423. *Mechanism of Elimination Reactions. Part XIII. Kinetics of Olefin Elimination from* iso*Propyl-,* sec.*-Butyl-, and* 1*-Phenylethyldimethylsulphonium Salts in Alkaline Alcoholic Media.*

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Data are recorded to show the effects of certain structural changes on the rates of the substitutions and eliminations which secondary alkyldimethylsulphonium ions undergo in bimolecular reactions with ethoxide ions in anhydrous ethyl alcohol as solvent. Elimination rates are analysed, where possible, in terms of the separate rates of establishment of the double bond in the different branches of the secondary alkyl groups. The structural effects studied relate to those of α-linked methyl, ethyl, and phenyl substituents, and to the effect of a β-linked methyl substituent on the rate of establishment of a double bond between C_α and C_β.

The substitutions are composite, since either methyl or the secondary alkyl group may be displaced from the sulphonium ion in bimolecular substitution. In the case of the dimethyl-1-phenylethylsulphonium ion, which shows an outstandingly large rate of total bimolecular substitution, it is shown that this effect of the phenyl substituent is due mainly to an increased rate of displacement of the 1-phenylethyl group itself, rather than to any effect of this phenylated group on the rate of displacement of methyl. The effect of the phenyl substituent is regarded as essentially polar.

In the bimolecular elimination of the *sec.*-butylsulphonium ion, the double bond mainly enters the shorter alkyl branch, in contrast to the corresponding reaction of *sec.*-butyl bromide. The effect of an α-methyl or α-ethyl substituent is to increase the rate of establishment of a double bond between C_α and C_β, the effect of an α-phenyl substituent is to increase it strongly, and the effect of a β-methyl substituent is to decrease it, in contrast to what is observed with alkyl bromides. The interpretation of the results is considered in Part XVI.

In the preceding paper a kinetic study was described the object of which was to establish the effect of structural changes in primary alkyl groups on the rates of the simultaneous substitutions and eliminations which arise in the decompositions of alkylsulphonium ions. The present paper describes a similar study of secondary alkyl groups combined in sulphonium ions.

Although, as compared with primary alkylsulphonium ions, secondary alkylsulphonium ions show an increased tendency to undergo unimolecular decompositions, these reactions are still difficult to realise in a mechanistically pure form. Therefore we again concentrated attention on the bimolecular reaction of substitution and elimination, which the simpler secondary, like the primary, alkylsulphonium ions undergo in the presence of a strongly nucleophilic reagent and in an appropriate solvent. We have, in fact, kinetically analysed the reactions between secondary alkyldimethylsulphonium ions ($sec.\text{-Alk}\overset{+}{\text{S}}\text{Me}_2$) and ethoxide ions, in dry ethyl alcohol as solvent, the conditions being generally similar to those used in already described investigations on primary alkyldimethylsulphonium ions.

The alkyl groups now examined in combination as dimethylsulphonium ions are *iso*propyl, *sec.*-butyl, and 1-phenylethyl, which may be regarded as derived from ethyl by introduction of the substituents α-Me, α-Et and α-Ph, respectively. A comparison of the behaviour of *iso*propyl and *sec.*-butyl will show the effect of introducing the substituent β-Me in the secondary alkyl series.

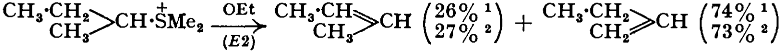
With all these sulphonium ions under the conditions indicated, unimolecular reactions proceed at rates which are negligible in comparison with the rates of the bimolecular processes. The total reaction is thus experimentally of the second order, consisting partly of bimolecular substitution (S_N2) and partly of bimolecular olefin-elimination ($E2$), and the proportion in which olefin is produced remains constant during the change. Our procedure has been, as before, to measure the total rate constant, k_2, and then split it into its components, $k(S_N2)$ and $k(E2)$, on the basis of measurements of the olefin proportion.

In all cases the substitution can consist of two simultaneous substitutions, since either a methyl group, or the secondary alkyl group, may separate from the sulphonium sulphur atom and combine with the attacking ethoxide ion, forming methyl ethyl ether, or a secondary alkyl ethyl ether. However, in our work these two substitutions have been measured together.

$$sec.\text{-Alk}\overset{+}{\text{S}}\text{Me}_2 + \overset{-}{\text{O}}\text{Et} \longrightarrow \begin{cases} \left.\begin{array}{l} \text{MeOEt} + sec.\text{-AlkSMe} \\ sec.\text{-AlkOEt} + \text{SMe}_2 \end{array}\right\} \quad \cdots\cdots \quad (S_N2) \\ \text{HO·Et} + \text{olefin} + \text{SMe}_2 \quad \cdots\cdots \quad (E2) \end{cases}$$

In the case of the *sec.*-butyl compound the elimination may consist of two simultaneous eliminations, since the olefinic double bond can be formed along either the shorter or the longer branches of the *sec.*-butyl group. These eliminations were in the first instance measured together; but it was important for our purpose to determine the rates of the separate processes, as given by the composition of the mixture of isomeric olefins formed in the reaction, because such figures must disclose the orientation laws for bimolecular olefin elimination in sulphonium salts, and must therefore help us to understand the rate relations.

The mixture of isomeric olefins formed in the decomposition of the *sec.*-butyl-sulphonium salt may contain but-1-ene and the *cis*- and *trans*-forms of but-2-ene. Two methods of analysis have been employed, following the pioneer work of Lucas, Dillon, and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 1949, 1953), who attacked the same problem in the example of butenes formed in the alkaline alcoholysis of *sec.*-butyl bromide. They recommended converting the butenes into their dibromides. They found that the boiling points of 1 : 2-, *meso*-2 : 3-, and racemic 2 : 3-dibromo-*n*-butane were too close together to allow an easy separation by distillation. They also found that the other physical constants which they measured were symbatic with the boiling points, so that it was undesirable to make the measurement of two such physical properties of the ternary mixture of bromides the basis of analysis. What was done was to employ one physical property, *viz.*, the density at 25°, and one chemical property, which had been found to be non-symbatic with the physical properties. This was the second-order rate-constant for the reaction with potassium iodide in methyl alcohol at 75°. We first used this method, employing pure synthetic but-1-ene in order to control the isolation of the analytical sample, and to correct for the effect of any slight differences of solvent, temperature, or other conditions between Lucas, Dillon, and Young's kinetic determinations and ours. Our second method consisted of a quantitative distillation of the butenes themselves, with the aid of a special column, which Dr. I. Dostrovsky had built, and which he helped us to apply in these analyses. The results obtained by both methods are given in the following scheme:



$$\left.\begin{array}{l}\text{CH}_3\text{·CH}_2\\ \text{CH}_3\end{array}\right>\text{CH·}\overset{+}{\text{S}}\text{Me}_2 \xrightarrow[(E2)]{\overset{-}{\text{O}}\text{Et}} \left.\begin{array}{l}\text{CH}_3\text{·CH}\\ \text{CH}_3\end{array}\right>\!\!\!=\text{CH} \begin{pmatrix}26\%^1\\27\%^2\end{pmatrix} + \left.\begin{array}{l}\text{CH}_3\text{·CH}_2\\ \text{CH}_2\end{array}\right>\!\!\!=\text{CH} \begin{pmatrix}74\%^1\\73\%^2\end{pmatrix}$$

[1] By kinetic and physical analysis of the dibromides.
[2] By quantitative distillation of the hydrocarbons.

The but-2-ene appeared to consist mainly of the *trans*-isomeride. The two methods of analysis agree in giving the result that most of the elimination which takes place in the alkaline decomposition of the dimethyl-*sec.*-butylsulphonium ion occurs along the shorter branch of the *sec.*-butyl chain. This is a striking contrast to Lucas, Dillon, and Young's results for the corresponding reactions of *sec.*-butyl bromide; and, accordingly, the opportunity of employing a modern column was taken to repeat their work. The outcome, as is mentioned in Part X (this vol., p. 2060), was that their findings were closely confirmed.

The results of the main series of measurements of the overall bimolecular rate-constants, and of the proportions in which olefins are formed in these reactions of the secondary alkyl-dimethylsulphonium ions, are assembled in Table I. In Table II these data are analysed in terms of the individual rate-constants for the total bimolecular reactions of substitution and the total bimolecular reactions of elimination. The substitution rate-constants are not further subdivided, but the elimination rate-constants are analysed in the last column of Table II into the rate-constants for elimination along the separate branches of the alkyl chain.

We shall comment first on the substitution rates. In the units employed in Table II, the substitution rate for the dimethylethylsulphonium ion, $CH_3\cdot CH_2\cdot\overset{+}{S}Me_2$, is given by $10^5k_2 = 395$ (preceding paper). Now it follows indirectly from the work of Ingold and Kuriyan on the aqueous alkaline decomposition of this ion (*J.*, **1933**, 991) that the substitution in alcoholic alkali will in this case proceed largely in the direction which involves the combination of one of the methyl groups with the attacking ethoxide ion to form methyl ethyl ether, but also to a significant degree in the direction in which the ethyl group is similarly displaced to form diethyl ether. No doubt the substitutions of the secondary alkyl-dimethylsulphonium ions will pursue two directions also, each of the observed substitution rates being, therefore, the sum of two components, one relating to the formation of a secondary alkyl ethyl ether and the other to the formation of methyl ethyl ether. Both these component rates are likely to be changed on passing from one alkyldimethylsulphonium ion to another, the former because of polar and

TABLE I.

Second-order rate constants (k_2 *in* $sec.^{-1}$ $g.$-$mol.^{-1}$ $l.$) *of, and percentages of olefin formed in, the reactions of secondary alkyl-dimethylsulphonium iodides and sodium ethoxide in dry ethyl alcohol at* 63·94°.

(Initially $[AlkSMe_2I]$ ~0·05 and $[NaOEt]$ ~0·095.)

Alk. in $(Alk\overset{+}{S}Me_2)\overset{-}{I}$.	10^5k_2.		% Olefin.	
	Individual values.	Mean.	Individual values.	Mean.
*iso*Propyl	1590, 1590, 1550	1580	65·8, 65·7, 65·6	65·7
sec.-Butyl	1200, 1210	1205	57·8, 57·6	57·7
1-Phenylethyl	—	9770 *	58·8, 58·4, 59·0, 60·4	59·1

* Extrapolated from the following results at lower temperatures, *viz.*,

$10^5k_2 = 27·4, 27·6$ (mean 27·5) at 19·98° ($T = 293·13°$)

,, $= 962, 960$ (mean 961) ,, 45·08° ($T = 318·23°$)

by means of the derived equation

$$\log_{10}k_2 = 16·00 - 26{,}230/(2·303 \times 1·986 \times T).$$

TABLE II.

Analysis of kinetic data for the reactions of alkyl-dimethylsulphonium iodides with sodium ethoxide in ethyl alcohol at 64°, *showing the variation of the rates of bimolecular substitution and elimination with changes in the structure of the alkyl group.*

Sulphonium ion.	10^5k_2.	% Olefin.	$10^5k(S2)$.	$10^5k(E2)$.	
				Total.	Each branch.
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot\overset{+}{S}Me_2$	1580	65·7	540	1040	520 520
$\begin{matrix}CH_3\cdot CH_2\\CH_3\end{matrix}\!>\!CH\cdot\overset{+}{S}Me_2$	1205	57·7	510	695	185 510
$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!CH\cdot\overset{+}{S}Me_2$	9770	59·1	4000	5775	— 5775

steric effects on the tendency of the alkyl group itself to be displaced by substitution, and the latter through an " orienting " effect of the secondary alkyl group on the rate of displacement of methyl. As yet we have no systematic data which enable these effects in general to be distinguished; but in the most extreme case, that of the dimethyl-1-phenylethylsulphonium ion, the total rate of substitution of which is much larger than that of any of the purely aliphatic sulphonium ions, we know that most of the rate is due to the relatively facile displacement of the 1-phenylethyl group to form ethyl 1-phenylethyl ether. It has in fact been directly confirmed in preparative experiments involving the decomposition of dimethyl-1-phenylethylsulphonium ions by ethoxide ions in ethyl alcohol, that such of the 1-phenylethyl radical as does not appear in the form of styrene can be recovered in high yield as ethyl 1-phenylethyl ether.* This effect is regarded as essentially polar.

Finally we direct attention to the following facts concerning the elimination rates. In contrast to bimolecular elimination in *iso*propyl and *sec.*-butyl bromides, for which the higher homologue has the larger rate (cf. Part X), the rate of bimolecular elimination drops from the dimethyl*iso*propyl- to the dimethyl-*sec.*-butyl-sulphonium ion. The fall of rate is due entirely to the slower establishment of the double bond in that alkyl branch which becomes lengthened in the *sec.*-butyl group, the rate of its entrance into the alkyl branches which remain similar in the two conpounds being only very slightly reduced. On the other hand, the rate of entrance of the double bond into the corresponding alkyl branch of the 1-phenylethyl group is very much increased, the 1-phenyl substituent of this sulphonium ion, unlike the 2-methyl substituent of the *sec.*-butyl-sulphonium ion, having a strong effect on the reaction of that alkyl branch to which it does not itself belong, *i.e.*, a strong " orienting " action. 1-Methyl and 1-ethyl substituents have a similar, but weaker, action, as may be seen by comparing the elimination rates for the *iso*propyl- and *sec.*-butyl-sulphonium ions with that of the ethyl-sulphonium ion (preceding paper). The theory of these relationships will be discussed in Part XVI.

EXPERIMENTAL.

Materials.—The required sulphonium iodides were all prepared from the secondary alkylthiols, by way of the secondary alkyl methyl sulphides, to which methyl iodide was added in nitromethane as solvent (cf. preceding paper). The 2-propyl and 2-*n*-butyl salts were purified by repeated precipitation at low temperatures from solution in anhydrous ethyl alcohol by addition of dry ether. The 1-phenylethyl salt readily became converted into an oil in the presence of solvents other than ether, and only went solid again when such solvents were removed by pumping. It was therefore purified by washing it with ether after it had largely solidified. The iodine contents of the salts were determined as a check on their purity: dimethyl*iso*propylsulphonium iodide gave I = 54·67% (Calc., 54·69%); dimethyl-*sec.*-butylsulphonium iodide gave I = 51·60% (Calc., 51·58%); and dimethyl-1-phenylethylsulphonium iodide gave I = 43·17% (Calc., 43·17%).

The ethyl alcohol employed in the kinetic measurements was prepared by drying commercial " absolute " ethyl alcohol by the method of Smith and Manske (preceding paper).

Methods for Measurements of Rates and Olefin Proportions.—The methods were the same as those given in the preceding paper. The special method there described for the preparation of solutions of dimethyl-2-phenylethylsulphonium iodide was not required for its more soluble isomeride, the 1-phenyl compound.

Results of Measurements of Rates and Olefin Proportions.—The results of the main series of measurements are summarised in Table I. In illustration of the experimental basis of these figures, we give in Table III the record of the first of the three rate measurements made at 63·94° on dimethyl*iso*propylsulphonium iodide, and in Table IV the third of the three olefin determinations made for this temperature on the same substance.

TABLE III.

Illustrating determinations of total second-order rate-constants (k_2 *in* $sec.^{-1}$ $g.-mol.^{-1}$ *l.*) *:*
*Dimethyl*iso*propylsulphonium iodide* (*Expt. A*).

(Solvent: EtOH. Temp. 63·94°. Initially [SMe_2PrI] = 0·0537M and [NaOEt] = 0·0981N. In the Table [SMePrI] and [NaOEt] are each expressed in c.c. of 0·02145N-acid per 5 c.c. sample.)

t (min.).	[NaOEt].	[SMe_2PrI].	$10^3 k_2$.	*t* (min.).	[NaOEt].	[SMe_2PrI].	$10^3 k_2$.
0	22·77	12·47	—	6	18·15	7·85	14·7
1	21·82	11·52	(13·7)	7	17·71	7·41	14·4
2	20·85	10·55	14·8	8	17·22	6·92	14·5
3	20·03	9·73	15·0	10	16·25	5·95	15·0
4	19·24	8·94	15·4	12	15·65	5·35	14·7
5	18·79	8·49	14·4	∞	10·30	—	—

(Mean $k_2 \doteq 14{\cdot}8 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l.; corrected for solvent expansion, $k_2 = 15{\cdot}9 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l.)

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* These experiments were carried out by Dr. S. H. Harvey. They were primarily directed to the solution of a problem relating to the Walden inversion, and will be published shortly in association with other work in that field.

The reaction with dimethyl-1-phenylethylsulphonium iodide went too rapidly at 63·94° to allow an accurate rate measurement. However, the proportion of olefin in the product of the completed reaction at this temperature was measured. The rate itself was obtained by extrapolation from rate measurements made at lower temperatures, as particularised in the footnote under Table I.

A few further measurements are recorded for convenience in Table V, although they are more relevant to Part VIII than to this paper (cf. this vol., p. 2049).

TABLE IV.

*Illustrating determinations of the proportion of formed olefin : propylene from dimethyl*iso*propylsulphonium iodide by the aspiration method (Expt. C).*

(Solvent: EtOH. Temp. 63·94°. Initially [SMe_2PrI] = 0·0507M and [NaOEt] = 0·0961N. In the Table the alkali is expressed in c.c. of 0·02125N-acid per 5 c.c. sample, whilst the olefin is given by the amount of bromine, measured in c.c. of 0·02925N-thiosulphate, which survives, out of a standard amount supplied, in a 10 c.c. sample of the reaction mixture.)

Initial readings.		Final readings.	
Alkali.	Bromine.	Alkali.	Bromine.
22·53	54·60	10·65	31·80, 32·65, 31·71
22·53	54·68	10·67	31·73, 31·84
22·53 (mean)	54·64 (mean)	10·66 (mean)	31·89 (mean)

(Alkali consumed : 11·87 c.c. Olefin formed : 22·75 c.c. Proportion of olefin = 65·6%.)

TABLE V.

Additional second-order rate-constant (k_2 *in* $sec.^{-1}$ *g.-mol.*$^{-1}$ *l.*) *and percentage of formed olefin for the reaction of dimethyl*iso*propylsulphonium iodide with sodium ethoxide (cf. Part VIII).*

(Solvent: EtOH. Temp. 45·08°.)

Initial concentrations.			
[SMe_2PrI].	[NaOEt].	10^5k_2.	% Olefin.
0·0201	0·0966	187	—
0·0207	0·0968	—	60·6 [1]

[1] Mean of six measurements ranging from 60·4 to 60·9%.

Experiments with But-1-ene and its Dibromide.—The hydrocarbon was prepared, as described by Lucas and Dillon (*J. Amer. Chem. Soc.*, 1928, **50**, 1460), by allowing allyl bromide to interact with methylmagnesium iodide, from which the ether used in its preparation had been largely removed by distillation. The gas evolved at about 75° was washed with 30% aqueous methyl alcohol and 37% perchloric acid, and dried with calcium chloride. Part of this material was used for the preparation of 1 : 2-dibromo-*n*-butane, as follows.

An all-glass apparatus was employed. The bromine was contained in a warmed glass bulb, and was carried as vapour in a stream of nitrogen through a capillary tube to the bottom of a second bulb, which contained the hydrocarbon and was cooled in a bath of ice and salt. The object of the arrangement was to secure good stirring where the bromine enters, and thus to avoid local excess of the halogen. The upper part of the bulb was fitted, by means of a ground joint, with a reflux condenser, consisting of a spiral tube sealed through the bottom of a container filled with ether and solid carbon dioxide. As soon as a permanent yellow colour appeared in the brominated hydrocarbon, this was washed successively with acidified sodium sulphite, sodium hydrogen carbonate, and water. It was then dried with calcium chloride and distilled at 50 mm. (barostat), with high reflux-ratio, through a " 15-plate " adiabatic column of glass helices. The boiling point (80·2—80·3/49·8 mm.) and physical constants agreed practically exactly with those given by Lucas, Dillon, and Young (*loc. cit.*).

This material was used in order to correlate the conditions of our kinetic analysis with those used by Lucas, Dillon, and Young. The chief conditions to which the rate-constants are sensitive are solvent-composition, temperature, and ionic strength. The object of the correlation was to enable us to use Lucas, Dillon, and Young's rate-constants for the dibromides of all the three butenes, by applying to the recorded figures a small percentage correction in order to bring them into correspondence with our slightly different solvent, temperature and ionic strength. The reaction studied was the interaction between the butene dibromides and potassium iodide in " 99% " methyl alcohol at 75°. A large batch of solvent was made up by the addition of the requisite amount of water to dry methyl alcohol : this material was used for all the rate measurements. Our thermostat ran at 74·98° ± 0·02°. After some preliminary trials, we settled to a standard procedure in which the initial concentration of potassium iodide was 0·27M and the initial concentration of dibromide was 0·064M. Under these conditions the second-order rate law was accurately obeyed, and the reaction with 1 : 2-dibromo-*n*-butane had the rate-constant 0·0800 min.$^{-1}$ g.-mol.$^{-1}$ l. For this substance, Lucas, Dillon, and Young record the rate-constant 0·0765 min.$^{-1}$ g.-mol.$^{-1}$ l., and hence it appears that 4·6% must be added to each of their rate-constants in order to obtain figures applying to our kinetic conditions.

Other portions of the synthetic sample of but-1-ene were employed in order to establish a process for the recovery of butenes from mixtures such as would arise by the decomposition of dimethyl-*sec.*-butylsulphonium ethoxide. In particular it was shown that but-1-ene, when recovered from a mixture containing ethyl alcohol and dimethyl sulphide by a process corresponding to that described below, gave a dibromide having properties identical with those of the above standard sample of dibromide.

Analysis of the Butenes derived from Dimethyl-sec.-*butylsulphonium Ethoxide* (*First Method*).—Dry ethyl alcoholic solutions of dimethyl-*sec.*-butylsulphonium iodide and of sodium ethoxide were mixed at 50° to give 2 l. of a solution 0·33M with respect to the sulphonium iodide and 0·66M with respect to sodium ethoxide. The temperature was raised to 70° during several hours, after which water at 70° was run in. There was a brisk evolution of gas, which passed through an ordinary reflux condenser, and was then condensed in a trap cooled in liquid air. The temperature of the reaction mixture was raised until the solvent boiled, and air was then passed through it in order to carry all the butenes into the cooled trap. The trap was warmed to −80°, and its contents were then added to a solution of mercuric chloride (15 g.) in ethyl acetate (62 g.) at −17°. The mixture, in which a heavy white precipitate had formed, was kept at this temperature overnight, and then distilled through a special column arranged for use at low temperatures.

This was a " 5-plate " column of Vigreux type, 80 cm. long and 7 mm. internal diameter, with low hold-up. Its purpose was to separate the butenes from other substances without separating the isomeric hydrocarbons from one another. It was lagged with 2 cm. of cotton wool surrounded by a double-walled jacket through which ice-cold water was pumped during distillation. It was connected by means of ground joints to the distillation vessel below, and, through a drip-indicator, to the first of two condensers above. The drip-indicator was observed through thick " Perspex " windows inserted into the lagging. The cooling jacket of the first condenser had three tubulures, two near the bottom and one at the top, so that its effective height could be altered to give any desired reflux ratio, including total reflux. The method was to pass the cooling fluid into, and out from, the bottom two tubulures, and keep the top one closed, after the height of the cooling liquid in the jacket had been adjusted by withdrawing from it, or letting in through it, the right amount of air. The top of this condenser was connected by a ground joint to the second condenser, which was designed to give total condensation, and which delivered, through another lagged drip-indicator, into a tube leading nearly to the bottom of a collecting flask, cooled with ether and solid carbon dioxide. The second condenser was also connected by way of a ground joint to a trap, and thence to a calcium chloride tube, both cooled with solid carbon dioxide. The cooling fluid for both condensers was dry ether at −80°. It was syphoned from a Dewar vessel, through a coil immersed in a mixture of chloroform, carbon tetrachloride, and solid carbon dioxide; and, having passed through either condenser jacket, it was collected in another Dewar vessel, which was substituted for the source vessel as necessary. The runs of tubing were lagged, except for short rubber sections possessing screw clips for regulating the rate of flow.

A eutectic alloy of sodium and potassium was made up in a flask having a ground joint which fitted the first condenser described above. The alloy was cooled to −80°, and the hydrocarbon distillate was added. The condenser was fitted, and the flask was allowed to warm until the butenes were boiling under total reflux. No hydrocarbon appeared in a CO_2-cooled trap attached to the top of the condenser, and there was very little discoloration of the alloy. After some hours the butenes were transferred by distillation through an all-glass connecting tube to the bromination apparatus, and brominated, exactly as described above for synthetic but-1-ene. The brominated butenes were washed and dried as described for 1 : 2-dibromo-*n*-butane, and then submitted to the following distillations, designed to remove any low-boiling, and also any high-boiling, non-isomeric impurities.

First, the mixture was put under the " 15-plate " column, and boiled with total reflux at 50 mm. pressure (barostat) until thermal equilibrium had been established. Then, very slowly, four drops were taken off as distillate. The temperature at the time of the fourth drop was 73·7°/50 mm. The distillation was then stopped, and the column allowed one hour to drain. The liquid in the distilling flask was then poured through it, and it was again allowed to drain. The four drops withdrawn as distillate would be insufficient appreciably to affect the proportions of the isomeric dibromides, but they could have removed an amount of non-isomeric impurity which would have been enough to upset the analysis. The second distillation process consisted of transferring the bromides by non-ebullient distillation at 50 mm., under conditions of negligible hold-up, from the distilling flask, which was finally heated on a boiling water-bath, to a receiving flask, which was cooled in ice and salt. The short ground-jointed connecting tube led nearly to the bottom of the cooled receiving flask, which was the only condenser. Its efficiency as a condenser was shown by the fact that no condensate collected in the CO_2-cooled trap, to which also it was connected. At this stage the density of the bromides was $d_{4^\circ}^{25^\circ}$ 1·78257. They were then again submitted to above-described distillations, first under the " 15-plate " column, and then from flask to flask. In the distillation under the column, three drops were taken off, the temperature at the time of the third being 78·5°/50 mm., and then three more drops were withdrawn, the temperature at the time of the sixth being still 78·5°/50 mm. It thus appeared that volatile non-isomeric impurities had been fully removed; and even the withdrawal of six drops could not seriously have affected the compositions of the isomeric dibromobutanes. After the non-ebullient distillation, the density was $d_{4^\circ}^{25^\circ}$ 1·78262. This was accepted as the correct value. Densities were measured with a 1 c.c. pyknometer and a microbalance, the technique being generally similar to that developed in these laboratories for work involving heavy hydrogen water or heavy oxygen water (cf., *e.g.*, *J.*, 1934, 498, 1593). The accuracy was about 3 in 10^6, *i.e.*, rather greater than corresponds to the number of figures we quote.

Two measurements were made, using this sample, of the rate-constant of the reaction with potassium iodide in " 99% " methyl alcohol at 74·98°, the conditions being as closely as possible identical with those employed in the experiments with synthetic 1 : 2-dibromo-*n*-butane. The results were as follows :

Initial concentrations.		k_2
[KI].	$[C_4H_8Br_2]$.	($min.^{-1}$ g.-$mol.^{-1}$ l.).
0·2661	0·06366	0·0755
0·2705	0·06385	0·0759

The mean of these rate-constants, in combination with density, gives the analytical composition already quoted.

*Analysis of the Butenes derived from Dimethyl-*sec.*-butylsulphonium Ethoxide* (*Second Method*).—The butene mixture was also analysed by the method of quantitative distillation. In this case twice the formerly used quantities of dimethyl-*sec.*-butylsulphonium iodide and sodium ethoxide were employed, the butenes being collected, and freed from sulphides by treatment with mercuric chloride in ethyl acetate, as before. On this occasion particular care was taken to remove the last trace of butenes from the solvent, which was used as a " chaser " in order to clear the butenes from the column at the end of the distillation. This meant that a quantity of the order of one drop of ethyl acetate became collected with the butenes, and that therefore the sodium–potassium alloy with which they were next treated became considerably tarnished. However, the treatment was continued with fresh portions of alloy until tarnishing no longer occurred. The butenes were then mixed with a little pure pentane (to act as a " chaser ") and distilled in the apparatus described below, the building and operation of which were supervised by Dr. I. Dostrovsky.

The bottom of the distillation bulb contained a thimble-shaped well through which a coil of fine platinum wire was sealed. Through this wire a controlled supply of heat could be introduced by the passage of an electric current. Adventitious heat-exchange was prevented by inserting the bulb, and its connexion to the column, into a Dewar vessel. The column, packed with small glass helices, was enclosed throughout its length with a silvered vacuum jacket, which was connected with a backed diffusion pump. At the head of the column was placed a thermometer, having its bulb in contact with the top of the packing. Above the thermometer, and surrounding its stem, was a reflux condenser, capable of condensing all the vapour that entered it. The top of the condenser was sealed. Between the bottom of the condenser and the top of the packing, a distance of about 2 cm., a narrow, upward-sloping side-tube was inserted, through which butene vapour, but not liquid, could be withdrawn. This tube led first to a wide U-tube, containing mercury through which gas could be bubbled by a small pressure difference, and thence, by a 3-way stopcock, to either of two large aspirators.

In preparation for a distillation, the column jacket was pumped to a hard vacuum, the condenser circuit was started and regulated, and the aspirators were filled. The cooling liquid for the condenser was dry ether which was drawn from a reservoir by means of a circulating pump, forced through a coil immersed in a mixture of chloroform, carbon tetrachloride, and solid carbon dioxide, and thence, by lagged tubes, through the condenser jacket, and back into the reservoir. Thermometers were provided for the measurement of the temperature of the ether as it entered and left the condenser jacket. These temperatures were regulated to be close to −25°, because this temperature gave adequate condensing power, and it had been found that a lower temperature over-cooled the refluxing butenes, so that the temperature at the head of the column fell below the boiling point. The aspirators were supplied with water made alkaline with potassium carbonate. The purpose of the alkali was to suppress any tendency for interaction between the butenes and the water. Losses due to the solubility of butenes in water were reduced by using the same liquid on each occasion.

The butene mixture, which had in the meantime been kept in the distilling bulb at −80°, was now heated by a current given by a 6-volt battery and controlled by a rheostat. Air was at first driven out through the mercury by the ascending vapour : the air was allowed to escape by way of a side-tube. Soon after the butenes had reached the head of the column, and had begun to condense, all passage of gas through the mercury ceased. The refluxing was allowed to continue for a further period in order to ensure thermal equilibrium in the column. Then the butene vapour was withdrawn by running water slowly out of the aspirators, and a series of readings was taken of the temperature at the head of the column and, simultaneously, of the volume of gas collected. A water manometer had been provided so that the pressure of the gas could be read, and its temperature was taken to be that of the emerging water : this was measured, thus permitting correction of the volumes to normal temperature and pressure. The whole of the butenes were eventually collected in the aspirators. When the pentane reached the top of the column the temperature rose sharply and the distillation was stopped.

The quantitative result has already been given. The effect of the distillation was to strip the but-1-ene (b. p. −6°) from the total but-2-enes (b. p. 2—3°) quite sharply. By turning the 3-way tap the isomerides could be collected in separate aspirators. The but-2-ene fraction appeared to consist mainly of the *trans*-isomeride, but the column could not have separated the stereoisomerides sharply, even if both had been present in substantial quantities.

(This method was also used for the analysis of the butenes evolved when *sec.*-butyl bromide is treated with ethyl-alcoholic potassium hydroxide. The result, which confirms an earlier analysis by Lucas, Dillon, and Young, has already been mentioned in Part X.)

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