801. *Mechanism of Elimination Reactions. Part XXII.* Anomalous Elimination from the Trimethylneomenthylammonium Ion.*

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The kinetics and products of the alkaline and neutral decompositions of menthyltrimethyl- and trimethylneomenthyl-ammonium ions in water or ethanol are examined, and indications in the previous literature that the alkaline neomenthyl reactions break the Hofmann rule for bimolecular 'onium eliminations are confirmed. An explanation is offered, which is based on non-synchronous timing in concerted *E*2 bond-changes, which in this case depart from simultaneity by relative advancement of the trimethylamine loss probably caused by instability in the reactive conformation of the quaternary ammonium ion.

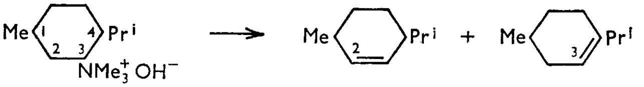
IN the preceding paper reference was made to two qualitatively anomalous reports on the orientation of olefin elimination. The older and more fully authenticated anomaly was discussed in that paper; the other is to be considered here.

It came to light in Hückel, Tappe, and Legutke's work[1] of 1940 on the relation of orientation in elimination to mechanism, though only then as a probable anomaly; for whilst these authors classified the reactions they discussed according to the elimination mechanism, *E*1 or *E*2, which the experimental conditions were thought to favour, their work contained no kinetic confirmation of the mechanisms assumed. The case now to be further considered, which is included by them, without details, in a report of olefin isomer-proportions, is that of the exhaustive methylation of neomenthylamine. They also examined, as we do for comparison, the exhaustive methylation of menthylamine. In menthylamine the 3,4-substituents are *trans*-related, and in neomenthylamine they are

* Part XXI, preceding paper.

[1] Hückel, Tappe, and Legutke, *Annalen*, 1940, **543**, 191.

cis-related; and the question of interest is whether menth-2-ene or menth-3-ene is mainly produced in these exhaustive methylations.



Read and Hendry [2] had previously carried through these reactions; menthyltrimethylammonium hydroxide gave 70% of menthyldimethylamine and 30% of a menthene; trimethylneomenthylammonium hydroxide gave 100% of a menthene. The authors suggested that the former hydrocarbon was menth-2-ene and the latter menth-3-ene. Hückel, Tappe, and Legutke analysed these menthenes, using the distinction that optically active menth-3-ene is racemised by acids in conditions in which menth-2-ene is optically stable; Read and McNiven repeated these analyses.[3] The two sets of figures are in Table 1.

TABLE 1. *Menthenes from menthyltrimethyl- and trimethylneomenthyl-ammonium hydroxide*: (*a*) *Hückel, Tappe, and Legutke*; (*b*) *Read and McNiven.*

	Menth-2-ene (%)	Menth-3-ene (%)
Menthyl-	(*a*) 100, (*b*) 96	(*a*) 0, (*b*) 4
Neomenthyl-	(*a*) 20, (*b*) 10·5	(*a*) 80, (*b*) 89·5

As we shall illustrate, it may not always be safe to assume that exhaustive methylations have the *E*2 mechanism, but it has always seemed rather likely that Hückel, Tappe, and Legutke's assumption that these particular reactions have that mechanism is correct. If this be granted, and if it be accepted that *E*2 eliminations require an *anti*-conformation of changing bonds, then Table 1 reveals an anomaly. In the menthylammonium ion, the 4-hydrogen atom is *cis*-related to the ammonium group; but one of the 2-hydrogen atoms is *trans*-related, and thus *trans*-elimination from this ion can give only menth-2-ene, which is what the ion does give. However, in the neomenthylammonium ion, *trans*-hydrogen atoms occur in both the 2- and the 4-position, and, with both alternatives open, polar factors should control the direction of elimination. There are two principal polar factors, but it is usually found that, for 'onium eliminations by the *E*2 mechanism, the inductive effect dominates, leading to Hofmann-type orientation, which in this case would mean a preponderating proportion of menth-2-ene—contrary to the observations. Of course, if the assumption of an *E*2 mechanism should be wrong, or, more generally, if any factor should markedly increase the unsaturation in the transition state of elimination, then the electromeric effect might dominate sufficiently to lead to Saytzeff-type orientation, and thus to a major proportion of menth-3-ene, as is observed.

It was obviously important to investigate the kinetics of these reactions, in association with determinations of olefin composition. We have thus examined the reactions of menthyltrimethyl- and trimethylneomenthyl-ammonium ions with hydroxide ions in water and with ethoxide ions in ethanol. We now summarise our observations on these reactions.

The reaction of menthyltrimethylammonium ion with hydroxide ion in water at 153—173° is essentially of second order, though kinetic observations are affected by several disturbances. One is a concurrent, and not always negligible, first-order reaction. It is, of course, the sole reaction in the absence of hydroxide ion; it is comparable in importance to the second-order process when the hydroxide ion is about 0·01N; and it is negligible when the hydroxide ion is above 1·0N. Another disturbance is a side-reaction of substitution of the recently reported fourth charge-type,[4] between a product and a factor of the main reaction:

$$R{\cdot}NMe_3^+ + NMe_3 \longrightarrow R{\cdot}NMe_2 + NMe_4^+$$

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[2] Read and Henry, *Ber.*, 1938, **71**, 2544.

[3] McNiven and Read, *J.*, 1952, 153.

[4] Hughes and Whittingham, *J.*, 1960, 806.

Naturally, this reaction disturbs only the later parts of runs, but it is quite important there, except when hydroxide ions are in considerable excess over the menthylammonium ion. The main reaction is subject to a negative salt effect, but this is not expected to be large in water, and is, indeed, not very obvious in the presence of the other disturbances.

Having understood the disturbances, it was easy to avoid or allow for them. We paid main attention to those parts of runs which occurred before an extensive production of tetramethylammonium ion set in. We determined separately the rate of the first-order reaction, by leaving out the alkali. Then, we dissected out the second-order rate from the mixed-order reaction in a way which has been illustrated many times before.[5] A knowledge of both the first- and second-order rate constants now enabled us to set up product-determining runs, which were either pure first-order or pure second-order reactions. In each case, about 70% of the total primary reaction consisted of elimination. The menthenes from the first-order decomposition contained 32% of menth-2-ene, and from the second-order reaction consisted wholly of menth-2-ene.

The reaction of menthyltrimethylammonium ion with ethoxide ion in ethanol at 80—100° was essentially one kinetic process. There was no appreciable first-order reaction, and no appreciable entry by formed trimethylamine into competition with ethoxide ion for menthyltrimethylammonium ion. We observed a second-order process, subject, however, to a considerable negative salt effect, so that it became necessary to compare rate-constants at approximately standardised ionic strengths. The second-order reaction gave 15% of olefin, and this consisted wholly of menth-2-ene.

The chief characteristic of the reaction of the trimethylneomenthylammonium ion with hydroxide ion in water at 153° was the relative prominence of a first-order process, which accounted for a substantial part of the reaction even in strongly alkaline conditions. We could observe the first-order process in the absence of the second-order by leaving out the alkali, but we could never follow the second-order process without some concurrent first-order reaction. However, having measured the first-order rate constant, we could extract the second-order rate constant from the mixed kinetics.[5] No disturbance arose from any reaction of formed trimethylamine. The second-order reaction probably had a somewhat small negative salt effect, but we could not obtain a reliable estimate of it from the mixed-order kinetics.

Both the first- and second-order reactions proved to be eliminations without concurrent substitution: and the menthenes, quantitatively formed in the first-order reaction, and in mixed-order reactions rich in their second-order component, were analysed. The first-order reaction gave 2% of menth-2-ene. From the olefin compositions given by the mixed-order reactions, and the first- and second-order rate constants, it could be computed that a pure second-order reaction would give 12% of menth-2-ene.

Unlike its reaction with hydroxide ion in water, the reaction of the trimethylneomethylammonium ion with ethoxide ion in ethanol at 65—80° was found to be a kinetically single process. It was of second-order, but was subject to a considerable negative salt effect. It was not an exclusive elimination, but gave about 70% of menthenes. This menthene mixture contained 35% of menth-2-ene. The figures illustrating the various descriptions just given are in Table 2.

The first theoretical point to be considered is what the kinetic orders mean in terms of mechanism. The fact that the menthyl cation experiences complete release from the stereospecific restriction to produce only menth-2-ene, when second-order kinetics give place to first-order, and that, after such release, the Saytzeff rule is followed, constitutes a clear demonstration that first-order kinetics signalise the unimolecular mechanism, and not a bimolecular reaction with a solvent molecule. If this is true for the menthyl cation, it must be true *a fortiori* for the neomenthyl cation, for which the general tendency to first-order reaction is much greater. Then, second-order kinetics must signalise the bimolecular

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[5] Hughes, Ingold, and Shapiro, *J.*, 1936, 231.

mechanism, and not the unestablished but often discussed mechanism of prior proton extraction to give primarily a carbanion. For the second-order reactions of the menthyl cation, this follows from the completeness of the bimolecular stereospecific restriction. It then follows *a fortiori* for the neomenthyl cation, because, for both cations, and for the latter especially, we observe a coexistence of the second-order process with what we have decided is the unimolecular mechanism, and the carbanion mechanism could not coexist with the unimolecular mechanism, with exclusion of the bimolecular mechanism, since the carbanion and unimolecular mechanisms differ in opposite directions from the bimolecular mechanism (cf. Part XX, Section 9, p. 4066): coexistence means that the second-order process is bimolecular. In Table 3 we translate our observed kinetics according to these theoretical principles, and show olefin isomer-ratios as functions of substrate and mechanism.

TABLE 2. *Rate constants (k_1 in sec.$^{-1}$, and k_2 in sec.$^{-1}$ mole^{-1} l.) and product compositions in the first-order reactions of menthyltrimethyl- and trimethylneomenthyl-ammonium ions in water, and in their second-order reactions with hydroxide ions in water, and with ethoxide ions in ethanol.*

Temp.	Rates and ionic strengths		1st Order		2nd Order		
	10^5k_1 (μ)	10^5k_2 (μ)	Elim. (%)	2-ene (%)	Elim. (%)	2-ene (%)	[B$^-$]
		Menthyl-NMe$_3^+$ + OH$^-$ in H$_2$O					
152·8°	0·011 (0·12)	1·65 (0·24)	—	—	~70	100	1·8
172·8	0·093 (,,)	9·5 (,,)	~70	32	—	100	2·5
		Menthyl-NMe$_3^+$ + OEt$^-$ in EtOH					
100·2	No reaction	114 (0·06)	No reaction		—	—	—
80·0		4·8 (0·10)			15	100	0·10
84·8		10·2 (,,)			—	—	—
90·1		19·2 (,,)			—	—	—
100·2		85·4 (,,)			15	100	0·10
80·0		3·4 (0·16)			—	—	—
84·8		7·6 (,,)			—	—	—
90·1		15·1 (,,)			—	—	—
100·2		53·0 (,,)			—	—	—
,,		40·0 (0·21)			—	—	—
		Neomenthyl-NMe$_3^+$ + OH$^-$ in H$_2$O					
152·8	6·2 (0·24)	61·0 (0·24)	100	1·9	100	8·5 *	0·23
,,	—	—	—	—	100	10·4 *	1·36
,,	—	—	—	—	—	11·6 †	∞
		Neomenthyl-NMe$_3^+$ + OEt$^-$ in EtOH					
80·0	No reaction	60·5 (0·05)	No reaction		—	—	—
,,		48·9 (0·075)			—	—	—
65·6		5·7 (0·10)			68	34	0·14
72·9		14·5 (,,)			—	—	—
80·0		39·8 (,,)			—	—	—
83·5		65·3 (,,)			71	36	0·10
80·0		31·6 (0·14)			—	—	—

* Not pure second-order kinetics.
† Extrapolated to pure second-order kinetics.

TABLE 3. *Olefin isomer ratios in unimolecular and bimolecular eliminations from menthyltrimethyl- and trimethylneomenthyl-ammonium ions.*

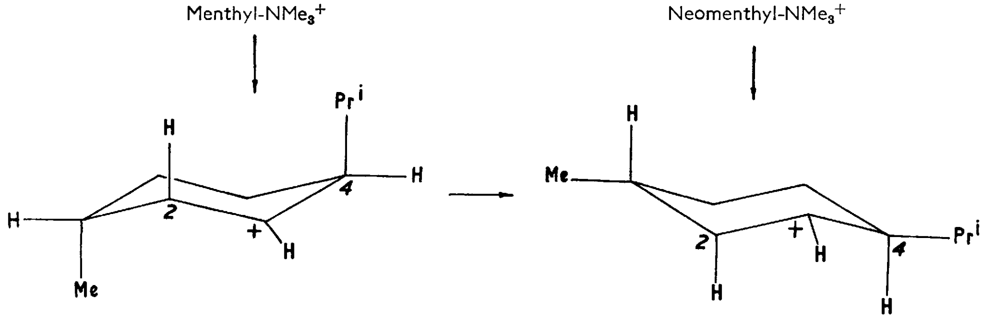
		Olefin isomers (%)			
		Menthyl reaction		Neomenthyl reaction	
Elimination mechanism	Reagent and solvent	Menth-2-ene	Menth-3-ene	Menth-2-ene	Menth-3-ene
*E*1	H$_2$O	32	68	2	98
*E*2	OH$^-$ in H$_2$O	100	0	12	88
,,	OEt$^-$ in EtOH	100	0	35	65

There is nothing qualitatively anomalous about the results given by the menthylammonium ion. Its *E*1 reaction follows the Saytzeff rule, as unimolecular eliminations should, and its *E*2 reactions obey the Hofmann rule, as bimolecular eliminations should, though the latter result has no polar significance, because the bimolecular reactions are going in the only direction stereochemically open to them.

The results given by the neomenthylammonium ion have the striking feature that, not only the *E*1 reaction, but also the *E*2 reactions follow the Saytzeff rule. The anomaly, which originally appeared in Hückel, Tappe, and Legutke's exhaustive methylation of neomenthylamine, supposing that one accepted their assignment of an *E*2 mechanism to this reaction, is therefore real; and it is not a sufficient explanation of it to suggest that a considerable proportion of the *E*1 reaction may have been present in their conditions, because we see here that pure *E*2 reactions of the neomenthyl cation also follow the Saytzeff rule.

We suppose that this is an effect of non-synchronous timing of concerted *E*2 bond changes, but of a timing-difference on the opposite side of simultaneity to that of the case considered in the preceding paper. There it was suggested that, because of a special factor of acidity in the system, the *E*2 mechanism deviated from simultaneity in the direction of the timing of the uncoupled bond-changes of the *E*1c*B* mechanism, *i.e.*, by advancement of the proton loosening. Here we suggest that, perhaps because of steric pressures in the axial conformation of the $C-N^+$ bond, which is the conformation needed for *E*2 elimination, the main lability in the system resides in that bond. We know that the *E*2 mechanism goes over very easily into the *E*1 mechanism in the neomenthyl eliminations, and it is reasonable to suppose that, even before the two bond-breaking processes become thus uncoupled, they will lose simultaneity in the direction of the uncoupled timing of the *E*1 mechanism, *i.e.*, loosening of the $C-N^+$ bond will gain advancement over the proton detachment. The result will be to produce some development of carbonium-ion character in the *E*2 transition state, which will bring in the electromeric effect, and therefore orientation according to the Saytzeff rule.

One other feature of Table 3 deserves comment. Since menthyl- and neomenthylammonium ions should produce the same carbonium ion, one might have expected their *E*1 eliminations to give menthene isomers in an identical ratio. However, the trimethylmenthylammonium ion gives much the more menth-2-ene, though, consistently with the Saytzeff rule, that is still the minor product. If we assume that, probably for reasons connected with hyperconjugation. the labile bonds of the cyclohexane structure are the axial bonds, *even in unimolecular reactions*, then the menthyltrimethylammonium ion, losing an axial trimethylamine residue, will produce its carbonium ion in the unstable conformation (I), which will subsequently pass into the stable conformation (II). On the other hand, the trimethylneomenthylammonium ion will produce the stable conformation (II) directly. Again, if an axial situation confers lability on protons in carbonium ions, then any proton loss from (I), prior to its conversion into (II), must lead to a higher



(I) (II)

proportion of menth-2-ene in *E*1 elimination from the menthyltrimethylammonium ion, than would be formed by way of (II), directly produced without the intervention of (I), in *E*1 elimination from the trimethylneomenthylammonium ion; for (I) contains an axial 2-proton but not an axial 4-proton, whereas (II) contains both, whilst polar orientation favours loss of the 4-proton.

EXPERIMENTAL

Materials.—(—)-Menthyltrimethylammonium iodide, prepared from (—)-menthylamine, had m. p. 190—191°, $[\alpha]_D^{25}$ —44·9° (*c* 4·5 in H_2O) (Found: C, 48·1; H, 8·7; I, 38·7. Calc. for $C_{13}H_{28}IN$: C, 48·0; H, 8·7; I, 39·0%), and the *nitrate* had m. p. 151—152°, $[\alpha]_D^{20}$ —51·1° (*c* 4·4 in H_2O) (Found: C, 60·0; H, 11·0; N, 10·7. $C_{13}H_{28}N_2O_3$ requires C, 59·9; H, 10·8; N, 10·8%). (—)-Trimethylneomenthylammonium iodide, prepared from (+)-neomenthylamine, had m. p. 160—161°, $[\alpha]_D^{20}$ —19·9° (*c* 3·5 in H_2O) (Found: C, 48·0; H, 8·7; I, 38·8%), and the *nitrate* had m. p. 114—115°, $[\alpha]_D^{20}$ —25·1° (*c* 4·3 in H_2O) (Found: C, 59·9; H, 10·8; N, 10·6%).

Kinetics in Water.—These reactions were run in batches of 12—16 silver tubes, each charged, by an automatic pipette, with 5·4 ml. of the reaction solution, made from standardised solutions of the quaternary ammonium hydroxide, alone, or with added sodium hydroxide, nitric acid, sodium nitrate, or water. The open ends of the tubes were nipped in a vice and welded, and, after reaction, the quenched tubes were opened by sawing off the seals. A pair of tubes, first withdrawn from the thermostat bath after sufficient time for the attainment of its temperature, marked the time-zero and gave the composition thereat. Analyses were performed by carrying off the products from the basic (if necessary basified) reaction solution in a stream of nitrogen at 70° for 30 min., and then titrating the non-volatile base with hydrochloric acid to Bromocresol Green–Methyl Red. Corrections to concentration were applied for the volume change between the temperature at which the reaction solutions were made up and the temperature of the reaction.

The first-order decompositions of both the menthyltrimethyl- and trimethylneomenthylammonium ions conformed so exactly to the first-order rate-law that they need not be numerically exemplified.

In the second-order reaction of menthyltrimethylammonium hydroxide, calculated second-order rate constants fell off at various stages, after about 35% of reaction when hydroxide ion was not in any excess over menthyltrimethylammonium ion, and at later periods when the hydroxide ion was in excess. This was due to the conversion of first-formed trimethylamine into tetramethylammonium hydroxide, which decomposed more slowly than the menthyltrimethylammonium hydroxide it replaced. This kinetic effect is illustrated in Table 4. The chemical explanation of it rests on the isolation of a tetramethylammonium salt from a reaction sample run for long enough to allow one to be formed. After the tertiary amines had been removed as usual, the solution was neutralised with hydrochloric acid and evaporated: tetramethylammonium chloride crystallised. It was identified by its physical properties, chlorine content (Found: Cl, 32·4. Calc. for $C_4H_{12}ClN$: Cl, 32·4%), and the rate of decomposition of the corresponding hydroxide, for which the rate constant at 172·8° in water, $k_2 = 1{\cdot}17 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l., was found, an authentic sample of tetramethylammonium chloride having given hydroxide with the decomposition rate $k_2 = 1{\cdot}22 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l. in the same conditions.

The decompositions of trimethylneomenthylammonium hydroxide were all mixed-order reactions, so that calculated second-order rate constants rose and first-order constants fell, as illustrated in Table 5. The second-order rate constant in Table 2 is taken, with greater accuracy, from runs in which the concentration of hydroxide ion was higher, and the drift in the calculated second-order constant was smaller, than is now illustrated. Correction of these apparent second-order constants for the concurrent first-order reaction was effected by Hughes, Ingold, and Shapiro's method.[5]

Kinetics in Ethanol.—Pyrex tubes were used. They were charged each with 5·4 ml. of the solution prepared by adding a known weight of the quaternary ammonium nitrate to a known volume of standard ethanolic potassium ethoxide, and filtering off the precipitated potassium nitrate in a sintered-glass crucible, the filtrate being analysed by titration with acid to check any change of concentration. The rest of the procedure was as for the kinetics in water, except that the contents of an opened tube were added to 35 ml. of water, before removal of volatile materials in nitrogen at 70°.

TABLE 4. (*Run* 6) *Decomposition of menthyltrimethylammonium hydroxide in water at* 172·8°. (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*)

(Initially, $[R{\cdot}NMe_3^+] = [OH^-] = 0{\cdot}1177$M, and $[Na^+] = [NO_3^-] = 0{\cdot}120$M.)

t (hr.)	1·0	2·0	3·5	5·5	7·75	12·0	23·75	30·75	49·5	120·0
OH^- reacted (%)	4·4	8·4	13·4	19·8	25·3	35·8	48·1	52·9	60·2	72·0
10^5k_2	1·08	1·08	1·05	1·06	1·03	1·00	0·92	0·86	0·72	—

TABLE 5. (*Run* 21) *Decomposition of trimethylneomenthylammonium hydroxide in water at* 152·8°. (*Apparent constants*, k_1^a *in sec.*$^{-1}$, *and* k_2^a *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*)

(Initially, $[R{\cdot}NMe_3^+] = [OH^-] = 0{\cdot}1001$M.)

t (min.)	15	30	45	60	80	100	120	150	180	210
OH^- reacted (%)	11·9	21·5	19·6	36·6	44·5	51·4	56·7	63·3	68·5	72·5
$10^5k_2^a$	150	152	156	160	167	176	182	192	201	214
$10^5k_1^a$	14·1	13·5	13·0	12·7	12·3	12·0	11·6	11·2	10·7	10·1

TABLE 6. (*Run* 30) *Decomposition of menthyltrimethylammonium ethoxide in ethanol at* 100·2° (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*).

(Initially, $[R{\cdot}NMe_3^+] = [OEt^-] = 0{\cdot}0967$M.)

t (min.)	15	30	60	90	120	180	240	360
OEt^- reacted (%)	6·8	12·9	23·0	32·2	39·6	51·3	59·2	71·8
10^5k_2	85·3	85·4	85·7	91·1	94·0	101	104	121

TABLE 7. (*Run* 47) *Decomposition of trimethylneomenthylammonium ethoxide in ethanol at* 80·0° (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*).

(Initially, $[R{\cdot}NMe_3^+] = 0{\cdot}0529$, $[OEt^-] = 0{\cdot}0992$, $[K^+] = 0{\cdot}0463$M.)

t (min.)	30	60	90	120	150	180	240	360
$R{\cdot}NMe_3^+$ reacted (%)	6·9	13·1	18·5	23·5	28·5	32·7	41·1	53·7
10^5k_2	40·3	40·7	40·3	41·0	40·8	40·9	42·2	43·2

There were no appreciable first-order reactions at our temperatures. The second-order reactions showed negative salt effects, both by the regular variation from run to run of initial second-order rate constants with initial ionic strength, and by the rise within runs of the second-order constants as ions became consumed. These upward drifts were naturally greater when the interacting ions were in equivalence than when one was in excess, as is illustrated by the examples in Tables 6 and 7.

Proportions of Olefin.—Pairs of tubes were simultaneously taken from the thermostat bath, one for determination of the total reaction by disappearance of alkali as already described, and the other for determination of olefinic product by hydrogenation with hydrogen and a platinum catalyst, after addition of the sample to excess of acetic acid. Table 8 shows an example of this type of determination.

TABLE 8. (*Run* 40) *Decomposition of menthyltrimethylammonium ethoxide in ethanol at* 100·2°. *Proportion in which reaction yields olefin.*

(Initially, $[R{\cdot}NMe_3^+] = [OEt^-] = 0{\cdot}0956$M. Alkali concentrations in ml. of 0·02834N-HCl per 5·00 ml. sample. H_2-uptake in ml. at N.T.P. per 5·00 ml. sample.)

t (hr.)	0	4	6	8	30	48
$[OEt^-]$	18·46	7·75	5·68	4·15	1·05	0·10
H_2	—	0·96	1·24	1·54	1·67	1·65
Olefin (%)	—	14	15	17	15	14

Mean: 15%

Olefin Isomer Ratios.—The reaction solutions were heated in silver or Pyrex vessels for 10 half-lives under the conditions of the kinetic runs, except that larger volumes, 150—500 ml., were now employed. The amines produced were retained in acid while the menthenes were extracted with ether. Menthyldimethylamine, subsequently isolated, had n_D^{25} 1·4558, α_D^{20} −51·0° (*l* 1 dm.) (Found: C, 78·8; H, 13·8; N, 7·6. Calc. for $C_{12}H_{25}N$: C, 78·6; H, 13·8; N, 7·6%), and gave a methiodide of the correct m. p. and optical rotation. Similarly isolated, dimethylneomenthylamine had n_D^{25} 1·4610 and α_D^{20} +50·9° (*l* 1 dm.). The menthenes were collected between 47° and 56° according to the pressure (8—14 mm.). They were analysed by

Hückel, Tappe, and Legutke's method.[1] After measurement of their optical rotation, they were refluxed for 6 hr. with 2 vols. of ethanolic toluene-*p*-sulphonic acid (5 g. of the monohydrate of the acid in 17 ml. of ethanol). The menthenes were then recovered by extraction with ether from the basified solution, and their optical rotation was again determined. Pure menth-2-ene has α_D^{20} +108° (l 1 dm.). When this rotation was observed, the treatment with toluene-*p*-sulphonic acid made no difference to it. When a lower rotation was found originally, it became lower still after the heating with toluene-*p*-sulphonic acid, and the residual rotation, reckoned as a fraction of 108°, gave the proportion of menth-2-ene in the mixture of isomers. From the losses of rotation under the acid treatment we could compute the rotation of the first-formed menth-3-ene, and so deduce that, when this was produced in unimolecular reactions, from the 'onium ions, it appeared in a partly racemised condition. The largest computed rotations of first-formed menth-3-ene were obtained in the essentially bimolecular reactions, and the consistency of the figures allowed us to conclude that bimolecular reactions produce this olefin in an unracemised state, with a rotation α_D^{20} +85·3°. Some examples of these analyses follow.

(No. 1) Initially, menthyltrimethylammonium ion 0·64M, and hydroxide ion 2·53M, were present in water at 172·8°. The menthenes (yield 61%) had n_D^{25} 1·4458, α_D^{20} +107·9°, and, after acid-treatment, α_D^{20} +108·0° (l 1 dm.); and, on hydrogenation, 0·1066 g. took up 17·2 ml. at N.T.P. of H_2 (calc. 17·3 ml.).

(No. 3) Initially, menthyltrimethylammonium ion 0·46M was present in neutral solution in water at 172·8°. The isolated menthenes (yield 67%) had α_D^{20} +52·5°, falling after acid-treatment to +34·1° (l 1 dm.).

(No. 6) Initially, trimethylneomenthylammonium ion 0·059M, and hydroxide ion 1·36M, were present in water at 152·8°. The menthenes (yield 98%) had α_D^{20} +87·6° (l 1 dm.), and 0·2000 g. took up 32·5 ml. of H_2 at N.T.P. (calc. 32·4 ml.); after treatment with acid, α_D^{20} was 11·2°, and 0·2012 g. took up 32·4 ml. of H_2 at N.T.P. (calc. 32·6 ml.).

(No. 9) Initially, trimethylneomenthylammonium ion 0·100M, and ethoxide ion 0·100M, were present in ethanol at 83·5°. The menthenes (yield 68%) had α_D^{20} 95·6°, reduced by acid treatment to α_D^{20} +42·6° (l 1 dm.). Of the latter material, 0·1009 g. took up 15·8 ml. of H_2 at N.T.P. (calc. 16·4 ml.). In the calculations a correction is applied for the 4% of saturated hydrocarbon, which may have come from a trace of paraffin caught up in the potassium used.

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