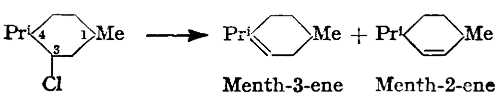
785. *Mechanism of Elimination Reactions. Part XIX.* Kinetics and Steric Course of Elimination from Isomeric Menthyl Chlorides.*

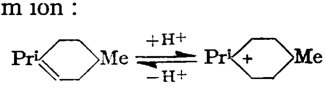
By E. D. Hughes, C. K. Ingold, and J. B. Rose.

The kinetics and products of second- and first-order elimination from menthyl and from *neo*menthyl chloride in alkaline or acid alcoholic solutions have been studied. The absolute rates, kinetic forms, and partitioned directions of these reactions furnish a picture of joint control by the electromeric effect, and by the stereochemical effects summarised in the already given rules, interpreted in the light of Hassel's *cyclo*hexane conformations.

One of the important groups of examples used by Hückel, Tappe, and Legutke, in order to illustrate their thesis that spatial specificity in elimination depends on mechanism, consisted in the formation of menthenes from menthyl and *neo*menthyl chloride (*Annalen*, 1940, **543**, 191). They examined the reactions of both chlorides with ethoxide ions in ethyl alcohol, and of the former chloride with the solvent in the absence of alkali, measuring the proportions in which menth-2- and -3-ene are formed, which are different in the three cases :



The method of analysis was based on the contrast between the stability of the rotatory power of menth-2-ene, and the ready racemisation of menth-3-ene in the presence of acids, an effect due, no doubt, to reversible 3-proton addition with the temporary production of a non-asymmetric 4-carbonium ion :



The above-named authors chose conditions calculated to favour certain mechanisms, but did not establish such mechanisms kinetically. It is, however, not safe always to assume pure bimolecular mechanisms in alkaline media; and we know that, for secondary chlorides, the balance between bimolecular and unimolecular solvolytic reactions is quite delicate. Indeed, the discussion which has been based (Dhar, Hughes, Ingold, Masterman, Maw, and Woolf, *J.*, 1948, 2117) on Hückel, Tappe, and Legutke's olefin compositions could not have been so definite had not part of the work now described already been carried through.

We first made a general kinetic study of the substitution and elimination reactions of menthyl and *neo*menthyl chloride, in alkaline and acidic conditions, in dry or aqueous

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* Part XVIII, preceding paper.

ethyl alcohol, with the object of establishing conditions for the second- and first-order processes. Then, in reactions thus controlled with respect to kinetic form, we measured the proportions of elimination and substitution, and the composition of the mixture of menthenes formed. Our menthene compositions agree well with those of Hückel, Tappe, and Legutke, where the mechanisms may be presumed to correspond. But we now have data for kinetic form and absolute rate to correlate with the olefin compositions; and the first-order reaction of *neo*menthyl chloride, which was not studied by the previous authors, is included in our comparisons. Our experimental findings are summarised in the next six paragraphs.

Menthyl chloride (Cl and Pr^{i} *trans*-related) is less prone to second-order reactions with alkali than are the simplest secondary alkyl chlorides. In dry ethyl alcohol at 160·4°, mixed-order kinetics apply over the more convenient range of alkali concentrations. But with more than 1·0N-sodium ethoxide, the reaction is of second order to the extent of more than 90%. This second-order reaction is presumed to be bimolecular, $S_N2 + E2$. With 1·0N-alkali, 95% of the total reaction is elimination, and a short extrapolation allows us to calculate that 98% of the total bimolecular reactions consists of the elimination $E2$. For this reaction the olefin is wholly menth-2-ene. The rate constant of the $E2$ process in dry ethyl alcohol at 160·4° is $9{\cdot}7 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l., whilst at 124·9° it is $0{\cdot}68 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l. The latter figure allows comparison with an unpublished value by Dr. J. F. Smith for the rate of second-order elimination from *cyclo*hexyl chloride to give *cyclo*hexene: for reaction with ethoxide ions in dry ethyl alcohol at 124·95°, his rate constant is 132×10^{-5} sec.$^{-1}$ mole^{-1} l., that is, 66×10^{-5} sec.$^{-1}$ mole^{-1} l. for the establishment of the double bond in each of two equivalent positions. (Smith finds a small salt effect, but we shall neglect it, since precise values are not important for the comparison.) Relatively to this rate standard, the formation of menth-2-ene from menthyl chloride is retarded by about 100 times, while the formation of menth-3-ene is very much more strongly retarded.

Menthyl chloride undergoes first-order solvolytic reactions at low alkali concentration and in the absence of alkali. In dry ethyl alcohol at 160·4°, more than 90% of the total reaction is of first order, when the concentration of sodium ethoxide is below 0·01N. For our study of the first-order process, we used also " 80% " aqueous ethyl alcohol, which is somewhat more favourable to this kinetic form. Although in this case, as in others in which secondary halides are involved, the distinction between unimolecular and bimolecular solvolysis—both reactions of the first order—is not easily made, our evidence on the whole indicates that we are dealing here with essentially unimolecular reactions. We therefore consider first the total unimolecular rate, which in this mechanism signifies the rate of ionic dissociation of the chloride, whatever may subsequently happen to the formed carbonium ion. In " 80% " aqueous ethyl alcohol at 124·9°, this rate is $0{\cdot}402 \times 10^{-5}$ sec.$^{-1}$. Dr. J. F. Smith has obtained the value $0{\cdot}887 \times 10^{-5}$ sec.$^{-1}$ for the rate of solvolysis of *cyclo*hexyl chloride in the same solvent at 124·95°. In other unpublished work, Dr. R. J. L. Martin derived the value $1{\cdot}53 \times 10^{-5}$ sec.$^{-1}$ for the rate of solvolysis of pinacolyl chloride in the same conditions; and in this case he was able to show that the solvolysis has the unimolecular mechanism exclusively. Evidently our solvolysis rate is of the order of magnitude which allows it to be understood as the unimolecular rate for a secondary chloride. In the absence of initially added alkali, conditions in which first-order processes are fully isolated, the proportion in which they lead to menthenes is 69%. The mixture of menthenes formed has the following composition: menth-3-ene, 68%; menth-2-ene, 32%.

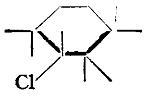
The menth-3-ene, formed in a medium which becomes acid during reaction, was optically inactive. This might have happened, either because, after having been formed in an active state by 4-proton loss from the 3-carbonium ion, the menthene was racemised by reversible 3-proton addition under the influence of liberated acid, or because it was originally formed in an inactive condition by a Wagner-type 4-to-3 migration of hydrogen. The former alternative has been shown to be the more correct by conducting the reaction in the presence of sodium acetate, the menth-3-ene then being formed under similar kinetics but with 90% of its maximal optical activity.

*neo*Menthyl chloride (Cl and Pr^{i} *cis*-related) has a stronger tendency than its isomer towards second-order reactions. In dry ethyl alcohol at 124·9°, more than 90% of the reaction is of the second order, when the ethoxide ions are in concentration 0·1N. With 1·0N-ethoxide, the second-order rate constant is 144×10^{-5} sec.$^{-1}$ mole^{-1} l. Of this total rate, 91% represents the elimination process *E*2, the rate constant for which is therefore 131×10^{-5} sec.$^{-1}$ mole^{-1} l. The menthene mixture formed has the composition : menth-3-ene, 78%; menth-2-ene, 22%. Thus, the partitioned rate constants are 102×10^{-5} and 29×10^{-5} sec.$^{-1}$ mole^{-1} l. for the respective olefins. Both these rates are of the order of magnitude of the rate of conversion of *cyclo*hexyl chloride into *cyclo*hexene, the value of which may be expressed as 66×10^{-5} sec.$^{-1}$ mole^{-1} l. for the establishment of the double bond in one individual position.

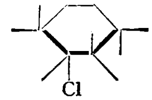
*neo*Menthyl chloride undergoes first-order solvolysis in very weakly alkaline or in non-alkaline alcoholic media. In " 80% " aqueous ethyl alcohol at 124·9°, the first-order rate constant is $16{\cdot}3 \times 10^{-5}$ sec.$^{-1}$, that is, about 20 times greater than the first-order rate constant for *cyclo*hexyl chloride. Either we are dealing here with a mildly accelerated unimolecular reaction, or the normal unimolecular reaction is being overlaid by a somewhat faster bimolecular solvolysis. We incline to the second view, mainly because the product compositions suggest that first-order reactions of menthyl and *neo*menthyl chloride cannot go through the same carbonium ion. The solvolysis of *neo*menthyl chloride consists of elimination to the extent of 96%, and the menthene mixture formed has the composition : menth-3-ene, *ca.* 99%; menth-2-ene, 1·2%. We thus assume that at least the menth-3-ene is formed mainly in a bimolecular manner.

This menth-3-ene is optically inactive, as recovered from solutions rendered acid by the liberated hydrochloric acid, but has more than 85% of its maximal optical activity when the solvolysis is conducted in the presence of sodium acetate, which does not otherwise alter the composition of the menthene, or change the kinetics in any significant way. It follows that a Wagner-type shift of hydrogen is not an essential feature of the process of elimination.

For the purpose of discussing the above results, we have to consider, not only polar effects on the rate and direction of reaction, but also the extent to which spatial requirements are, or can be, fulfilled. In the latter connexion, it is necessary to take account of Hassel's concept of the stable, strainless, *cyclo*hexane ring with a six-fold alternating axis, six bonds being directed radially from the circumference (κ) and six parallel to the unique axis of symmetry (ε). Then *cis*-1 : 3-pairs of substituents have to be radially attached in the stable state, since they would overlap strongly, if bound in directions parallel to the axis. *cyclo*Hexyl chloride may be considered in two important forms of not very different stability (I and II), menthyl chloride in two forms, (III) much more stable than (IV), and *neo*menthyl chloride in two forms not greatly differing in stability (V and VI).



(I)



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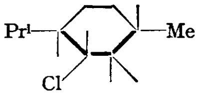

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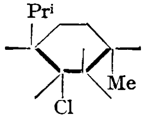

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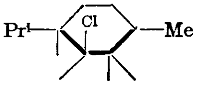

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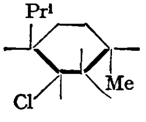

(VI)

It may reasonably be assumed that second-order elimination from menthyl chloride takes place so much more slowly than from *cyclo*hexyl chloride, because, as an *E*2 reaction, it is subject to the *anti*-elimination rule. Therefore, the reaction of menthyl chloride is compelled to go through form (IV) of that molecule, which is very unstable, because it has axially bound *cis*-1 : 3-substituents. Even then, under the same rule, elimination is permitted only in one direction, which is not that favoured by electromeric hyperconjugation. Thus only menth-2-ene is obtained in this reaction, and it is produced 100 times more slowly than might have been expected.

Because of the difficulty attending bimolecular elimination from menthyl chloride, we are fairly safe in assuming that its first-order elimination is unimolecular. If we assume that the first-order reaction of *cyclo*hexyl chloride, like that of *iso*propyl chloride, is largely unimolecular, it becomes intelligible that the rates of these reactions are the same to within a small multiple. In unimolecular elimination, the direction of reaction should be controlled essentially by electromeric hyperconjugation, without much interference from stereochemical factors; and thus it is consistent that in this reaction of menthyl chloride a preponderating quantity of menth-3-ene is produced.

The stereochemical situation places no restriction on bimolecular elimination from *neo*menthyl chloride. Furthermore, since the reactive form is (V) under the *E*2 rule, elimination in either direction is sterically possible, and thus electromeric hyperconjugation is free to control the direction of reaction. Consistently, we find second-order elimination from *neo*menthyl chloide proceeding at a rate of quite the same order of magnitude as that of the corresponding reaction of *cyclo*hexyl chloride, and, moreover, producing a preponderating quantity of menth-3-ene.

The mildly accelerated first-order reaction of *neo*menthyl chloride is believed to arise from a predominating bimolecular solvolysis. It is really faster in one direction, but slower in the other, than our standard of comparison, the orientation being qualitatively as expected for control by electromeric hyperconjugation, but quantitatively more extreme than is commonly associated with this effect when, as is frequently the case, an anion is the attacking reagent. This may be because the reagent is now a neutral solvent molecule. There is some evidence for the conclusion that hyperconjugation produces larger and more strongly differentiated kinetic effects where reagents are neutral than where they are charged. It was thus that we explained (Dhar *et al.*, *loc. cit.*) how, in bimolecular elimination, the Saytzeff rule replaces the Hofmann rule when we go over from alkyl 'onium salts to alkyl halides as substrates. In the field of electrophilic aromatic substitution, de la Mare has similarly explained (*J.*, 1949, 2871; cf. de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12s) the larger kinetic effects produced by alkyl substituents in chlorination by molecular chlorine than in nitration by the nitronium ion. Perhaps in all such cases, the binding in the transition state is more quantal and less electrostatic, so that more unsaturation has to be developed, in the absence than in the presence of ionic charges.

EXPERIMENTAL

Materials.—The chlorides employed were obtained by treatment of (−)-menthol with phosphorus pentachloride, with or without ferric chloride, at regulated temperatures. The reaction produced (−)-menthyl chloride and (+)-*neo*menthyl chloride, in proportions which varied with the conditions, together with 4-chloromenthane and menthenes (cf. Hückel and Pietrosk, *Annalen*, 1939, **540**, 250).

When (−)-menthyl chloride was required, menthol (320 g.) was chlorinated with commercial phosphorus pentachloride (500 g.) and ferric chloride (100 g.) in light petroleum (1100 c.c.) at 0°. After the acids had been removed with aqueous sodium carbonate, the (−)-menthyl chloride was crystallised and collected at −80°, and recrystallised several times from ethyl alcohol at that temperature, the progress of purification being followed by the optical rotation. The material was finally dissolved in ether, freed from alcohol by washing with aqueous sodium chloride, recovered, and given a non-ebullient distillation in a good vacuum at 25°, the receiver being cooled in liquid air. The pure liquid chloride had α_D^{20} −49·6° (*l* 10 cm.).

We obtained (+)-*neo*menthyl chloride only as a concentrate still containing (−)-menthyl chloride, but this permitted study of the kinetics and products of the elimination processes of the former, more reactive chloride. Menthol (120 g.) was now chlorinated with *pure* phosphorus pentachloride (200 g.) in light petroleum (450 c.c.) at 80—100°. After the acids had been washed out and the organic solvent removed, the product was shaken with concentrated sulphuric acid (10 c.c.) in order to eliminate olefins. The residual chlorides were separated, given a non-ebullient distillation in a good vacuum, and then heated at 64° for 15 hr. with "80%" aqueous ethyl alcohol in order to destroy the 4-chloromenthane. The material, recovered by pouring of the reaction product into aqueous sodium chloride, extraction with light petroleum, and distillation of the solvent, was treated, as before, with concentrated sulphuric acid, for the purpose now of removing the solvolysis products, and was then re-dissolved in light petroleum, washed with aqueous sodium carbonate, and given a final non-ebullient distillation in vacuum. The main central fraction (60 g.) had α_D^{20} +19·6° (*l* 10 cm.) (Found: C, 68·3; H, 10·9; Cl, 20·9. Calc. for $C_{12}H_{15}Cl$: C, 68·7; H, 11·0; Cl, 20·3%). It was shown by kinetic analysis, and by its rotatory power, to contain 1% of 4-chloromenthane, 21% of (−)-menthyl chloride, and 78% of (+)-*neo*menthyl chloride.

Kinetics.—The solvent was either dry ethyl alcohol, or "80%" aqueous ethyl alcohol, *i.e.*, a mixture of 4 vols. of the alcohol with 1 vol. of water. The temperatures being somewhat high, the sealed-tube method was used, second-order rate constants being corrected for expansion of the solvent. Introduced concentrations of the organic chlorides and of sodium ethoxide were obtained by direct weighing and by volumetric measurements respectively, and the losses of these substances by reaction as the tubes were attaining the temperature of the thermostat were obtained from a determination of chloride ion in the tubes withdrawn at what was to be the time-zero. Cooled tubes were broken under dilute nitric acid, and the reaction was followed by potentiometric titration of chloride ion.

The reactions of menthyl chloride with sodium ethoxide in comparable proportions were of mixed order, and the second-order rate constants were therefore obtained by using the alkali in constant excess, measuring the resulting first-order constant, k_1', subtracting the independently determined solvolytic rate constant, k_1, and dividing by the alkali concentration: $k_2 = (k_1' - k_1)/[\text{NaOEt}]$.

The solvolytic constant k_1 had to be measured by extrapolation methods owing to the loss of chloride ion in acid solution through the reaction of hydrochloric acid with ethyl alcohol. In one such method, the reaction was started with a deficit of alkali, so that the solution became acid while the reaction rate was still easily measurable. Integrated first-order constants, k_1', were then computed for successive intervals of time while the alkali was disappearing, and these constants were plotted against the relevant mean alkali concentrations, thus giving by extrapolation the value of k_1 at zero alkali concentration. In the "80%" solvent at 124·9° the attack of hydrochloric acid on ethyl alcohol is not very fast, and thus the reaction could be studied by starting it in neutral solution, the integrated first-order constants k_1', being extrapolated backwards to give the initial constant k_1.

The rates of reaction of *neo*menthyl chloride were examined by using the mixture of chlorides of rotatory power $\alpha_D = +19·8°$ (*l* 10 cm.). In alkaline solution a reaction curve of normal type, due to *neo*menthyl chloride, was succeeded by a slightly sloping continuation curve, due to menthyl chloride, which could be treated as linear for the times occupied by the reaction of *neo*menthyl chloride. Back-production .of this linear curve gave the correction for the simultaneous reaction of menthyl chloride, which was to be applied in computing the amount of reaction of *neo*menthyl chloride. The axial intercept of the curve produced gave the composition of the original mixture of chlorides: in runs at different temperatures, and with different solvents, and different concentrations of alkali, this was found to be within 1% of the composition already noted. Rate constants were computed from the record of the first 75% of the reaction of *neo*menthyl chloride, a range in which the correction for the simultaneous reaction of menthyl chloride was not above 2%. The reaction of *neo*menthyl chloride in alkaline solution was found to be much more nearly of the second order than the corresponding reaction of menthyl chloride, but the simultaneous solvolytic reaction was not negligible. Allowance was made for it by conducting the alkaline reaction in such conditions that good apparent second-order rate constants, k_2', could be calculated from the results, and then subtracting the independently determined solvolytic rate constant divided by the mean alkali concentration: $k_2 = k_2' - k_1/[\text{NaOEt}]$.

The solvolytic rate for *neo*menthyl chloride was determined in runs which were started in neutral solution and thus became acid, allowance being made for the reaction of menthyl chloride with the aid of the first-order rate constant already measured for that substance. In principle the error caused by the reaction of hydrochloric acid with the solvent was eliminated by the second of the extrapolation methods already described; but in practice, owing to the relative rapidity of the solvolysis of *neo*menthyl chloride, the correction involved was unimportant.

In some runs conducted in the presence of sodium acetate the disappearance of chloride ion by reaction with the solvent did not take place, and first-order rate constants of solvolysis could be computed in the ordinary way.

Proportions of Olefin.—Menthenes were estimated in some cases at the conclusion of reaction, and in others at the time-zero and at various later stages during the progress of reaction.

The determination of menthenes by halogen uptake proved difficult, and we therefore resorted to quantitative hydrogenation with Adams's platinic oxide catalyst, the platinum being produced in a mixture of equal volumes of ethyl alcohol and acetic acid, before the ethyl alcoholic solution of the menthenes to be reduced, together with an equal volume of acetic acid, both saturated with hydrogen, were introduced with careful exclusion of air. The reaction vessel being provided with a jacket at 25° and shaken mechanically, the uptake of hydrogen became complete within 30 min., and could be read on the gas-burette. Experiments with weighed samples of the menthenes in about 0·05M-solution gave results good to within 2%.

Kinetic Results.—The more important results are summarised in Table 1. The last group of entries requires some further explanation.

During our experiments on the preparation of concentrates of *neo*menthyl chloride, a sample of mixed isomers was obtained from which the 4-chloromenthane had not been removed. It had α_D^{20} +8·0° (*l* 10 cm.), and was subsequently shown by kinetic analysis to contain 19% of the tertiary chloride. This is the most rapidly solvolysed chloride, and the opportunity was taken to measure its first-order rate of solvolysis, the method being the same as that already described for finding the solvolysis rate of *neo*menthyl chloride in the presence of more slowly reacting menthyl chloride. As can be seen from the last two entries in the Table, the rate constant was the same in acid and alkaline solution.

TABLE 1. *Rate constants and proportions of olefin formed in alcoholic solvents from isomers of menthyl chloride in the presence or absence of alkali.*

Run no.	Initial [RCl]	Initial [NaOEt]	$10^5k_1'$ (k_1' in sec.$^{-1}$)	$10^5k_2'$ (k_2' in sec.$^{-1}$ mole^{-1} l.)	10^5k_1 (k_1 in sec.$^{-1}$)	10^5k_2 (k_2 in sec.$^{-1}$ mole^{-1} l.)	Olefin (%)
(−)-*Menthyl chloride in dry* EtOH *at* 160·4°.							
5	0·1796	1·027	~10·1	—	—	~10	95
6	0·0520	1·026	10·9	—	—	10·0	96
8	0·0402	0·978	10·6	—	—	10·1	—
29	0·0177	0·936	9·84	—	—	9·7	—
9	0·0512	1·396	15·3	—	—	10·5	—
7	0·0448	1·917	21·1	—	—	10·7	97
10	0·0505	2·047	22·2	—	—	10·5	—
11	0·0490	2·385	25·4	—	—	10·4	—
12	0·2030	2·050	—	—	—	—	97
14	0·0382	0·0177	1·10—0·92	—	0·92	—	—
15	0·0381	0·0188	1·08—0·91	—	0·89	—	—
16	0·1920	—	—	—	—	—	74
(In this series, the olefin was determined at the conclusion of reaction.)							
(−)-*Menthyl chloride in dry* EtOH at 124·9°.							
13	0·1014	1·914	1·23	—	—	0·74	93
(The rate-constant is not corrected for a small amount of simultaneous solvolysis. Olefin was determined at the end of reaction.)							
(−)-*Menthyl chloride in* " 80% " *aq.* EtOH *at* 124·9°.							
17	0·1164	—	0·39—0·27	—	—	0·402	—
18	0·1177	—	—	—	—	—	69
(Olefin was determined at the end of reaction.)							
(+)-neo*Menthyl chloride in dry* EtOH *at* 124·9°.							
20	0·0940	0·1580	—	193	—	170	91, 93
21	0·0994	0·3640	—	161	—	153	90, 90, 90
22	0·0674	1·023	—	146	—	144	93
23	0·0613	1·483	—	141	—	140	89
24	0·0374	0·0171	5·8—2·1	—	2·2	—	—
(+)-neo*Menthyl chloride in dry* EtOH *at* 99·5°.							
30	0·1050	1·702	—	18·4	—	18·4	—
(+)-neo*Menthyl chloride in* " 80% " *aq.* EtOH *at* 124·9°.							
26	0·0921	—	16·3	—	16·3	—	—
27	0·0884	—	—	—	—	—	96, 96, 95
(In the above eight runs, [RCl] refers to the *neo*-isomer, not the total chlorides. Olefin was determined at known times in the course of reaction.)							
4-*Chloromenthane in* " 80% " *aq.* EtOH *st* 64·0°.							
33	0·0396	—	25·4	—	25·4	—	—
34	0·0418	0·0512	25·9	—	25·9	—	—
([RCl] refers to the 4-chloromenthane only.)							

Analysis of the Menthenes.—The menthene mixtures to be analysed were isolated from experiments in which about 25 g. of menthyl or *neo*menthyl chloride were decomposed in conditions such that the rate and kinetic constitution of the reactions were known. The alcoholic solution of the decomposition products was poured into aqueous sodium chloride and extracted with pentane, and the menthene mixture was isolated by distillation under reduced pressure, and redistillation over sodium. The analysis was effected by measurement of the optical rotation, and its remeasurement after the menth-3-ene had been racemised by being heated with ethyl-alcoholic toluene-*p*-sulphonic acid, the menthene mixture being recovered as before.

Analytical Results.—The conditions of the principal experiments are in the upper part of Table 2, while the corresponding results are given in the lower part.

According to Hückel, Tappe, and Legutke, to whom the analytical method is due (*loc. cit.*), menth-2-ene has α_{D}^{20} 107° (l 10 cm.). On the assumption that no racemisation occurs to menth-3-ene bimolecularly produced in alkaline solution, our data lead to the conclusion that menth-3-ene has the maximum rotation α_{D}^{20} $+76{\cdot}2°$ (l 10 cm.).

TABLE 2. *Proportions of menth-2- and -3-ene in the mixed menthenes formed from menthyl and from* neo*menthyl chloride by reaction in alcoholic solvents in the presence or absence of alkali.*

(A) *Conditions of reaction.*

Product run no.	Chloride	Mean [NaOEt]	EtOH solvent	Temp.	Time (hr.)	Order of olefin-forming reactions
P 1	Menthyl	2·4	Dry	160·4°	12	97% 2nd, 3% 1st
P 2	Menthyl	None	" 80% "	124·9	192	100% 1st
P 4	73% *neo*- + 27% menthyl	2·0	Dry	99·5	4	99% 2nd of *neo*- 1·2% 2nd of menthyl
P 5	73% *neo*- + 27% menthyl	None	" 80% "	124·9	4	98% 1st of *neo*- 1·8% 1st of menthyl

(B) *Composition of menthenes.*

Product run no.	α_{D}^{20} (l 10 cm.) before rac.	α_{D}^{20} (l 10 cm.) after rac.	Menth-2-ene (%) in total	Menth-2-ene (%) in main reaction
P 1	+106·7	+104·2	98	100 in 2nd order of menthyl
P 2	+ 33·6	+ 34·2	32	32 in 1st „ „
P 4	+ 83·4	+ 24·6	22·8	22 in 2nd „ *neo*menthyl
P 5	+ 2·4	+ 1·8	1·7	1·2 in 1st „ „

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