Il convient de noter qu'une propriété conformationnelle des liquides purs, le nombre moyen de conformations gauches, est capables non seulement d'ordonner les alcanes normaux et ramifiés en familles, mais encore de conserver cet ordre lors de la représentation du volume d'excès des solutions de ces alcanes dans un alcane de référence, en fonction de $Z_g$.

Il est permis de penser qu'il existe une contribution conformationnelle aux volumes d'excès, qui serait due à une modification de la fonction stérique de partition des alcanes lors de leur mise en solution.

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# 60. The Mass Spectrometric Fragmentation of 1-Heptyl Ions Derived from the Corresponding Halides

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(27. XI. 73)

*Summary.* We have studied the fragmentation of 1-heptyl ions resulting from the loss of halogen from the corresponding halide ions. All positions had been labelled with D and $^{13}$C, some positions even doubly labelled. The main processes are the loss of propene and, to a lesser extent, ethylene as neutral fragments. All carbon atoms have a definite probability of being lost with the olefin, those which are terminal having the smallest chance; this precludes an important contribution by direct scission. The source-and the metastable-decomposition produced much the same isotopic distribution in the fragments. The terminal hydrogen atoms also have a small chance of being rearranged, whereas those at non-terminal positions show extensive scrambling. It seems that the fragmentation proceeds *via* cyclic structures which are rapidly attained and equilibrated amongst each other, but our results do not warrant suggestion of a detailed model.

**1. Introduction.** – The mass spectrometric fragmentation of alkanes has been summarized [1] and is characterised by the loss of an olefin or alkyl group neutral fragment. This might proceed by a simple mechanism or result from a series of re-arrangements [2]. The rearrangement of hydrogen has especially attracted interest and has been reviewed recently [3–4]. The alkyl ion being one of the most important fragments, we undertook an intensive research program to elucidate the mechanism of its decomposition. In a first paper of this series we investigated the fragmentation of butyl ions formed by loss of halogen from the corresponding halide ions [5]. We were able to show that the scrambling of hydrogen atoms is a relatively 'slow' reac-

tion $(k \sim 2 \cdot 10^{-9}/\text{s})$ whereas the equivalence of the carbon atoms is immediately attained. We explained the results by assuming the formation of a protonated four-membered ring where the loss of methane and ethylene competes with hydrogen scrambling *via* proton. In this present work we are concerned with heptyl ions formed from the corresponding halide ions. In forthcoming publications we shall deal with alkyl ions from pentyl to nonyl and study the dependence of the fragmentation pattern on the mode of formation of the initial ion; preliminary results show that alkyl ions up to pentyl behave like butyl, that heptyl and higher homologues follow a different reaction mechanism, and that hexyl seems to be a somewhat particular case.

**2. Experimental.** – The mass spectra were obtained with a double focussing instrument (*CEC* 21–110 B), equipped for using the metastable defocussing technique. Its resolution was on the average 25 000 for a 10% valley. The identification of the fragments obtained from samples containing $^{13}C$ and/or D was by peak matching. The standard conditions were a source temperature of $120 \pm 5°$ and pressure of about $10^{-5}$ Torr, an electron energy of 70 eV. All the results given are mean values of several determinations, frequently on different samples.

Table 1. *Low-resolution mass spectra of heptyl iodides, deuterated in different positions.* Uncorrected spectra; only fragments without halogen are given

| $m/e$ | $C_7H_{15}I$ | $1\text{-}d_2$ | $2\text{-}d_2$ | $3\text{-}d_2$ | $4\text{-}d_2$ | $5\text{-}d_2$ | $6\text{-}d_2$ | $7\text{-}d_3$ |
|---|---|---|---|---|---|---|---|---|
| $\Sigma\,(M\text{-}I)^+$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ | $\equiv 100$ |
| 86 | | | | | | | | 0.1 |
| 85 | | 0.6 | 0.6 | 0.6 | 0.55 | 0.6 | 0.6 | 0.05 |
| 84 | | 0.15 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 |
| 83 | 0.9 | 0.2 | 0.25 | 0.25 | 0.25 | 0.25 | 0.3 | 0.5 |
| 74 | | | | | | | | 9.9 |
| 73 | | 16.4 | 9.7 | 14.9 | 9.6 | 12.7 | 7.1 | 9.4 |
| 72 | | 11.1 | 10.1 | 20.8 | 15.0 | 17.1 | 11.8 | 10.7 |
| 71 | 21.6 | 21.2 | 17.6 | 27.1 | 19.7 | 21.7 | 8.1 | 2.7 |
| 70 | 13.2 | 14.7 | 14.0 | 14.0 | 11.3 | 10.8 | 7.4 | 3.1 |
| 69 | 25.2 | 15.2 | 11.3 | 11.9 | 8.2 | 10.4 | 12.9 | 12.4 |
| 60 | | | | | | | | 617 |
| 59 | | 803 | 625 | 658 | 333 | 478 | 339 | 128 |
| 58 | | 278 | 669 | 925 | 453 | 667 | 545 | 132 |
| 57 | 1618 | 458 | 339 | 372 | 372 | 257 | 251 | 350 |
| 56 | 29 | 48 | 50 | 99 | 94 | 55 | 59 | 24 |
| 55 | 175 | 90 | 66 | 70 | 56 | 53 | 82 | 86 |
| 46 | | | | | | | | 198 |
| 45 | | 166 | 114 | 172 | 102 | 100 | 139 | 72 |
| 44 | | 122 | 195 | 421 | 276 | 205 | 209 | 83 |
| 43 | 640 | 371 | 320 | 451 | 317 | 198 | 263 | 270 |
| 42 | 113 | 160 | 174 | 316 | 331 | 155 | 258 | 114 |
| 41 | 525 | 253 | 212 | 334 | 317 | 133 | 337 | 238 |
| 40 | 24 | 42 | 40 | 102 | 102 | 30 | 79 | 34 |
| 39 | 146 | 84 | 70 | 106 | 157 | 44 | 174 | 103 |
| 32 | | | | | | | | 66 |
| 31 | | 27 | 19 | 45 | 11 | 15 | 160 | 43 |
| 30 | | 46 | 47 | 122 | 146 | 45 | 114 | 69 |
| 29 | 247 | 160 | 146 | 270 | 194 | 171 | 165 | 82 |
| 28 | 37 | 49 | 42 | 108 | 78 | 31 | 149 | 62 |
| 27 | 161 | 85 | 72 | 233 | 174 | 52 | 197 | 107 |

Table 2. *Low-resolution mass spectra of heptyl iodides with* $^{13}C$ *in different positions.* Uncorrected spectra

| Mass | 1-$^{13}$C | 2-$^{13}$C | 3-$^{13}$CD$_2$ | 4-$^{13}$C | 5-$^{13}$C | 6-$^{13}$C | 7-$^{13}$CD$_3$ | 1,7-2$^{13}$C | 2,6-2$^{13}$C | 3,7-2$^{13}$C |
|---|---|---|---|---|---|---|---|---|---|---|
| $^{13}$C$_2$C$_5$X$_{15}$I$^+$ | | | | | | | | 34.7 | 38.8 | 39.0 |
| $^{13}$CC$_6$X$_{15}$I$^+$ | 64.5 | 57.5 | 64.5 | 59 2 | 64.5 | 58.5 | 63.2 | 46.2 | 47.3 | 47.0 |
| C$_7$X$_{15}$I$^+$ | 35.5 | 42.5 | 35.5 | 40.8 | 35.5 | 41.5 | 36.8 | 19.1 | 13.9 | 14.0 |
| $(M$-I$)^+$ | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 | ≡ 100 |
| 87 | | | | | | | 0.4 | | | |
| 86 | | | 1.4 | | | | 0.3 | | 0.5 | 0.3 |
| 85 | 2.6 | 1.2 | 2.4 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.9 | 1.6 |
| 84 | 1.3 | 0.9 | 1.5 | 1.7 | 1.6 | 1.5 | 0.4 | 1.4 | 0.8 | 1.9 |
| 83 | 1.3 | 0.9 | 5.1 | 1.4 | 1.0 | 1.3 | 2.5 | 1.0 | 0.4 | 1.7 |
| 75 | | | | | | | 5.8 | | | |
| 74 | | | 5.9 | | | | 8.9 | | | |
| 73 | | | 13.6 | | | | 8.6 | 3.0 | 2.3 | 3.8 |
| 72 | 11.6 | 6.0 | 17.4 | 7.9 | 9.2 | 9.9 | 6.6 | 9.9 | 8.8 | 10.3 |
| 71 | 20.2 | 13.1 | 13.9 | 14.7 | 14.5 | 14.5 | 2.3 | 16.5 | 9.9 | 19.5 |
| 70 | 21.4 | 16.4 | 8.0 | 16.3 | 17.3 | 11.1 | 3.0 | 27.2 | 11.6 | 12.1 |
| 69 | 17.4 | 13.2 | 5.0 | 10.3 | 10.3 | 17.9 | 9.4 | 21.2 | 6.7 | 9.7 |
| 61 | | | | | | | 389 | | | |
| 60 | | | 146 | | | | 267 | | | |
| 59 | | | 408 | | | | 108 | 214 | 85 | 130 |
| 58 | 792 | 415 | 447 | 498 | 496 | 478 | 102 | 1025 | 548 | 508 |
| 57 | 1214 | 960 | 194 | 933 | 888 | 1114 | 312 | 805 | 473 | 482 |
| 56 | 70 | 69 | 50 | 83 | 84 | 71 | 24 | 238 | 83 | 81 |
| 55 | 108 | 124 | 42 | 77 | 123 | 140 | 65 | 233 | 56 | 62 |
| 47 | | | | | | | 122 | | | |
| 46 | | | 48 | | | | 103 | | | |
| 45 | | | 143 | | | | 65 | 34 | 6 | 18 |
| 44 | 149 | 120 | 216 | 101 | 235 | 172 | 87 | 523 | 205 | 231 |
| 43 | 480 | 486 | 240 | 428 | 430 | 516 | 239 | 706 | 279 | 261 |
| 42 | 155 | 221 | 145 | 200 | 294 | 232 | 91 | 923 | 256 | 242 |
| 41 | 264 | 464 | 181 | 335 | 425 | 483 | 216 | 1033 | 241 | 224 |
| 40 | 30 | 73 | 40 | 48 | 106 | 67 | 26 | 439 | 84 | 69 |
| 39 | 64 | 153 | 54 | 93 | 139 | 174 | 93 | 602 | 81 | 72 |
| 33 | | | | | | | 36 | | | |
| 32 | | | 9 | | | | 392 | | | |
| 31 | | | 32 | | | | 413 | 4 | 1 | 1 |
| 30 | 15 | 37 | 62 | 60 | 53 | 100 | 46 | 51 | 105 | 94 |
| 29 | 127 | 336 | 141 | 210 | 367 | 289 | 106 | 77 | 189 | 173 |
| 28 | 30 | 87 | 52 | 81 | 118 | 115 | 53 | 62 | 127 | 98 |
| 27 | 58 | 227 | 117 | 160 | 274 | 240 | 102 | 73 | 134 | 148 |

The following positions were labelled with isotopes:

deuterium: 1-C$_7$H$_{15}$I: 1-d$_2$; 2-d$_2$; 3-d$_2$; 4-d$_2$; 5-d$_2$; 6-d$_2$; 7-d$_3$;

1,3-d$_4$; 1,5-d$_4$; 1,7-d$_5$.

1-C$_7$H$_{15}$Br:7-d$_3$

carbon $^{13}$C:1-C$_7$H$_{15}$I:1-$^{13}$C; 2-$^{13}$C; 3-$^{13}$CD$_2$; 4-$^{13}$C; 5-$^{13}$C; 6-$^{13}$C; 7-$^{13}$CD$_3$;

1,7-$^{13}$C$_2$; 2,6-$^{13}$C$_2$; 3,7-$^{13}$C$_2$

1-C$_7$H$_{15}$Br:3-$^{13}$CD$_2$; 4-$^{13}$C; 5-$^{13}$C; 6-$^{13}$C.

The degree of deuteration was always higher than 98%. The $CO_2$ used for the synthesis contained between 56–64% of $^{13}C$; for samples marked with two carbon atoms this value turned out to be too small for precise results. The isotopic distribution was corrected for the natural abundance of the non-labelled atoms and the measured distribution for the labelled carbon atom for all results except Tabs. 1 & 2. The enrichment calculated from the molecular ion always corresponded with that given for the labelled $CO_2$ used for synthesis, with the exception of 1,7-$^{13}C$-heptyl iodide where the process of purification apparently introduced some traces of unlabelled product. Classical syntheses were generally used viz.: reduction of esters with $LiAlD_4$, preparation of the bromide, followed by chain prolongation with $CO_2$ or ethylene oxyde. The label in position 7 was introduced by a 'statistical' synthesis from 1,6-$C_6H_{12}Br_2$ with dimethyl-copper-lithium. All products were purified by gas-chromatography prior to use.

**3. Results.** – For the iodides, the sum of the molecular ion and the fragments containing halogen amounts to about 50% of the corresponding alkyl ion or to 1% of the total ionisation; the latter is somewhat higher for the bromides. For this reason we have concentrated on the iodides and in Tab. 1 only the uncorrected fragmentation patterns for fragments not containing halogen are given; the 'parent' ion is normalised to 100. In Tab. 2 we include the percentage distribution of the molecular ion in order to show the enrichment in $^{13}C$. By far the most important reaction with which this paper is chiefly concerned, is the elimination of propene, substantiated by a strong metastable transition. The peaks at $m/e = 43$ correspond, at least partially, to the loss of methane from the butyl ion as we have shown previously [5]. We were unable to measure a metastable transition $97 \rightarrow 43$ due to our experimental conditions (the direct loss of butene from the parent alkyl ion); the same is true for the peak at $m/e = 41$. The loss of ethylene forms the peak with the highest mass in the group of fragments with five carbon atoms; although qualitatively unimportant, this is a conspicuous reaction and the influence of labelling can be followed. The fragmentation reactions are summarized in Tab. 3, from which it can be seen that on a longer time-scale (metastable decomposition), only the loss of propene and perhaps that of ethylene are of importance.

Table 3. *Fragmentation scheme for $C_7H_{15}^+$ in %*

|  | $C_6H_{11}^+$ | $C_5H_{11}^+$ | $C_5H_{10}^+$ | $C_5H_9^+$ | $C_4H_9^+$ | $C_4H_8^+$ | $C_4H_7^+$ | $C_3H_7^+$ |
|---|---|---|---|---|---|---|---|---|
| Source | 0.1 | 0.8 | 0.5 | 1.0 | 64 | 1.1 | 7.5 | 25 |
| metastables | <0.1 | 0.1 | 0.1 | 1.1 | 98 | <0.1 | 0.1 | 0.4 |

**4. Discussion.** – 4.1. *Elimination of ethylene.* Since we have labelled all the positions of the $C_7$-skeleton, we are able to calculate the probability of every position to be lost, as part of an ethylene fragment, from the heptyl ion. The probabilities are as follows:

*Scheme 1*
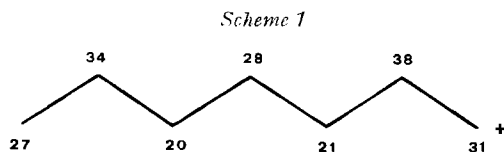


Their sum amounts to 199% instead of 200%; the system is thus internally consistent with an absolute error of about 1%. The distribution shows that the loss of ethylene corresponds by no means to a simple scission of the bond between the

second and the third carbon atom, nor is it due to a complete randomisation of the carbon atoms, as could be predicted for a possible seven-membered ring, as in the latter case every position would have an equal probability (28.7%) of being lost; most of our values are significantly different from this figure. Furthermore, the measured distribution is slightly dissymetric, favouring the loss from the side that originally carried the halogen atom. We could try to rationalize the results by assuming the following four possible intermediate states[1]:

*Scheme 2*
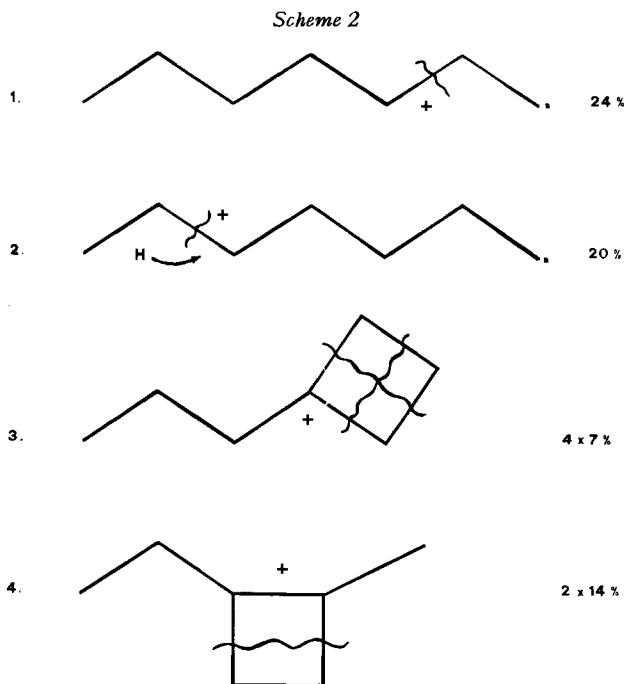


The first reaction corresponds to a simple bond scission, the second necessitates the migration of a hydrogen atom from position 6 or 7, the third and fourth require the formation of four-membered rings, where we assumed equal probability for each end of the molecule. The percentages given are the contributions of each configuration and were obtained by trial and error and in order to explain the observed distribution. We have some confirmations of these figures by checking the loss of $C_2H_4$ from the doubly labelled species: for 1,7-$^{13}C_2$, we measured 40% for a calculated value of 42%; for 2,6-$^{13}C_2$ the corresponding figures are 30% and 28% and for 3,7-$^{13}C_2$, 48% and 52% respectively. The correlation is as good as can be expected, without having adequate experimental evidence for a fragmentation scheme which, for a minor reaction, seems complicated.

4.2. *Elimination of propene.* The elimination of propene is by far the most important fragmentation reaction; it can also be conveniently studied in the meta-

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[1] The assumption of a four-membered ring is entirely arbitrary. A five- or six-membered ring or a combination would probably do as well.

stable decomposition of the labelled species. The distribution of the deuterium in the propene lost for the different positions within the molecule – for the decomposition in the source (fast reactions, up to 0.1 $\mu$s) and metastables (decay after about 1 $\mu$s) – is given in Fig. 1. At both sides of the figure, the expectance for complete randomisation of two, resp. three deuterium atoms are given. Several observations can be made: the fragmentation is apparently preceeded by some rearrangement of the deuterium atom since, for the non-terminal position, the probability to lose one D-atom from a specified position is largest. The distribution however does not correspond to a complete randomisation contrary to what is usually accepted [4]. There is no tendency to approach the statistical distribution in the slow metastable process as has been observed for butyl ions [5]. The terminal groups are somewhat particular as they have a tendency to lose either all or none of their D-atoms. It seems to us that the non-terminal positions undergo a randomisation process prior to an elimination that involves the terminal position only in a minor sense. In Tab. 4 the

Table 4. *Distribution of propenes eliminated from* $C_7H_{11}D_4{}^+$

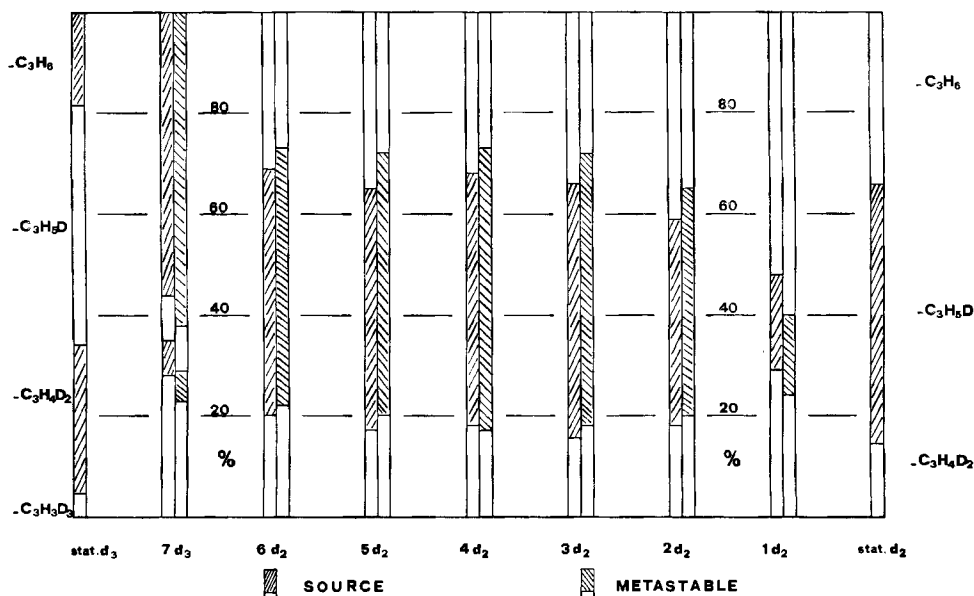| Fragment lost | 1,3-$D_4$ | | | 1,5-$D_4$ | | | 4 D statistical |
|---|---|---|---|---|---|---|---|
| | source | meta-stables | calc. | source | meta-stables | calc. | |
| —$C_3H_6$ | 19 | 22 | 17.7 | 11 | 10 | 18.2 | 9.2 |
| —$C_3H_5D$ | 32 | 37 | 32.9 | 35 | 37 | 31.8 | 36.9 |
| —$C_3H_4D_2$ | 26 | 24 | 27.6 | 36 | 35 | 28.2 | 39.6 |
| —$C_3H_3D_3$ | 18 | 12 | 17.4 | 15 | 14 | 17.0 | 13.2 |
| —$C_3H_2D_4$ | 5 | 5 | 4.4 | 3 | 4 | 4.8 | 1.1 |



Fig. 1. *Elimination of propene from 1-heptyl ions deuterated in different positions*

distribution of D, in propene lost, is given for molecules labelled in two positions and is compared with the distribution calculated for complete randomisation ('statistical'). Under the heading 'calc.' the figures given are those obtained on the assumption that the deuterated positions lose their deuterium independently, according to the data in Fig. 1. The results for deuteration in the 1,5-positions correspond rather well with the statistical distribution, but since this is not true for 1,3-positions, this agreement must be accidental. In the latter case the figures agree rather well with the calculated ones; this means that there is little exchange between the 1- and the 3-positions, an unastonishing result since we have already shown that the terminal positions show little randomisation. Only 5% of the propene lost from 1,3-$d_4$-heptyl ion contain four D-atoms. This shows that the direct scission of the C(3)–C(4) bond without previous scrambling of H atoms is, at most, a minor process. The small differences between the distributions for the fast and the slow reaction show that the rearrangement must be fast.

The probability of losing a specific fragment of three carbon atoms as propene is obtained from the series of molecules labelled with $^{13}C$ and is given in the following diagram:

*Scheme 3*
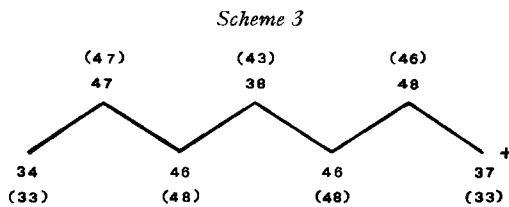


The values in parentheses are for the metastable decomposition. The sum of all probabilities is 296% (298%), again showing the internal consistency with an average error of about 1%. As in the case of the loss of ethylene, all positions participate in
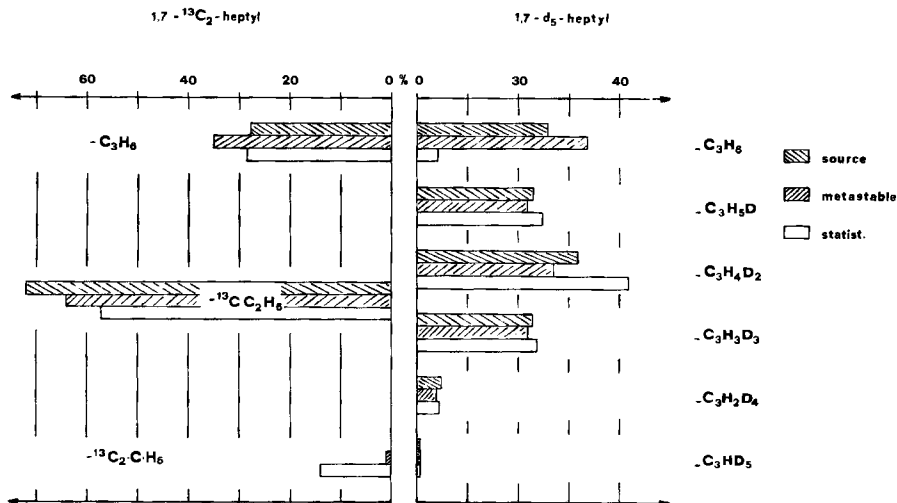


Fig. 2. *Elimination of propene from 1-heptyl ions labelled in the terminal positions*

this reaction, the terminal carbon atoms having the smallest probability. The loss of propene must mainly proceed by rearranged intermediate products that are rapidly formed, since the slow reactions do not differ much from the fast ones. The main difference is the decreased probability of loss of the terminal positions in the slow processes, which is to be expected on the basis that part of the terminal losses might originate from direct fragmentations without rearrangement. The latter reaction results from molecules with internal energy and therefore must be fast in order to compete successfully with rearrangement processes; such molecules will have little tendency to appear as metastables. The statistical probability for losing any one position is 42.8%. Most of the measured values differ significantly from this value. In Fig. 2 the distribution of the propene that results from doubly labelled molecules in the terminal positions is illustrated, together with the expectancy for complete randomisation. The probability of losing the two terminal positions as the same fragment is very small, however it must be admitted that the calculation for the fragments $^{13}C_2CH_6$ and $^{13}CC_2H_6$ are not very precise because of the too small enrichment of $^{13}C$. One third of the molecules lose propene without any participation of the terminal positions; this fraction increases for the slow reactions. Labelling with D does not significantly change the results, and in this case the distribution is very far from random.
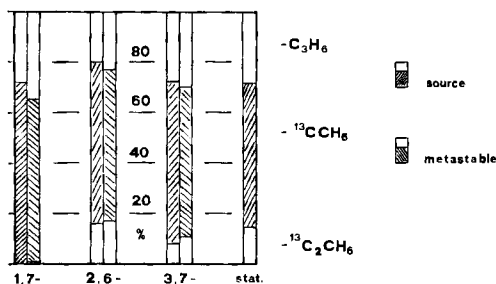


Fig. 3. *Elimination of propene from 1-heptyl ions with two carbon atoms labelled*

In Fig. 3 we present the results for the elimination of propene from some doubly labelled molecules. It can be seen that there is a fair chance of losing either carbon at positions 2 and 6 or 3 and 7 together. The calculated values are again obtained from the probabilities of each position and on the assumption that the fragments are lost independently of each other. They are different from the measured values, but in all cases the change in distribution from the values for source reactions to those of the metastables, i.e. from fast reactions to slow ones allowing more time for possible scrambling reactions, is in the same direction. It might be possible to explain the results by assuming a series of intermediate products. Besides the direct scission of the bond between positions 3 and 4 we can postulate a similar scission between positions 4 and 5 with a concurrent transfer of a hydrogen atom. Furthermore, we assume protonated dimethylcyclopentane, ethylcyclopentane and methylcyclohexane to be intermediates. This model introduces a number of adjustable parameters, but cannot explain the simultaneous loss of two $^{13}C$-carbons from the doubly labelled molecules; moreover, parameters cannot be found to explain the values for

the terminal positions. It is not unreasonable to assume that the different forms can rearrange into one another, but in this case the number of parameters is so high that any attempt to adjust them becomes a mere gamble. However, we intend to study the fragmentation of protonated rings in order to gain some insight into their reaction paths. For the moment we must be content with the conclusion that the fragmentation of heptyl ions proceeds by one or more apparently rather specific rearrangements that are as yet unknown.

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# 61. Isolierung und Strukturaufklärung von Chlamydocin

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(24. I. 74)

*Summary.* The constitution of Chlamydocin – a metabolite of *Diheterospora chlamydosporia* with pronounced cytostatic activity – is proposed on the basis of chemical reactions and physical data. The synthesis of a derivative of a new amino acid is described. The biological activities of this compound and of derivatives of Chlamydocin are discussed.

Chlamydocin (**1**) wurde aus Kulturfiltraten von *Diheterospora chlamydosporia* (S 3440) mit Äthylenchlorid extrahiert[1]) und nach Chromatographie an Kieselgel als einheitlicher farbloser Schaum erhalten. Die durch Hochauflösungsmassenspektrum und Analyse ermittelte Bruttoformel von $C_{28}H_{38}N_4O_6$, sowie die Absorptionen im IR.-Spektrum (s. Fig. 1) bei 3400, 3300 und 1680 cm$^{-1}$, die für Amidbindungen charakteristisch sind, liessen das Vorliegen eines Peptids vermuten.

Nach saurer Hydrolyse konnten mittels Aminosäureanalyse Phenylalanin, Prolin und α-Aminoisobuttersäure im Verhältnis 1:1:1 nachgewiesen werden. Daneben traten noch mehrere kleinere Pike auf, die von keiner üblichen Aminosäure herrührten. Auch konnte es sich nicht um unvollständig hydrolysierte Peptidfragmente handeln, da das Verhältnis Peptid-Aminosäuren (Phe, Pro, Iabu) schon nach 90 Min. Hydrolyse konstant blieb, sondern um eine Aminosäure neuen Typs, die wir vorläufig mit «X» bezeichnen. Die absolute Konfiguration der Aminosäuren wurde durch Abbau mit D- und L-Aminosäureoxydase bestimmt [1]. Phenylalanin und die unbekannte Aminosäure X liegen in der L-Form, Prolin in der D-Form vor.

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