135, shown in Table 2. The former is ascribable to an ion d (R=Me) and the latter to an ion e (Scheme 3). Namely, one of the four axial hydrogens migrates to the acetal part when α-bond with respect to the acetal group in the cyclopropane ring is cleaved, resulting in the formation of the ions d and e . Further study for (V) and (VI) is in progress and will be reported in detail.



(V) R=Me
(VI) R=Et

Scheme 3

Table 2 Mass spectra of 11,11-dimethoxy[4.4.1]propellane (V) and 11,11-diethoxy[4.4.1]propellane (VI) at 14 eV and 70 eV.

Acetals	m/e(I%rel.)	
	14 eV	70 eV
(V)	210(100,$M^{+}_{\cdot}$) 75(69)	210(54) 135(35) 75(100)
(VI)	238(100,M^{+}) 135(19)	238(20) 135(100) others

REFERENCES AND NOTES

1a) Part II; A.Kunai, K.Yorihiro, T.Hirata, and Y.Odaira, *Tetrahedron*, 29, 1679 (1973).

b) Further evidence for cyclobutane cleavage was obtained using a deuterium labelled propellanone (Ib).

c) A certain spiro ketone is known as a cyclanone without α-cleavage; W.D.Weringa, Org. Mass Spectrometry, 5, 1055 (1971).

2) Each acetal (IIIa)-(VI) was thermally stable liquid, and was purified by preparative glpc.

3) D.B.Ledrie, *J. Org. Chem.*, 37, 1439 (1972).

4) It is well known that a common cyclanone ethylene acetal, such as cyclopentanone ethylene acetal, generates the α-cleavage ion a ,exclusively; H.Budzikiewicz, C.Djerassi, and D.H.Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco (1964).

5) The deuterated acetal (IIIb) was obtained from (Ia) and ethylene glycol-d_4, and the acetal (IIIc) was obtained by acetalization of deuterated propellanone (Ib).

6) The skeleton of (IIIa) may be composed of a nearly planar cyclobutane, a puckered cyclopentane, and a chair cyclohexane (minimizing H-H and H-O repulsion between rings). Similarly, the skeleton of (IV) may be composed using a chair cycloheptane in place of the cyclohexane.

7) Dioxycarbene species are generated by pyrolysis, photolysis, or electron impact in the case of highly strained acetals having no hydrogen to be abstracted, such as norbornadienone acetals[7a)] and 2,3-diphenylcyclopropenone ethylene acetal.[7b)]

a) R.W.Hoffmann et al., *Tetrahedron Lett.*, 4819 (1970).

b) T.Teramoto, T.Ishii, K.Kimura, and Y.Odaira, unpublished data.

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