Tetrahedron, 1961, Vol. 12, pp. 163 to 167. Pergamon Press, Inc. Printed in Northern Ireland

THE ANALYSIS OF MIXTURES OF OCTALINS

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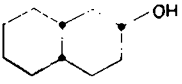
(*Received* 16 *September* 1960)

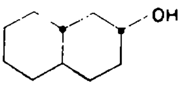
Abstract—A method of analysis is described, based on gas-liquid chromatography at moderate (ca. 2000 plates) efficiency on Apiezon L and benzyldiphenyl, whereby any octalin can be recognized. Any mixture of octalins can be tested for contamination by any bicyclo[5:3:0]decene by chromatography after hydrogenation. Quantitative analysis of binary mixtures of octalins is discussed; it is usually accurate, although an indirect method is necessary for mixtures of the $\Delta^{1,9}$- and *cis*-Δ^{1}-isomers.

In order to study the effects of conformation on the pyrolysis of the diazodecalins, it was necessary to devise techniques for the quantitative analysis of the six isomeric octahydronaphthalenes ("octalins"). In earlier work by Hückel *et al.*, chemical degradation,[1] nitrosochloride formation,[2] and ultra-violet spectroscopy applied to the derived iodine complexes[3] have all been employed, while more recently gas-liquid chromatography has also been used.[4] For the sake of simplicity, we sought to rely exclusively on the last-mentioned technique, and have examined it systematically.

The six octalins were prepared by rational methods in the form of five different binary mixtures. Pyrolysis of the *cis*- and *trans*-β-decalol methylcarbonates, derived from the alcohols, m.p. 105° (I) and 75° (II) respectively, gave in each case a mixture of the Δ^{1}- and Δ^{2}-octalins. Pyrolysis of the methylcarbonates of the *cis*- and *trans*-α-decalols, m.p. 93° (III) and 63° (IV), gave similar binary mixtures, which this time had one component (clearly $\Delta^{1,9}$-octalin) in common.



I



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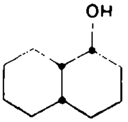

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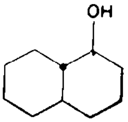

IV

The other component was, in each case, identical chromatographically with one of the two pyrolysis products from the corresponding β-decalol; this was therefore the Δ^{1}-octalin, while the other pyrolysis product from the β-decalol ester must have been, in each case, the Δ^{2}-octalin. Finally, reduction of napthalene with lithium in liquid ammonia is known[5] to give Δ^{9}-octalin, with a little of the $\Delta^{1,9}$-isomer; in the mixture so obtained, one new product, the major component, was found, together with about 10 per cent of the $\Delta^{1,9}$-isomer, already recognized from the pyrolysis experiments. Thus every octalin could be identified with certainty, although no one isomer had been obtained pure.

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[1] W. Hückel and H. Naab, *Liebigs Ann.* **502**, 136 (1933).

[2] W. Hückel, R. Danneel, A. Schwartz and A. Gercke, *Liebigs Ann.* **474**, 121 (1929).

[3] W. Hückel and O. Fechtig, *Chem. Ber.* **92**, 693, (1959).

[4] W. Hückel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanck, M. Heinzel, A. Hubele, J. Kurz, M. Maier, D. Maucher, G. Näher, R. Neidlein and R. B. Rashingkar, *Liebigs Ann.* **624**, 142 (1959).

[5] R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, *J. Amer. Chem. Soc.* **77**, 3230 (1955).

In any reaction involving the elimination of a functional group at the α-position in a decalin derivative, the possibility of rearrangement to a derivative of bicyclo[5,3,0]-decane has to be borne in mind. Analysis of mixtures of octalins, therefore, required a method of identifying the bicyclo[5,3,0]-decanes in the hydrogenation products. A mixture of the two forms (ratio 82:18) of this hydrocarbon was readily prepared by the hydrogenation of azulene in ethyl acetate; it is interesting that hydrogenation over platinum in acetic acid led to almost exclusive (ca. 98:2) formation of one component.

The retention times observed when a number of liquid phases were employed are listed in Table 1, together with values for naphthalene and tetralin. All are quoted ("R_D values") relative to *trans*-decalin = 100. With the apparatus available, the determination of R_D values for Apiezon L and benzyldiphenyl sufficed to identify any octalin, or to identify either of the perhydroazulenes in the presence of both decalins.

Quantitative analysis was attempted only for the five binary mixtures discussed above, and some favourable cases of more complex mixtures. It requires complete separation of the components and knowledge of the relationship between the area under the observed detector-response/time curve and the weight of material present. The first requirement involves the resolution of the column used; in the present work a difference in R_D values of about 7 per cent was called for, and the separation of $\Delta^{1,9}$- and *cis*-Δ^1-octalins was therefore impossible with any of the liquid phases investigated. The separation of *trans*-Δ^1- and -Δ^2-octalins was incomplete, even on Apiezon L, so that only an approximate value could be given for the relative peak areas; it should, however, be reliable to ±5 per cent. The other three mixtures were completely separated on one or other of the chosen stationary phases, and results should be reliable to ±2 per cent.

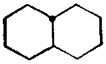
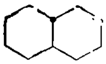
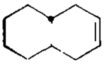
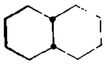
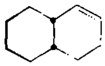
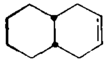
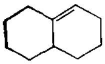
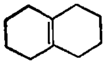
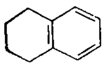
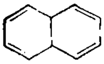
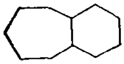
The detector used was of the flame ionisation type, and has recently been described.[6] While a linear relationship between weight and peak area has been claimed for a number of compounds,[7] it was necessary to test this for the substances under consideration. Accordingly, mixtures of *trans*-decalin with available binary octalin mixtures were prepared in a known weight ratio, and the signal areas compared. In all cases, the ratios were identical to within 2·5 per cent.

There remained the problem of analysing mixtures of *cis*-Δ^1-octalin and $\Delta^{1,9}$-octalin, which were inseparable, though not indistinguishable, on any of the columns used. It seemed that preferential isomerization of the trisubstituted olefine to an equilibrium mixture of this with the Δ^9-isomer might provide a solution; indeed, mixtures containing $\Delta^{1,9}$-octalin sometimes showed a peak corresponding to Δ^9-octalin, presumably formed by catalysis by adventitious acidic contaminants. Various isomerizing agents were investigated, using for convenience a mixture of *trans*-Δ^1- and $\Delta^{1,9}$-octalins. This mixture could be analysed directly, so that the unreactivity of the disubstituted olefine could be checked simultaneously. The results were of considerable interest and will be published in detail later; but for the present purpose a solution of perchloric acid (0·25 M) in acetic acid proved to be one of the most selective and convenient reagents examined. It gave a mixture which after reaction-times of between 1 and 100 minutes at 30° remained constant (within a range

[6] I. G. McWilliam and R. E. Dewar, *Nature Lond.* **181**, 760, (1958).

[7] I. G. McWilliam and R. A. Dewar, *Gas Chromatography* p. 142. Butterworths, London (1958).

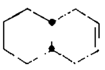
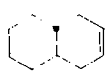
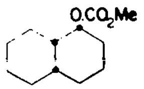
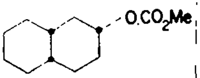
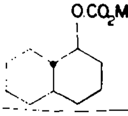
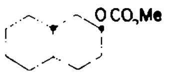
TABLE 1. RELATIVE RETENTION TIMES

Stationary Phase	Apiezon L	Squalene	Dinonyl Phthalate	Benzyl Diphenyl	Tricresyl Phosphate	AgNO$_3$/poly-ethylene glycol
Column Length	400 cm	260 cm	170 cm	250 cm	200 cm	250 cm
Column Temperature	120°	100°	100°	90°	100°	40°
	100	100	100	100	100	100
	105	102	110	132	133	155
	111	107	110	137	140	177
	125	130	130	144	144	155
	120	119	127	160	159	210
	125	126	136	179	178	235
	117	119	127	161	157	200
	124	135	145	192	182	240
	177			430		
	217			680		
	120 124			133 164		

of 2 per cent) containing as much *trans*-Δ^1-octalin as was originally present and Δ^9- and $\Delta^{1,9}$-octalins in a ratio of 9:1, evidently the equilibrium proportions.

When the same analytical procedure was applied to the mixture of *cis*-Δ^1- and $\Delta^{1,9}$-octalins a mixture of Δ^9-octalin and (*cis*-Δ^1 + $\Delta^{1,9}$)-octalins was formed for which the relative areas of the two peaks obtained remained constant, within 2 per cent, after reaction-times of between 1 and 30 minutes. This was taken to imply that the conversion of the *cis*-Δ^1-octalin to the equilibrium mixture, though undoubtedly faster than that of the *trans*-Δ^1-octalin (cf. the stabilities of the *cis*- and *trans*-decalins[8]), was still much slower than the interconversion of the $\Delta^{1,9}$- and Δ^9-isomers. It was then a simple matter to subtract 11 per cent of the Δ^9-octalin peak (the equilibrium amount of $\Delta^{1,9}$-octalin present) from the ($\Delta^{1,9}$- + *cis*-Δ^1-) octalin peak, and thus obtain the amount of *cis*-Δ^1-octalin finally (and originally) present in the mixture.

TABLE 2. PRODUCTS OF THE PYROLYSIS OF THE DECALOL METHYL CARBONATES

					
	25%	75%			
		52%	48%		
	59%			41%	
				55%	45%

With the reservations made, the methods described should be useful in the study of the conformational requirements of various reactions. Indeed, the pyrolysis of the methylcarbonates of four of the decalols, as described above, provides an example; the results are listed in Table 2. In general, these results are consistent with earlier discussions.[9] The formation of as much as 25 per cent of $\Delta^{1,9}$-octalin from the ester of the alcohol (III) underlines the real possibility of *trans*- (presumably di-equatorial) elimination[10] in ester pyrolyses.

EXPERIMENTAL

To eliminate the effects of minor variations in temperature, column packing, etc., it is convenient to use an internal standard, and for the present purpose, *trans*-decalin was preferred. All retention times were expressed as relative to that of *trans*-decalin, taken as 100, and are denoted as R_D values. When these were close to 100, it was necessary to use *trans*-decalin before and after the sample injection

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[8] N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.* **81**, 4080 (1959).

[9] *inter alia* see D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. De Puy, *J. Amer. Chem. Soc.* **81**, 643 (1959); W. J. Bailey and W. F. Hale, *Ibid.* **81**, 647 (1959).

[10] F. G. Bordwell and P. S. Landis, *J. Amer. Chem. Soc.* **80**, 2450 (1958).

rather than as an internal label; such chromatographic runs were accepted only when the retention times of *trans*-decalin differed by less than 2%.

The following columns were employed: Apiezon L (a high-vacuum grease composed of aliphatic hydrocarbons, 400 cm); squalane (260 cm); dinonyl phthalate (170 cm); benzyldiphenyl (250 cm); tricresyl phosphate (200 cm); and silver nitrate (13%) in polyethylene glycol (250 cm). The R_D values obtained on these columns are summarized in Table 1.

The first two stationary phases were similar in behaviour; benzyldiphenyl and tricresyl phosphate were also similar to each other. Dinonyl phthalate was intermediate between the essentially aliphatic and the essentially aromatic solvents, as expected, and showed no advantages. The silver nitrate column showed remarkable behaviour; generally, it lowered the stability of the detector, and it gave retention times which depended upon the other components present, and peaks of unpredictable widths. To avoid the need for many control experiments, we abandoned its use. Apiezon L and benzyldiphenyl were chosen as standard stationary phases; neither was adequate in itself for identifying the six octalins when used under the conditions employed, as R_D values differing by 1-2% cannot be distinguished with certainty.

In all quantitative analyses two samples were examined and gave peak-area ratios and relative retention times constant to ±2%. Minor constituents amounting to 1% were readily identified. In any work with octalins it is necessary to examine samples immediately after preparation, to avoid loss, not necessarily at the same rate for all components, due to autoxidation.

Acknowledgement—One of us (J. W. P.) thanks the Department of Scientific and Industrial Research for a research scholarship.