Tetrahedron. 1967. Vol. 23. pp. 321 to 333. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES IN MASS SPECTROMETRY—XVIII[1]

THE RELATIVE EASE OF LOSS OF ALKYL RADICALS FROM ETHYLENE ACETALS AND KETALS UPON ELECTRON IMPACT

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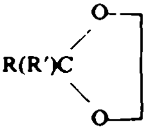
Abstract—Since compounds of the general formula  fragment specifically by loss of R and R′ radicals upon electron impact, the mass spectra of an extensive series of ethylene acetals (R = alkyl and R′ = H) and ketals (R and R′ = alkyl) have been used to indicate the relative ease of loss of alkyl radicals in the mass spectrometer. It is found that the ease of loss of n-alkyl radicals follows the order heptyl > hexyl > pentyl > butyl > propyl > ethyl > methyl ≫ hydrogen. In general, a tertiary radical is more readily expelled than an isomeric secondary radical, which in turn is expelled more readily than a primary radical. Although the results follow an order which might be expected in terms of relative radical stabilities, it is concluded that the method can only give a rough qualitative guide to the relative stabilities of radicals.

INTRODUCTION

THE fragmentation reactions which occur in ethylene acetals[2] and ethylene ketals[3-8] are known to be some of the most specific which are induced by electron impact. For example, the ethylene ketals (I) derived from simple acyclic ketones consistently show only two principal cleavages;[6] these correspond to the loss of the radicals $R^{1}\cdot$ and $R^{2}\cdot$ and account for about 50% of the total ion current in 70 eV spectra. To illustrate this behaviour, the mass spectrum of 2-n-pentyl-2-methyl-1,3-dioxolane (II) is reproduced in Fig. 1. The spectrum contains no molecular ion, but exhibits only two significant peaks in the high mass region at *m/e* 140 (*a*, M—CH_3) and *m/e* 87 (*b*, M—n-C_5H_{11}). The remaining significant peak in the spectrum occurs at *m/e* 43 ($CH_3C{\equiv}O^{+}$, h.r.[9]) and is shown by an appropriate metastable peak in this spectrum (and also by metastable peaks in the spectra of related compounds) to arise from *b* by the elimination of C_2H_4O.[10]

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[1] Part XVII, *Tetrahedron* **23**, 305 (1967).

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

[3] G. V. Mutzenbecher, Z. Pelah, D. H. Williams, H. Budzikiewicz and C. Djerassi, *Steroids* **2**, 475 (1963).

[4] Z. Pelah, D. H. Williams, H. Budzikiewicz and C. Djerassi, *J. Amer. Chem. Soc.* **86**, 3622 (1964).

[5] H. Audier, A. Diara, M. Durazo, M. Fétizon, P. Foy and W. Vetter, *Bull. Soc. Chim. Fr.* 2827 (1963).

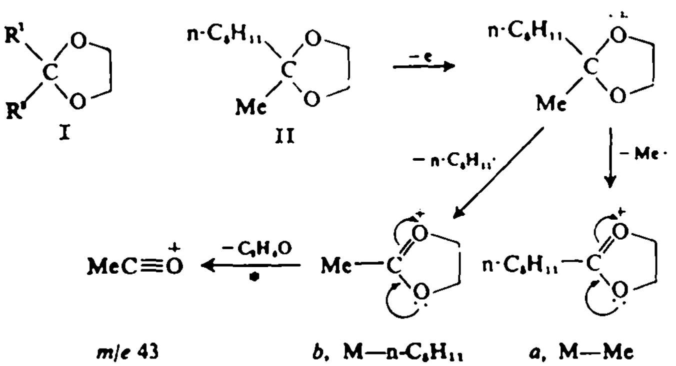
[6] H. Audier, M. Fétizon, J.-C. Gramain, J. Schalbar and B. Waegel, *Bull. Soc. Chim. Fr.* 1880 (1964).

[7] H. Audier, J. Bottin, A. Diara, M. Fétizon, P. Foy, M. Golfier and W. Vetter, *Bull. Soc. Chim. Fr.* 2292 (1964).

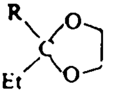
[8] H. Audier, M. Fétizon and J.-C. Gramain, *Bull. Soc. Chim. Fr.* 3088 (1965).

[9] The abbreviation "h.r." is used to signify ions whose composition has been established by high resolution measurements.

[10] Consistent with our formulation *b*, all ethylene ketals derived from methyl ketones which we have investigated give appreciable *m/e* 43 ions in 70 eV spectra, whereas the corresponding ketals from ethyl ketones furnish *m/e* 57 ions ($C_2H_5C{\equiv}O^{+}$).



The fragmentation reactions are thought to be specific because either of the oxonium ions, formed by loss of R^1 or R^2 as radicals from the molecular ion of I, may be stabilized by delocalization of the positive charge between the two equivalent oxygen atoms and the intervening sp^2 hybridized carbon atom (see *a* and *b*). It is apparent, both from Fig. 1 and from published data,[6] that in these two specific fragmentation reactions, groups R^1 and R^2 are lost to different extents. Fétizon *et al.*[6] comment that a substituent in the α-position of R^1 or R^2 facilitates the elimination of that group and illustrate this with a series of ethylene ketals derived from butyl ethyl ketones (III–V). The greater the α-branching of the butyl group, the greater the proportion of the total ion current carried by the $M—C_4H_9$ ion.



III, R = n-Bu
IV, R = s-Bu
V, R = t-Bu

It was decided to investigate the mass spectra of a wide variety of ethylene acetals (I, R^1 = H, R^2 = alkyl) and ethylene ketals (I, R^1 and R^2 = alkyl) prepared from simple acyclic aldehydes and ketones, respectively. The aim was to evaluate precisely the effect of the relative size of R^1 and R^2 (see I), and of branching in R^1, on the relative abundance of $M—R^1$ and $M—R^2$ ions. The final objective was, if possible, to reach generalizations or conclusions about the relative ease of loss of alkyl radicals in mass spectrometry.

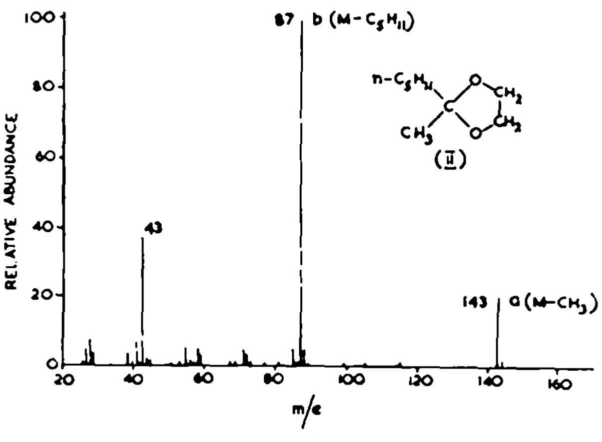
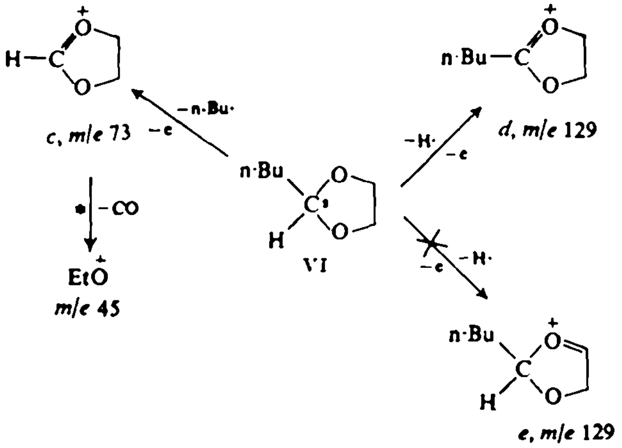


Fig. 1. The 70 eV mass spectrum of 2-n-pentyl-2-methyl-1,3-dioxolane (II).

DISCUSSION

The spectrum (Fig. 1) of a typical ketal (II) has been illustrated in the introductory section. For purposes of clarity, the spectrum (Fig. 2) of a typical acetal, 2-n-butyl-1,3-dioxolane (VI) is reproduced at the outset of the discussion. The only abundant ions are *m/e* 73 (*c*, M—C_4H_9) and *m/e* 45. There is no molecular ion, but a 4% M—H peak which is due to species *d*. The possibility that the M—H ion could correspond significantly to an ion *e*, formed by loss of hydrogen from C-4 or C-5, is excluded by the observation that the mass spectra of ethylene *ketals*, which have no hydrogen in the C-2 position do not contain M—H ions. Characteristic of all ethylene acetal spectra which we have obtained is the ion at *m/e* 45 (usually 10–20% of the base peak in 70 eV spectra) which has the composition $C_2H_5O^+$ (h.r.). Metastable peaks in the spectra establish its formation from *m/e* 73 (*c*, $C_3H_5O_2^+$, h.r.) by the elimination of carbon monoxide.



If one makes the statement that since the relative abundances of M—CH_3 and M—C_5H_{11} ions from II are 21% and 100% (see Fig. 1), the relative ease of loss of a n-pentyl radical is 4·8 times greater than that of a methyl radical, a number of assumptions and approximations are made which should be discussed.

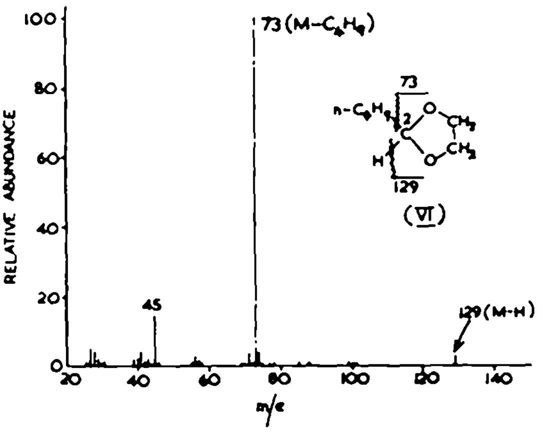


FIG. 2. The 70 eV mass spectrum of 2-n-butyl-1,3-dioxolane (VI).

First, since a metastable peak has established the decomposition of *m/e* 87 (*b*, Fig. 1) to *m/e* 43, the relative abundance of *m/e* 87 does not completely express the extent of the reaction in which a pentyl radical is eliminated. However, this error may be effectively eliminated by obtaining the spectra at 15 eV instead of 70 eV. In the 15 eV spectra of 12 ethylene ketals derived from methyl alkyl ketones no less than 85% of the total ion current is on average carried by the $M—R^1$ and $M—R^2$ ions under discussion, as opposed to an average of only 56% in the 70 eV spectra (the 15 eV spectrum of II is reproduced in Fig. 3). The corresponding figures for the 10 ethylene acetals investigated are 91% of the total ion current on average carried by M—H and M—R ions in the 15 eV spectra, against an average of 61% in the 70 eV spectra. *Therefore, the assumption that the relative abundances of* $M—R^1$ *and* $M—R^2$ *ions (or* M—H *and* M—R *ions) measure the relative extent to which the molecular ion chooses to eliminate the alternative radicals is a realistic assumption for* 15 eV *spectra.*

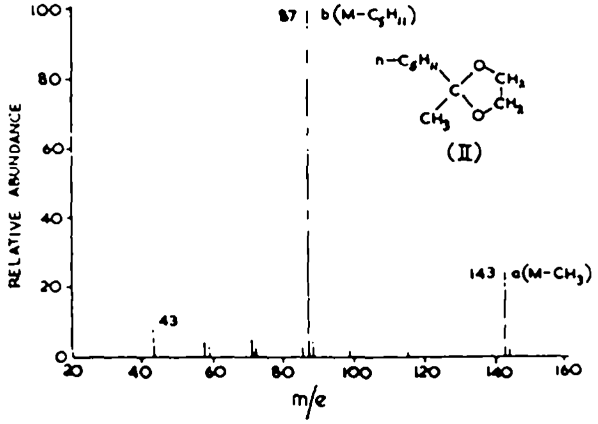


FIG. 3. The 15 eV mass spectrum of 2-n-pentyl-2-methyl-1,3-dioxolane (II).

Second, the statement assumes that the difference in energy of formation of the radicals is much greater than that of the ions, and so is the controlling factor. For example, it is assumed that the difference in energy of formation of CH_3 and C_5H_{11} controls the relative abundances of *a* and *b*. This assumption is intuitively reasonable since ions *a* and *b* have very similar chemical structures and identical delocalised systems. Indeed, if there were any significant difference in energy of formation between *a* and *b*, *a* should be favoured relative to *b* because of greater stabilisation of the positive charge by the larger inductive effect of a n-pentyl group relative to a methyl group.[11] Experimentally, *b* is greatly favoured over *a*, (see Fig. 1), as would be expected if the difference in energy of formation of the CH_3 and C_5H_{11} radicals were the controlling factor.

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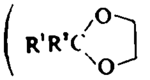
[11] This argument (by analogy to ground state mechanistic organic chemistry) assumes that the oxonium ions are formed in their ground states. Since the mass spectra of ethylene ketals[3-8] can be precisely predicted in terms of ground state mechanistic concepts, this assumption seems reasonable, especially for 15 eV spectra. With reference to this argument, it is noteworthy that the $C_7H_5O^+$ ion, occurring in the mass spectra of a series of benzoyl compounds, is formed in the ground state.[12]

[12] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.* **88**, 528 (1966); see also P. Natalis and J. L. Franklin, *J. Phys. Chem.* **69**, 2935, 2943 (1965).

Finally, conclusions as to the relative ease of loss of two radicals R^2 and R^3 formed from similar ketals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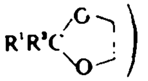
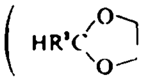


or acetals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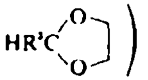
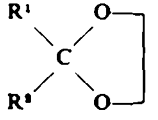
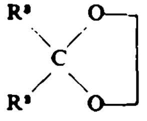


will only be valid if the two ketals or two acetals have very similar ground state energies. Any cases where this condition seems unlikely to be satisfied will be indicated subsequently.

Having demonstrated that our two basic assumptions are realistic at 15 eV, we may conclude that if the M—R^1 ion from I is of greater abundance than the M—R^2 ion, then the formation of the radical R^1 is energetically more favourable than of R^2. The difference in the relative abundances of M—R^1 and M—R^2 ions will give a qualitative measure of the difference in stability between the R^1 and R^2 radicals. Moreover, if an M—R^2 ion from a ketal VII containing R^2 and R^3 groups is more abundant than the M—R^3 ion, then clearly the formation of the R^1 radical is greatly favoured over the formation of the R^3 radical; the deduction is possible from the spectra of the ketals I and VII, because these compounds contain a common alkyl group (R^2).


I


VII

Experimental conditions

If we are to reach valid generalizations about the relative ease of loss of alkyl radicals in the mass spectrometer, it is essential that the relative abundances of ions in the spectra studied should be reproducible. The effect of the following variables on the spectra was therefore investigated.

A. *Heated inlet temperature.* A series of spectra of 2-n-butyl-2-ethyl-1,3-dioxolane (III) were obtained at temperatures of the heated inlet system ranging from ambient up to 250°. There was no significant effect on the relative intensities of ions over this temperature range.

B. *Source temperature.* Spectra of the same ethylene ketal (III) were also studied at various source temperatures in the range 150–330°. A consistent trend towards greater abundance of lower mass fragments occurred as the source temperature was raised.

The ions M-29 and M-57 are the two principal fragments caused by elision of ethyl and butyl groups respectively, while *m/e* 57 and *m/e* 29 are the two next most abundant ions at 70 eV. This latter pair of ions increases in relative abundance by a factor in excess of 1·5 over the source temperature range 150–330° (see Table 1). The M—C_2H_5 ion shows a slight decrease in intensity relative to the M—C_4H_9 ion; presumably the former fragments slightly more easily at the higher temperatures.

So it was concluded that the most consistent results were to be obtained if the spectra were obtained at the lowest constant source temperature. In fact, most of the ketals and acetals showed a much smaller temperature sensitivity.

C. *Random variation*. Consecutive spectra of the same compound were shown to be virtually identical. If there was a time interval between two spectra, or the mass spectrometer had been re-adjusted, some quantitative differences were apparent. So for a series comparison the best results were obtained by running the spectra in the shortest possible time, and preferably consecutively.

There were still some random variations in relative abundances, to allow for which, it was necessary *either* to obtain several consecutive spectra of each compound *or* to obtain one spectrum for each, but to repeat the whole series several times. All results presented have therefore been averaged in one of these ways.

TABLE 1. VARIATIONS IN RELATIVE ABUNDANCE OF FRAGMENTS OF 2-n-BUTYL-2-ETHYL-1,3-DIOXOLANE WITH SOURCE TEMPERATURE

Source Temp	Relative abundances			
	M-29	M-57	*m/e* 57	*m/e* 29
150°	67%	100%	33%	16%
170	67	100	34	17
190	67	100	36	18
210	59	100	37	18
240	64	100	46	24
270	66	100	44	23
300	63	100	49	27
330	61	100	51	29

D. *Electron beam energy*. Variation of electron beam energy was shown to have a significant effect on the relative intensities as indicated previously. Fig. 4 shows the variation of ion current carried by the two principal cleavages (as percentage of total, higher than *m/e* 40) with electron beam energy.

The curves show the percentage ion current remaining steady or falling a little from 70 eV to the 40–50 eV region when it begins to rise quickly. It continues to do so until the lowest value of beam energy capable of ionising and fragmenting the molecules (10–12 eV) when well over 90% of the total ion current is carried by the two main cleavages.

However certain disadvantages were found when running a series of compounds at low energies. For instance there was a relatively high random error. A difference in energy of less than 0·5 eV would alter the general intensity and relative intensities of a spectrum by a significant amount. In general much greater care was necessary to ensure that conditions were identical and even then errors were slightly greater. It was decided to obtain two sets of results—one exclusively at low electron beam energies, and the other at the standard figure of 70 eV.

RESULTS

The results obtained from a series of ethylene acetals at an electron beam energy of 70 eV are shown in Table 2. The corresponding results for 15 eV spectra are summarized in Table 3. The total ion current values are based upon the summation of all ions above *m/e* 40.

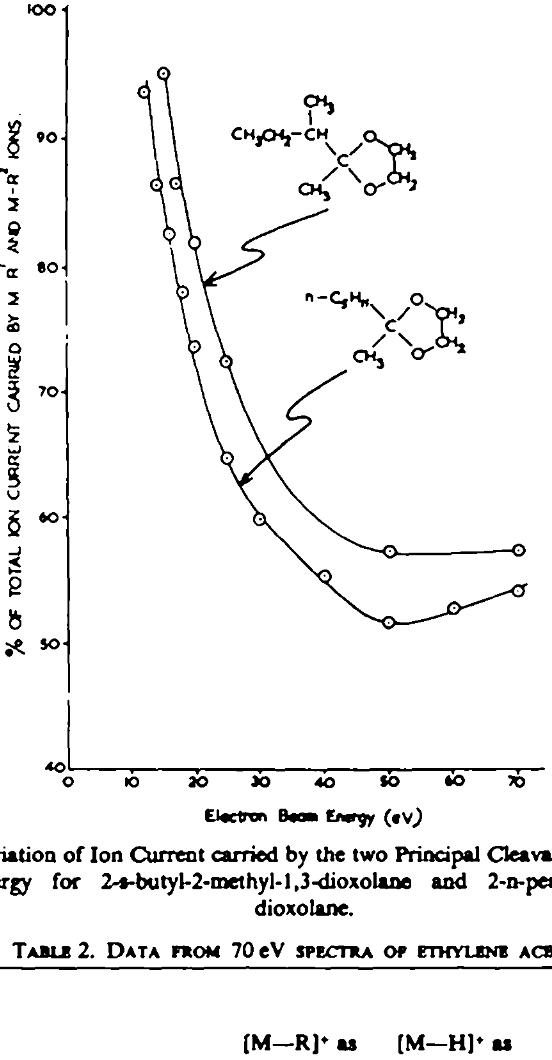


FIG. 4. Variation of Ion Current carried by the two Principal Cleavages with Electron Beam Energy for 2-s-butyl-2-methyl-1,3-dioxolane and 2-n-pentyl-2-methyl-1,3-dioxolane.

TABLE 2. DATA FROM 70 eV SPECTRA OF ETHYLENE ACETALS

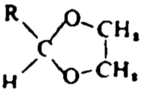
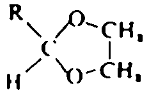
Group R in compounds 	Ratio of intensity $[M-R]^+/[M-H]^+$	$[M-R]^+$ as percentage of total ion current	$[M-H]^+$ as percentage of total ion current	$[M-R]^+ + [M-H]^+$ as percentage of total ion current
Me	9·1 : 1	43·0	4·8	47·8
Et	17·0 : 1	57·3	3·2	61
Pr^n	23·3 : 1	60·6	2·5	63
Bu^n	27·8 : 1	68·0	2·4	70
Pen^n	31·3 : 1	72·3	2·2	75
Hex^n	40·0 : 1	78·0	1·7	80
Hep^n	47·0 : 1	80·0	1·7	82
Pr^n	23·3 : 1	60·6	2·5	63
Pr^i	31·3 : 1	64·8	1·9	67
Bu^n	27·8 : 1	70·0	2·3	72
Bu^{sec}	37·0 : 1	72·6	1·8	74
Bu^t	52·7 : 1	65·6	1·1	67

TABLE 3. DATA FROM 15 eV SPECTRA OF ETHYLENE ACETALS

Group R in Compounds 	Ratio of intensity $[M-R]^+/[M-H]^+$	$[M-R]^+$ as percentage of total ion current	$[M-H]^+$ as percentage of total ion current	$[M-R]^+ + [M-H]^+$ as percentage of total ion current
Me	9·1:1	62·3	6·9	69
Et	17·0:1	75·0	4·4	79
Pr^n	20·9:1	82·1	3·4	85
Bu^n	23·3:1	84·6	3·4	88
Pen^n	26·4:1	93·9	3·6	98
Hex^n	31·3:1	93·7	2·7	96
Hep^n	33·3:1	94·6	2·6	97
Pr^n	20·9:1	82·1	3·4	85
Pr^i	31·3:1	92·9	2·8	96
Bu^n	23·3:1	84·6	3·4	88
Bu^{sec}	33·3:1	93·6	2·6	96
Bu^t	52·7:1	90·8	1·6	92

In Fig. 5 and Fig. 6 the ratio of the relative abundances of M—R and M—H ions is plotted against the number of carbon atoms in R for both 70 eV (Fig. 5) and 15 eV (Fig. 6) spectra. It was shown earlier that at 15 eV the sum of M—R and M—H ion abundances represented such a high proportion of the total ion current that the relative abundances must closely represent the actual differences in ease of loss of the alkyl radical (R·) and a hydrogen atom (H·), and Fig. 6 therefore summarizes these differences. At 70 eV (Fig. 5), the proportion of the total ion current carried by M—R plus M—H fragments is considerably lower, and it can no longer be assumed that secondary fragmentation of either M—R or M—H has not distorted the original abundance. However, although there are some quantitative differences in the ratios, the results summarized in Fig. 5 and Fig. 6 are qualitatively the same. Both figures show that the ease of loss of a straight chain alkyl radical is greatly favoured over loss of a hydrogen radical in the order heptyl > hexyl > pentyl > butyl > propyl > ethyl > methyl.[13] An isopropyl radical is lost more readily relative to a hydrogen radical than a n-propyl radical,[14] and similarly a s-butyl radical is eliminated more

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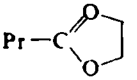
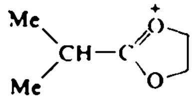
[13] Views as to the effect of radical size on ease of radical elimination from ion-radicals have been expressed previously and are consistent with our findings; see H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* p. 29. Holden-Day, San Francisco (1964) and S. J. Di Mari, J. H. Supple and H. Rapoport, *J. Amer. Chem. Soc.* **88**, 1226 (1966).

[14] The nature of the results for propyl versus isopropyl groups convincingly supports our arguments. The change in ratios (see column 2 in Table 2 and Table 3) must either be explained in terms of a greater stability of A over B *or* in terms of easier elimination of an isopropyl radical relative to a propyl radical. The latter is clearly the most reasonable explanation.



A



B

readily than a n-butyl radical. At either 15 eV (Fig. 6) or 70 eV (Fig. 5) the t-butyl radical is most readily expelled and all the results are consistent with an order of radical stabilities, tertiary > secondary > primary; this latter result is consistent with previous literature data.[15,16]

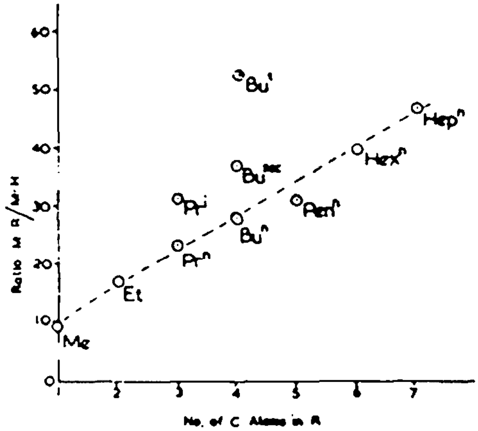
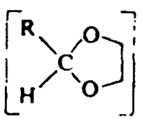


FIG. 5. Plot of M—R/M—H Abundance Ratio against no. of C-Atoms in R for a series of 70 eV spectra of Ethylene Acetals



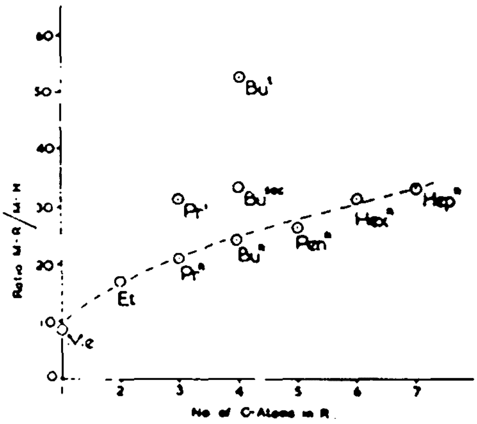
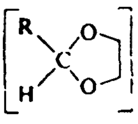


FIG. 6. Plot of M—R/M—H Abundance Ratio against no. of C-Atoms in R for a series of 15 eV spectra of Ethylene Acetals



The corresponding results obtained for a series of ethylene ketals at 70 eV and 15 eV are shown in Table 4 and Table 5, respectively, and in Fig. 7 and Fig. 8, respectively.

The plots in Fig. 7 and Fig. 8 of $M-R/M-CH_3$ against the number of carbon atoms in R very much resemble the corresponding plots of M—R/M—H (Fig. 5 and Fig. 6) for the straight chain alkyl groups; the order of ease of loss of the straight chain alkyl radical is exactly that observed for acetals (heptyl > hexyl > pentyl > butyl > propyl > ethyl).

However, when R is a branched chain alkyl group, there is one rather surprising difference between the results obtained from acetals and those obtained from ketals. When R is iso-propyl there is the expected jump in the ratio compared to R as n-propyl. Similarly, the s-butyl radical is formed considerably more easily, relative to the methyl radical, than the primary n-butyl radical; but the t-butyl group actually registers a lower ratio than the s-butyl group (contrast Fig. 5 and Fig. 6 with Fig. 7

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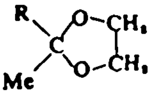
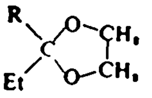
[15] For example, the observation that the bond dissociation energy (D) follows the order $D(C_4H_9—H) > D(s\text{-}C_4H_9—H) > D(t\text{-}C_4H_9—H)$ [D. P. Stevenson, *Disc. Faraday Soc.* **10**, 35 (1951)] may be interpreted in terms of greater stability of more substituted radicals.

[16] C. Walling, *Free Radicals in Solution* pp. 50–51. Wiley, New York (1957); V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities*, p. 123 Arnold, London (1966).

TABLE 4. DATA FROM 70 eV SPECTRA OF ETHYLENE KETALS

Group R—in compounds 	Ratio of intensity $[M-R]^+/[M-Me]^+$ or $[M-R]^+/[M-Et]^+$	$[M-R]^+$ as percentage of total ion current	$[M-Me]^+$ or $[M-Et]^+$ as percentage of total ion current	$[M-R]^+ + [M-Me]^+$ as percentage of total ion current (or $[M-R]^+ + [M-Et]^+$)
Et	3·45:1	30·9	9·1	40
Pr^{n}	4·00:1	40·9	10·1	51
Bu^{n}	4·23:1	44·4	10·5	55
Pen^{n}	4·68:1	48·8	10·3	59
Hex^{n}	5·27:1	51·5	9·8	61
Hep^{n}	5·50:1	54·5	9·9	64
Pr^{n}	4·00:1	40·9	10·1	51
Pr^{i}	6·25:1	46·5	7·3	54
Bu^{n}	4·23:1	44·4	10·5	55
Bu^{sec}	7·51:1	51·1	6·8	58
Bu^{t}	5·56:1	49·9	9·0	59
Bu^{n}	4·23:1	44·4	10·5	55
Bu^{i}	4·49:1	45·4	10·1	56
Pen^{n}	4·68:1	48·8	10·3	59
Pen^{i}	5·56:1	49·7	9·0	60
Pen^{neo}	7·70:1	48·6	6·4	55
				
Bu	1·49:1	37·2	25·0	62
Bu^{i}	1·54:1	37·7	24·5	62

and Fig. 8).[17] These results are consistently reproducible. While one should not be too glib about proposals to rationalise this apparent single anomaly, it is pertinent to note that 2-t-butyl-2-methyl-1,3-dioxolane is, of all the compounds examined, the one whose ground state energy might be expected to be modified most by steric factors.[18] Finally, when the alkyl group is branched at a site which does not directly affect the primary, secondary, or tertiary nature of the radical, the effect of the branching seems to slightly assist the loss of the group (see points for isobutyl

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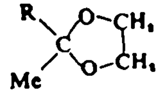
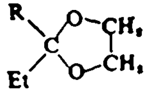
[17] This apparent anomaly is not observed in the results of Fétizon *et al.*[6] which indicate that t-Bu· is expelled slightly more readily from 2-t-butyl-2-ethyl-1,3-dioxolane (V) than is s-Bu· from 2-s-butyl-2-ethyl-1,3-dioxolane (IV). However, the significance of this result in the context of the present paper is open to question, since the instrumental conditions were probably different in the two studies.

[18] At very low energies (~12 eV), the result for the tert-butyl group becomes "normal" (i.e., M—t-Bu/M—Me > M—s-Bu/M—Me). That the 2-t-butyl-2-methyl-1,3-dioxolane definitely behaves anomalously at higher energies is established by the observation that the M—R/M—Me ratio for this compound *increases* with *decreasing* energy of the electron beam; for all other ketals this ratio *decreases* with *decreasing* energy (cf. Tables 4 and 5).

TABLE 5. DATA FROM 15 eV SPECTRA OF ETHYLENE KETALS

Group R—in compounds 	Ratio of intensity $[M-R]^+/[M-Me]^+$ or $[M-R]^+/[M-Et]^+$	$[M-R]^+$ as percentage of total ion current	$[M-Me]^+$ or $[M-Et]^+$ as percentage of total ion current	$[M-R]^+ + [M-Me]^+$ as percentage of total ion current (or $[M-R]^+ + [M-Et]^+$)
Et	2·78:1	50·5	17·9	68
Pr^n	3·13:1	69·4	22·0	91
Bu^n	3·57:1	65·7	18·4	84
Pen^n	3·85:1	65·8	17·1	83
Hex^n	3·92:1	67·9	18·4	86
Hep^n	4·08:1	70·6	17·6	88
Pr^n	3·13:1	69·4	22·0	91
Pr^i	5·00:1	78·1	15·5	94
Bu^n	3·57:1	65·7	18·4	84
Bu^{sec}	5·81:1	79·4	13·6	93
Bu^t	5·71:1	79·6	14·0	94
Bu^n	3·57:1	65·7	18·4	84
Bu^i	3·64:1	66·8	18·6	85
Pen^n	3·85:1	65·8	17·1	83
Pen^i	4·16:1	60·6	14·7	75
Pen^{neo}	5·00:1	62·4	12·7	75
				
Bu^n	1·23:1	44·7	36·4	81
Bu^i	1·28:1	47·2	37·1	84

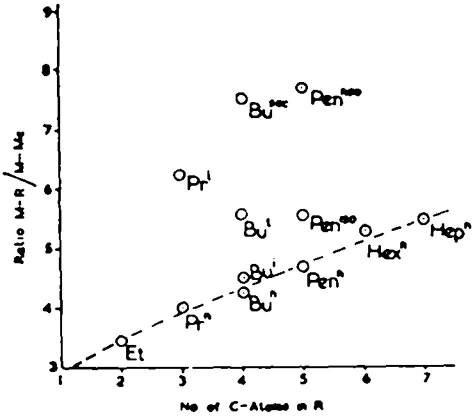
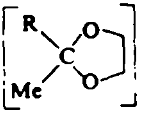


FIG. 7. Plot of M—R/M—CH$_3$ Abundance Ratio against no. of C-Atoms in R for a series of 70 eV spectra of Ethylene Ketals



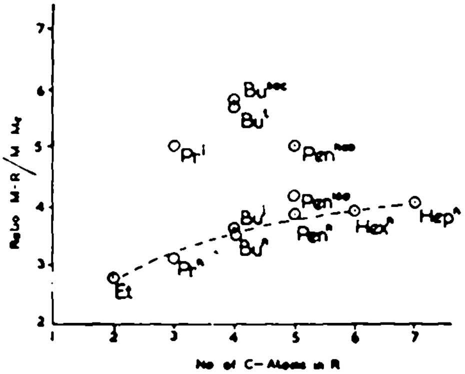
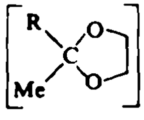


FIG. 8. Plot of M—R/M—CH$_3$ Abundance Ratio against no. of C-Atoms in R for 15 eV spectra of Ethylene Ketals



[$(Me)_2CHCH_2$], isopentyl [$(Me)_2CHCH_2CH_2$] and neopentyl [$(Me)_3CCH_2$] compounds at 15 eV in Fig. 8).[19]

CONCLUSIONS

The results obtained from both acetals and ketals at 70 eV and 15 eV are sufficiently consistent to establish an ordered pattern which may be related to alkyl radical stabilities. Quantitative arguments are ruled out owing to lack of proof of the assumption that it is ease of radical formation *alone* that controls the fragmentation. Almost certainly there will be some contribution from energy differences between ionic species. It is thought that this contribution is small, if not negligible, but it is not possible to prove this rigorously.

TABLE 6. RATIO OF LOSS OF R· TO H·

R	"Obs." (Acetals)	"Calc." (Ketals)
Me	9	9
Et	17	25
Pr^n	21	29
Bu^n	23	32
$Pent^n$	26	35
Hex^n	31	36
$Hept^n$	33	37

So the results give a qualitative, rather than quantitative guide to radical stability. We have summarized this qualitative guide in Table 6, in which the "observed" values are the results from acetal spectra at 15 eV, whereas the "calculated" values, are derived from the 2-methyl-2-alkyl-1,3-dioxolane (ketal) spectra at 15 eV; these ketal results (which were originally expressed relative to loss of CH_3· in Fig. 7 and Fig. 8) have been converted to factors relative to loss of H· by multiplying the observed ratios by 9·1 (which measures the ease of loss of a methyl radical over a hydrogen radical—see Fig. 6). There is a satisfactory qualitative agreement between the two series. By far the greatest difference for an increase of CH_2 is of course observed between hydrogen and methyl radicals and thereafter the difference decreases fairly regularly for each CH_2-group added. It is hoped that our results provide some detailed evidence for the statement, frequently seen in papers dealing with mass spectrometry, that given a choice between the expulsion of two alkyl radicals, the larger radical will be expelled more readily.

EXPERIMENTAL

All mass spectra were obtained using an A.E.I. MS 9 double-focusing mass spectrometer. The heated inlet system was maintained at 200°, and the ion source equilibrium was 215–235°. The electron beam energy was set at 70 eV unless otherwise stated.

Exact mass measurements were made with the resolution set better than 10,000 (10% valley definition) and were correct to within 15 ppm. Heptacosafluorotributylamine was the usual mass standard, but for ions below *m/e* 69 common solvents were used such as acetone.

The sample pressure in the flask was regulated so that the monitor current registered 500–700 arbitrary units (background 30–60). For spectra at 70 eV the multiplier was set by trial and error

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[19] These conclusions are slightly less secure than earlier ones, since the percentage of total ion current carried together by the M—R and M—CH_3 ions when R is isopentyl or neopentyl is less (75%) than in all other cases (>83%) even at 15 eV (see Table 5). However, in support of these conclusions, it has recently been shown [S. Sample and C. Djerassi, *J. Amer. Chem. Soc.* **88**, 1937 (1966)] that n-amyl isoamyl sulphide eliminates an isobutyl radical in preference to an n-butyl radical in undergoing α-cleavage.

until the base peak came within 2 cm of the top of the chart paper. This ensured that the measurement of relative abundance was done under optimum conditions, and was of similar error for any given series of spectra.

The value of the electron multiplier employed ensured that a normal background (other than air peaks) did not contribute to any significant extent to the mass spectra.

At low electron beam energy the electron multiplier was set higher, but the background ions, which were usually hydrocarbon fragments had, in general, completely disappeared at these energies.

The mass spectra of the whole series of acetals and ketals were obtained on three separate occasions, and the results tabulated are the averages of these runs.

Preparation of ethylene acetals and ethylene ketals

The acetals and ketals were prepared from commercially available aldehydes and ketones which were not in general purified further. Standard procedures were used in the preparations.[8]

Equimolar quantities of ethylene glycol and the carbonyl compound were refluxed with a trace of acid catalyst (*p*-toluenesulphonic acid) and an excess of benzene. The water produced in the reaction was azeotropically removed from the mixture and collected in a Dean and Stark water separator. The reaction times ranged from a few minutes for the lower aldehydes to 6–7 hr for the higher ketones.

The resulting acetals and ketals were twice distilled and checked for purity by IR spectroscopy (absence of carbonyl stretching frequency) and gas chromatography (6 ft. apiezon column). Yields were in the range 30–70%.