Brèves communications - Kurze Mitteilungen
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The Electron-Induced Dissociation of some Monoterpenoids

The studies previously reported upon certain steroids and triterpenoids have now been extended to some monoterpenoids and their derivatives.

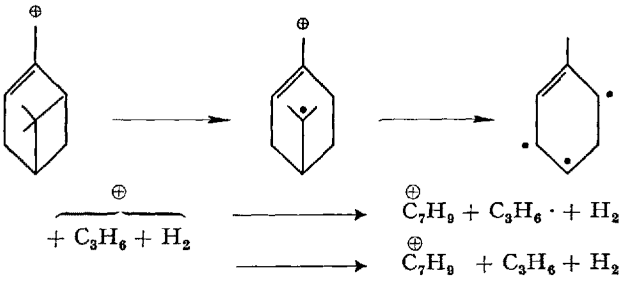
These experiments were generally conducted with an electron beam energy of some 12–15 electron volts, a practice previously described[1] which has the effect of simplifying the mass-spectrum. Comparison with many of the published mass-spectra[2] which have been obtained under more usual conditions show little alteration in the main features of the 'cracking-pattern' and although relative intensities of the fragment ions within a spectrum may change somewhat with the electron beam energy the order of intensities is unaffected.

The results are shown in the following Table.

A comparison of the fragmentation patterns of the hydrocarbons shows that the probability of elimination of a methyl group is related to the molecular structure and diminishes along the series Δ^3 carene, camphene, α- and γ-fenchene, tricyclene, cyclofenchene, to α-pinene and dipentene, and camphane. This effect is in agreement with the observations previously discussed[1] that (*a*) the presence of *gem*-dimethyl groups and (*b*) the methyl group being allylic to a double bond are two conditions which facilitate group elimination. When both occur together, as in camphene, the elimination is very much more marked than when only one is present. In the absence of both, the loss of the methyl group is not very marked, the exceptional case being Δ^3 carene. In this compound the parent molecular ion is small under the present experimental conditions the most prominent peak corresponding to a mass of 121. Thus ring strain may be involved in determining the nature of the fragmentation process.

A second feature common to the compounds camphene, α- and δ-fenchene, tricyclene, cyclofenchene, and α-pinene is that the base peak i.e. the most abundant fragment ion present corresponds to the loss of 43 mass units. This may be readily correlated with the loss of the bridge structure C_3H_6 and a further hydrogen. Such reactions which involve hydrogen transfer are known to occur with very great facility. It is considered by McLafferty[3] that such re-arrangements, especially those that allow the formation of double-bonds, are favoured over simple bond fissions as they result in the formation of one bond for each bond broken. Moreover, such re-arrangements involve the migration of a hydrogen atom on the β-carbon atom to the ruptured bond. This is supported by all the cases listed by the observation that the largest fragment of low mass obtained has $M/_e = 41$ resulting from the extraction of one hydrogen atom from each fragment with the formation of a hydrogen molecule; a particularly common form of re-arrangement.

A typical fragmentation process may therefore be written



$$\overset{\oplus}{\overline{\qquad}} + C_3H_6 + H_2 \longrightarrow \overset{\oplus}{C_7H_9} + C_3H_6\cdot + H_2$$

$$\longrightarrow \overset{\oplus}{C_7H_9} + C_3H_6 + H_2$$

The presence of an allylic system must obviously favour the initial rupture of the C_3H_6 fragment. The alternative mode of break-down which might occur, namely, the migration of a hydrogen atom from the ring to the C_3H_6

Compound	154	138	136	123	Mass of Ion										
					121	95	93	81	79	68	57	55	43	41	28
Δ^3 Carene . . .	—	—	—	—	*B*										
Camphene . . .	—	—	W		S		*B*							VS	
α-Fenchene . .	—	—	M		MS		*B*		S					VS	
δ-Fenchene . .	—	—	M		MS		*B*		S					VS	
Tricylene . . .	—	—	M		M		*B*							M	
Cyclofenchene .	—	—	W		M		*B*							M	
α-Pinene	—	—	VW		W		*B*							M	
Dipentene . . .	—	—	W		W		S			*B*				S	
Camphane . . .	—	—	M	M		VS		S				*B*	M	VS	
Camphor . . .	W	—	W										M	*B*	S
Pulegone . . .	MS	—	MS								*B*		S	S	MS

B the most abundant ion MS 50–65% S 65–80% of B W 15–30%
VS 80–90% of B M 30–50% VW 15%

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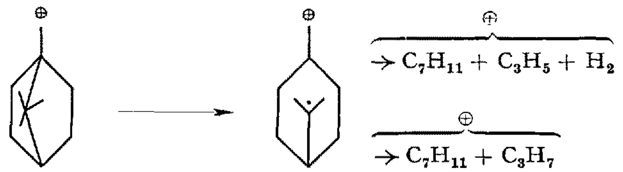
[1] R. I. Reed, J. chem. Soc. *1958*, 3432.

[2] A. P. I. Reports, Project No. 44.

[3] F. W. McLafferty, *A.S.T.M.E-14 Committee on Mass Spectrometry*, May 1958.

system does not seem to do so in these systems. This is, however, observed in the break-down of the camphane molecular ion



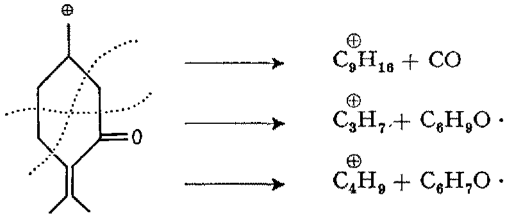
$\rightarrow \overbrace{C_7H_{11} + C_3H_5 + H_2}^{\oplus}$

$\rightarrow \overbrace{C_7H_{11} + C_3H_7}^{\oplus}$

where the ions of masses 95, 43, and 41 are very abundant. Ring-strain seems an important factor in all these systems as the presence of the *gem*-dimethyl bridge system gives a conformational rigidity to the molecule. This is supported by the fact that the elimination of 43 units from 1-methyl-4-*iso*propylcyclohexane while marked is not as intense as in the systems discussed[2].

Other prominent fragments which occur in certain of the spectra, namely mass 68 in dipentene, and 75 in Δ^3 carene may readily be interpreted as allylic-bond fissions. The prominent peak of mass 79 in the α- and δ-fenchenes is not readily explained on this basis without postulating hydrogen migrations also and this system is to be further examined.

These studies have been extended to pulegone and to camphor to allow of comparison with the hydrocarbons. In accordance with previous observations[4,5] the predominant process seems to be the elimination of carbon monoxide. The remaining fragments may be obtained as follows

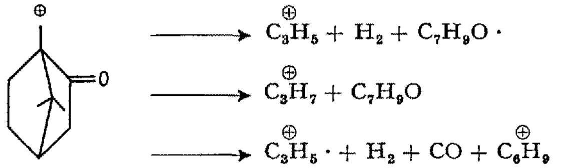


$\rightarrow \overset{\oplus}{C_9H_{16}} + CO$

$\rightarrow \overset{\oplus}{C_3H_7} + C_6H_9O\,\cdot$

$\rightarrow \overset{\oplus}{C_4H_9} + C_6H_7O\,\cdot$

giving fragment ions of 57,43, and 28. In a similar way camphor yields fragments of masses 41,43, and 81.



$\rightarrow \overset{\oplus}{C_3H_5} + H_2 + C_7H_9O\,\cdot$

$\rightarrow \overset{\oplus}{C_3H_7} + C_7H_9O$

$\rightarrow \overset{\oplus}{C_3H_5}\cdot + H_2 + CO + \overset{\oplus}{C_6H_9}$

The other significant fragment ion at low energies, 55, is not so readily interpreted.

It is concluded, therefore, that the principal fragment ions obtained in this series of compounds may, with two exceptions, be obtained directly from the carbocyclic skeletons. They do not at least at the low energies used require re-arrangements of this skeletal structure for their interpretation.

We acknowledge with gratitude the provision of a sample of pulegone by Dr. G. Buchanan, The University of Glasgow, of Δ^3 carene by Dr. L. N. Owen of the Imperial College of Science and Technology, London, and part of the mass-spectrum of camphor by Mr. W. Snedden of The University of Glasgow.

T. Gilchrist (in part)
and R. I. Reed

Chemistry Department, The University of Glasgow, July 27, 1959.

Résumé

Les auteurs ont trouvé quelques corrélations entre la formation des ions les plus abondants et la disposition des liaisons-éthyléniques dans les ions moléculaires de quelques terpènes.

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[4] J. H. Beynon, personal communication.

[5] J. H. Beynon, R. G. Lester, and A. E. Williams, *A.S.T.M. E-14 Committee on Mass Spectrometry*, May 1959.

The Effects of Nucleases on Photosynthetic CO_2 Fixation

The occurrence of nucleic acids in chloroplasts has been recognised for quite sometime[1] but very little is known about their function, except possibly an involvement in the propagation of chloroplasts. It has been indicated that the activity of RNA[2] could be linked to the synthesis of specific proteins i.e. enzymes involved in photosynthesis[3]. In view of some recent observations on nucleic acid control of protein and polysaccharide syntheses it was considered of interest to study whether and to what extent the CO_2 fixation reactions in photosynthesis are nucleic acid dependent processes.

Young cultures of *Chlorella pyrenoidosa* and *Nostoc muscorum* were used. The cells were centrifuged in the cold in an MSE centrifuge, suspended in phosphate buffer of pH 7·0 and incubated with deoxyribo- or ribonucleases for 2–2·5 h at 37°C. The cells were then centrifuged again, resuspended in phosphate buffer allowed to metabolise $NaH^{14}CO_3$ (obtained from the Radiochemical Centre, Amersham, England) for a further period of 2 h at 25°C. The cells were extracted in hot 80% ethanol, filtered and the residue washed in 80% ethanol. An aliquot of the filtrate was transferred to stainless steel planchets for counting with an end window β-counter and another chromatographed two dimentionally on Whatman No. 1 filter paper with phenol-water butanol acetic water (4:1:1) as the developing solvent[4]. The radioactive areas on the chromatograms were located by exposure to X-Ray films and counts were taken directly on paper. The DNase (1 × cryst) used was obtained from the Nutritional Biochemical Corporation, Cleveland, Ohio, U.S.A. and RNase (5 × cryst.) was supplied by Sigma Chemical Co., St. Louis, Missouri, U.S.A.

Nuclease treatment resulted in slight inhibition (less than 10%) of the incorporation of ^{14}C into the 80% ethanol-insoluble fraction. Examination of the ethanol soluble fraction however revealed rather severe effects on the synthesis and metabolism of $^{14}CO_2$ fixation products. The effect of nuclease treatment on the total incorporation of ^{14}C into the alcohol-soluble fraction and the more important products of $^{14}CO_2$ fixation during a 2 h photosynthesis is shown in the Table. It appears that the CO_2 fixation process in *C. pyrenoidosa* is more susceptible to nuclease

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[1] E. I. Rabinowitch, *Photosynthesis and related processes*, Vol. 2, Part 2 (Interscience Publishers, Inc., New York 1956).

[2] The following abbreviations have been used: DNA, deoxyribonucleic acid; RNA, ribonucleic acid; DNase deoxyribonuclease; RNase, ribonuclease.

[3] G. Brawerman and E. Chargaff, Biochim. biophys. Acta *31*, 164 (1959).

[4] B. B. Biswas and S. P. Sen, Nature *181*, 1219 (1958).