637. *Reactions related to the Pinacol–Pinacone Rearrangement. Part II.*[1] *The Fate of the Carbonium Ion derived from* 2-*Methylpropane*-1 : 2-*diol.*

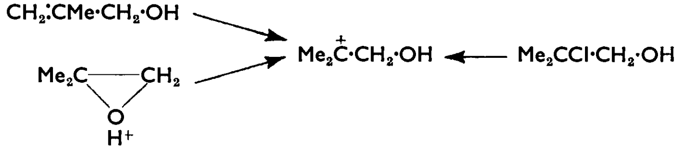
By J. B. Ley and C. A. Vernon.

2-Methylallyl alcohol in aqueous acid gives *iso*butyraldehyde and 2-methylpropane-1 : 2-diol in the ratio *ca.* 1 : 3. The unimolecular solvolysis of 2-chloro-2-methylpropan-1-ol gives the same products in approximately the same ratio, and the two reactions are considered to proceed through a common carbonium ion. The acid-catalysed ring opening of 1 : 2-epoxy-2-methylpropane also gives the same products, but in a different ratio. The reasons for this are discussed. The results are used to interpret the course of the acid-catalysed rearrangement of 2-methylpropane-1 : 2-diol.

In Part I [1] the acid-catalysed rearrangements of 2-methylpropane-1 : 2-diol and its dimethyl ether were shown to proceed *via* the carbonium ions (I) and (II) respectively. In water both ions give ultimately *iso*butyraldehyde. The analogous process in methanol was shown to proceed, for ion (II), by internal hydrogen shift. Other possible reactions of the ions are combination with solvent, and loss of a proton from a methyl group. Since the first process would produce either the original substrate [from ion (I)], or a substance difficult to distinguish from the original substrate [from ion (II)], and the second would produce the readily protonated 2-methylallyl alcohol or its methyl ether, neither could be conveniently studied in the course of the acid-catalysed rearrangement of the glycol or its diether.

(I) $Me_2\overset{+}{C}\cdot CH_2\cdot OH$ $\qquad$ $Me_2\overset{+}{C}\cdot CH_2\cdot OMe$ (II)

Other reactions proceeding through ion (I) and with experimental conditions such that 2-methylpropane-1 : 2-diol and 2-methylallyl alcohol would be stable were therefore sought. Three reactions expected to produce ion (I) are (*a*) acid-catalysed hydration of 2-methylallyl alcohol, (*b*) acid-catalysed ring opening of 1 : 2-epoxy-2-methylpropane, and (*c*) S_N1 hydrolysis of 2-chloro-2-methylpropan-1-ol. These three have now been studied and from the results conclusions have been drawn about the relative ease of the various reactions of ion (I).



Results

Acid-catalysed Rearrangement of 2-*Methylallyl Alcohol.*—This compound in aqueous perchloric acid at 72·9° rearranged completely to *iso*butyraldehyde. The rate of production of aldehyde, initially rapid, decreased until, towards the end of the reaction, the rate was the same as that of rearrangement of 2-methylpropane-1 : 2-diol at the same acidity and temperature. This suggested that the initial reaction produced both the glycol and the aldehyde, the former slowly rearranging to the latter. At lower temperatures, where the glycol was relatively stable, the reaction was followed both by polarographic estimation of *iso*butyraldehyde (A) and by periodate estimation of the glycol (G). The results indicated that, for at least 70% of reaction, the percentage of aldehyde [100A/(A + G)] formed was sensibly constant. First-order rate coefficients were, within experimental error, the same when calculated from either set of analytical data, and were reasonably constant throughout any one reaction. In Table 1

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[1] Part I, Ley and Vernon, *J.*, 1957, 2987.

results are given for the rearrangement of 2-methylallyl alcohol ($3{\cdot}03 \times 10^{-2}$M) in perchloric acid (2·16M) at 44·6°; k_A and k_G are the first-order rate coefficients calculated from the analytical data for the aldehyde and glycol respectively.

TABLE 1.

Time (min.)	Concn. of aldehyde (10^{-2}M)	Concn. of glycol (10^{-2}M)	$\frac{100A}{A + G}$	10^2K_A (min.$^{-1}$)	10^2K_G (min.$^{-1}$)
0·0	0·087	0·306	22·1	—	—
5·0	0·173	0·582	22·9	2·94	2·96
10·0	0·259	0·810	24·3	3·18	2·91
16·0	0·343	1·106	23·8	3·25	2·95
20·0	0·404	1·190	25·2	3·49	2·89
25·0	0·436	1·332	24·6	3·21	2·89
35·0	0·504	1·608	23·9	3·07	3·00
45·0	0·543	1·778	23·4	2·82	2·90
∞ (calc.)	0·722	2·305	—	—	—

In the range of acid concentrations, *ca.* 1·0—2·7M, the percentage of aldehyde formed in the reaction was sensibly constant (mean value, 23·2); the rate of the reaction, however, increased faster than the stoicheiometric acidity, the logarithms of the first-order rate coefficients against H_0 giving a straight line of slope $-1{\cdot}26$. Table 2 refers to measurements made at 44·6°.

TABLE 2.

$HClO_4$ (M)	100A/(A + G)	10^3K_A (min.$^{-1}$)	10^3K_G (min.$^{-1}$)
1·08	23·5	0·70	0·65
1·62	21·4	1·75	1·55
2·16	23·8	3·14	2·93
2·69	24·2	6·04	5·92

Acid-catalysed Ring-opening of 1 : 2-*Epoxy*-2-*methylpropane*.—This reaction was too fast, even at 0°, for kinetic study. Estimations of the amounts of 2-methylpropane-1 : 2-diol (G) and of *iso*butyraldehyde (A) formed in mixtures containing 1·08M-perchloric acid were made; in Table 3, the percentages are calculated from the initial amounts of substrate.

TABLE 3.

Temp.	(G) (%)	(A) (%)
0	96·8	2·7
44·6	92·5	4·9

Solvolysis of 2-*Chloro*-2-*methylpropan*-1-*ol in Water*.—The preparation of this compound by reduction of α-chloro-α-methylpropionyl chloride with lithium aluminium hydride gave a material whose chlorine content was low. The impurity appeared to be 2-methylpropane-1 : 2-diol formed by hydrolysis of the chloro-compound during working up, and it could not be removed by fractionation, presumably because of azeotrope formation. Accurate analysis of the amount of this impurity by periodate titration was not possible because of the hydrolysis of the chloro-compound under the conditions of the estimation. Since it was desired to estimate the amount of 2-methylpropane-1 : 2-diol formed in the solvolysis of the chloro-compound, a material initially containing this substance, in amounts not accurately known, was unsuitable.

The reaction of hydrogen chloride and the oxide in anhydrous ether at −10° gave a mixture of 2-chloro-2-methylpropan-1-ol and its isomer, 1-chloro-2-methylpropan-2-ol. Separation by fractional distillation proved impracticable. Chlorine analysis indicated that no other substance was present. Since the two isomers solvolysed in water at enormously different rates, the reaction of the faster reacting 2-chloro-2-methylpropan-1-ol could easily be studied in the presence of its isomer. It was shown that the inert isomer had no effect on the analytical procedures and underwent no change in the course of the reaction studied. Estimations of chloride ion (C) and of *iso*butyraldehyde (A) were made at suitable points throughout the course of the reaction; 2-methylpropane-1 : 2-diol (G) was estimated in the final product. Table 4 shows the results obtained at 25°.

It will be seen that, when the initial substrate concentration is calculated from that of the chloride ion at complete reaction, the amounts of glycol and aldehyde formed account for *ca.* 96% of the reaction. *A priori*, the discrepancy might be due to the formation of a small

TABLE 4.

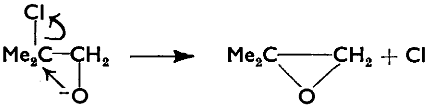
Time (min.)	[Cl⁻] (10^{-3}M)	[A] (10^{-3}M)	[G] (10^{-3}M)	[A]100/[Cl⁻]	100[A]/([A] + [G])
0	3·73	0·99	—	26·7	—
10	8·15	1·81	—	22·2	—
20	12·35	2·28	—	18·5	—
32	16·85	3·44	—	20·4	—
45	21·3	3·68	—	17·3	—
60	26·0	5·21	—	20·5	—
∞	53·5	12·3	39·8	22·7	23·6

amount of 2-methylallyl alcohol. This substance is difficult to detect specifically, and consequently solvolysis of a relatively large amount of chloro-compound was carried out and the product was carefully fractionated. No 2-methylallyl alcohol was found and the discrepancy in Table 4 is most probably due to experimental error.

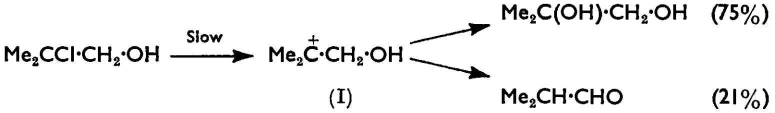
First-order rate coefficients for the solvolysis were calculated from results referring to the rate of production of chloride ions, and were found to be constant, within experimental error, throughout a run. The mean values obtained on using the mixture of isomers and the substance prepared by reduction of α-chloro-α-methylpropionyl chloride were virtually identical, *i.e.*, 10·1 and 10·2 × 10^{-3} min.$^{-1}$ respectively. In 40% (v/v) aqueous ethanol the reaction was much slower ($k_1 = 2{\cdot}34 \times 10^{-4}$ min.$^{-1}$).

DISCUSSION

The solvolysis of 2-chloro-2-methylpropan-1-ol in water cannot be shown to be unimolecular by the usual criterion of non-dependence of rate on alkali concentration, since in the presence of sufficient base the reaction

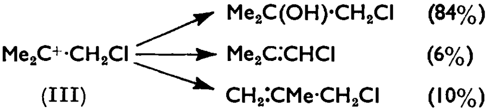


occurs, and an order in base appears in the rate equation. Nevertheless, there are good reasons for believing the solvolysis to be unimolecular : (*a*) the compound is structurally akin to *tert.*-butyl chloride, the solvolysis of which, in water, is certainly unimolecular; (*b*) the related 1 : 2-dichloro-2-methylpropane has been shown [2] to undergo unimolecular solvolysis in water; (*c*) the increase in rate on change of solvent from 40% aqueous ethanol to pure water is as expected for a unimolecular mechanism.[3] If these arguments are accepted, the rate-controlling stage must be formulated as the formation of the carbonium ion (I), which then undergoes reaction to give 2-methylpropane-1 : 2-diol and *iso*-butyraldehyde, *i.e.* :



The percentages given for the two products have been calculated as mean values from the data in Table 4. However, although 2-methylallyl alcohol was not detected among the products in a large-scale experiment, the possibility that small amounts are formed cannot be excluded.

It is of interest to compare these results with those obtained by de la Mare and Salama [2] for the solvolysis of 1 : 2-dichloro-2-methylpropane. This compound reacts through the intermediate ion (III) and gives the products as shown. The two reactions give similar



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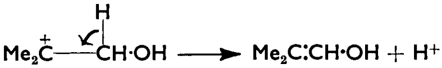
[2] de la Mare and Salama, *J.*, 1956, 3337.

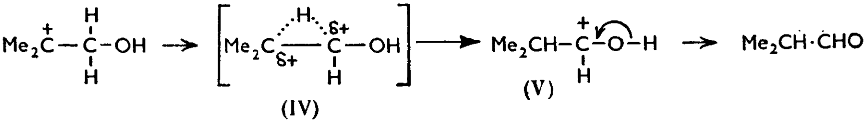
[3] de la Mare, Leffek, and Salama, *J.*, 1956, 3686.

relative amounts of substitution product; the main difference is that, whereas elimination from a methyl group, giving an allylic derivative, occurs readily for ion (III) and accounts for 10% of the products, no similar process has been detected for ion (I). The interpretation of this difference involves considering the mechanism of formation of *iso*butyraldehyde. There are two possibilities; first, proton loss giving the enol form of the aldehyde:



$$Me_2\overset{+}{C}—\overset{H}{CH}·OH \longrightarrow Me_2C{:}CH·OH + H^+$$

and, secondly, internal proton migration giving ion (V) which, by proton loss, gives the aldehyde in the keto-form:



The first of these processes would be analogous to the formation of 1-chloro-2-methylpropene from ion (III) and should occur the more readily since, in the transition state, the greater conjugative power of the hydroxyl group than of a chlorine atom, would be more effective in stabilising the incipient double bond. However, the second process, which has not been found for ion (III),* but has been shown to take place with ion (II) (Part I), is, since ions (I) and (II) are closely related, probably that which actually occurs. If this is so, its greater ease, compared with processes involving proton loss, can plausibly be attributed to stabilisation, by conjugation of the hydrogen group, of the partial positive charge on the α-carbon atom in the synartetic ion (IV).

Acid-catalysed hydration of 2-methylallyl alcohol gives the same products as hydrolysis of 2-chloro-2-methylpropan-1-ol, and in approximately the same relative amounts (see Table 5). The rate of the reaction is dependent on Hammett's acidity function, and this recalls a similar finding by Taft[4] in his work on the hydration of olefins. The exact significance of this dependence of rate on acidity function in the hydration of olefins is not clear. Taft supposed the rate-determining step to be a slow isomerisation of a π-complex, present in equilibrium amounts, to give the classical carbonium ion. de la Mare, Hughes, Ingold, and Pocker[5] suggested that, in reactions involving the addition of a proton to carbon, only the bare proton, or at least some freer form of protons than the normal electronic state of covalent H_3O^+, is effective; the scheme

TABLE 5.

Substrate	(A) (%)	(G) (%)
2-Methylallyl alcohol	23·2	76·8
2-Chloro-2-methylpropan-1-ol	21	75
1 : 2-Epoxy-2-methylpropane	4·9	92·5

The figures refer to 44·6°; values for 2-methylallyl alcohol are means over the range 1·0—2·6M-$HClO_4$.

$$H_3O^+ \overset{\text{Fast}}{\rightleftharpoons} H_2O + H^+$$

$$H^+ + \text{Olefin} \xrightarrow{\text{Slow}} \text{Carbonium ion}$$

is consistent with a rate dependent on Hammett's acidity function since it contains a pre-equilibrium step. On the other hand Long and Paul[6] pointed out that olefin hydration

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* For ion (III) the two processes lead to different products; internal hydrogen migration would give *iso*butyraldehyde. For ion (I) the product is the same in the two cases.

[4] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372.

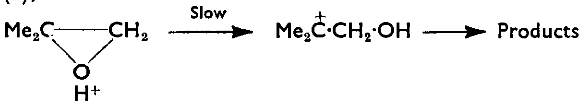
[5] de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.

[6] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

may involve a slow proton-transfer as the rate-determining step and that proportionality of rate and H_0 is, in certain circumstances, plausible for this mechanism.

This controversy, however, is not vital to the present argument, since, on any view, ion (I) would be a reaction intermediate. The close similarity in the relative proportions of aldehyde and glycol formed in the reaction and in the solvolysis of 2-chloro-2-methylpropan-1-ol is consistent with this, and it may be concluded that both reactions proceed *via* ion (I).

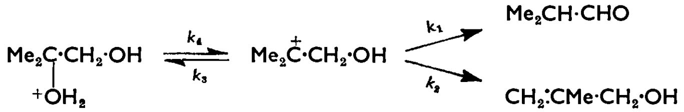
The acid-catalysed hydrolysis of 1 : 2-epoxy-2-methylpropane would also be expected to proceed *via* ion (I), *i.e.*



The evidence in favour of this scheme is strong. Long and Pritchard [7] have shown, by ^{18}O tracer technique, that in acid conditions bond fission occurs almost entirely at the tertiary carbon atom. They have also shown [8] that, typically, the rates of hydrolysis of ethylene oxides are dependent on Hammett's acidity function. Although this could not be shown for 1 : 2-epoxy-2-methylpropane itself, because its hydrolysis was too rapid, there is no reason to suppose it an exception to the general rule.

In the present study it was found, consistently, that both *iso*butyraldehyde * and 2-methylpropane-1 : 2-diol were produced in the reaction of the epoxide, but the amount of the former product was very much less than in the other reactions proceeding through ion (I) (see Table 5). This difference in product ratio is not difficult to explain. When the ion is formed from the oxide, the oxygen atom moves away from the incipient carbonium centre towards whatever equilibrium position it takes up in the stable conformation. At any point before this state is reached the interaction between the oxygen electrons and the positive centre is greater than at equilibrium and, correspondingly, the distortion of the bond angles from the tetrahedral values at the primary carbon atom is also greater. Internal hydrogen migration is less likely to occur in these strained conformations than in the equilibrium one; proton loss from the primary carbon atom is also less likely since conjugation of the hydroxyl group with the incipient double bond would be reduced. Substitution at the tertiary centre would, however, be unaffected, except that the shielding effect of the departing oxygen atom would tend to orientate the incoming group so as to produce configurational inversion. The consequences of assuming that ion (I), when formed from the oxide, undergoes substitution before reaching its equilibrium conformation are, then, twofold: (*a*) the substitution product should be formed in relatively greater proportion; and (*b*) there should be an inversion at the tertiary centre. These consequences are consistent with the present findings and with the known tendency for essentially complete inversion to occur in the acid-hydrolysis of epoxides with suitable optically active centres.[9]

The acid-catalysed rearrangement of 2-methylpropane-1 : 2-diol, as was shown in Part I, also proceeds through ion (I). If, as seems probable, the ion under these conditions is divided between its various products in the same way as in the hydrolysis of 2-chloro-2-methylpropan-1-ol and, as in the hydration of 2-methylallyl alcohol, a more detailed picture of the reaction can be built up, *viz.*:



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* This substance had not previously been identified as one of the products of this reaction.

[7] Long and Pritchard, *J. Amer. Chem. Soc.*, 1956, **78**, 2663.

[8] Pritchard and Long, *ibid.*, p. 2667.

[9] Winstein and Henderson, "Heterocyclic Compounds," Vol. I, Chap. 1, John Wiley and Sons Inc., New York, 1950.

The important conclusions are : (*a*) the ratio k_1/k_3 is *ca.* 3 ; (*b*) k_2 is small compared with k_1 and k_3. It is interesting to compare the ratio k_1/k_3 obtained here with the corresponding ratio for the pinacol–pinacone rearrangement (*ca.* 1·5) determined by Bunton, Hadwick, Llewellyn, and Pocker [10] using ^{18}O tracer technique. In view of the considerable differences between the two systems, the relative tendencies of the two ions to return by substitution to the original substrate or to undergo group migration are remarkably similar, and this is consistent with the view that a common mechanism is involved and that, in neither case, is there major assistance to the formation of the carbonium ion by the migrating group.

The magnitude of the rate coefficient k_4 compared with k_3 and k_1 is, of course, unknown, but the reaction scheme shown includes the possibility that the step to which k_4 refers, *i.e.*, the formation of the carbonium ion (I), may not be entirely rate-determining. In these circumstances, as Deno has pointed out,[11] correlation of rate with acidity intermediate between H_0 and J_0 might be found, and it is possible that the high slopes of the Hammett plots for the rearrangement of 2-methylpropane-1 : 2-diol and its dimethyl ether might have arisen in this way.

EXPERIMENTAL

Materials.—2-Methylallyl alcohol was prepared by hydrolysis of the corresponding chloride and had b. p. 114—114·5°, n_D^{20} 1·4232.

1 : 2-Epoxy-2-methylpropane was prepared by alkaline hydrolysis of 1-chloro-2-methylpropan-2-ol and had b. p. 50—51°, n_D^{25} 1·3700.

A mixture of 1-chloro-2-methylpropan-2-ol and 2-chloro-2-methylpropan-1-ol was prepared by dropwise addition of the epoxide (56 g.) to a solution of hydrogen chloride in dry ether (200 c.c.) at −10°. Anhydrous potassium carbonate was then added and the mixture set aside for 1 hr., then filtered and evaporated under reduced pressure at room temperature. Fractionation of the residue at 17 mm. gave a product, b. p. 36·5—38·5°, containing the two isomers in roughly equal amounts. Fractionation at higher temperatures or for prolonged times resulted in some decomposition of the tertiary chloro-compound to *iso*butyraldehyde and hydrogen chloride.

An attempt was made to prepare 2-chloro-2-methylpropan-1-ol by reducing α-chloro-α-methylpropionyl chloride with lithium aluminium hydride. After addition in the normal way of the acid chloride to an ether suspension of lithium aluminium hydride, the product was added dropwise to 10% aqueous sulphuric acid, thus ensuring that the chlorohydrin did not come into contact with aqueous alkali. The best sample obtained had b. p. 59—60°/50 mm., n_D^{25} 1·4313, and contained 74% of the chloro-compound. The compound is so readily hydrolysed by water and so sensitive to distillation that it appears unlikely that a pure product can be obtained in this way.

Kinetic Measurements.—The rate of production of acid in water from the mixture obtained by the action of hydrogen chloride on the oxide was followed by the conventional method of titrating aliquot portions, taken at suitable intervals, with standard alkali. The following experiment, with 0·109M-RCl at 25° is typical. Titrations are of 5 c.c. aliquot parts with $2·21 \times 10^{-2}$M-sodium hydroxide.

The primary chloride was unchanged at 25°, and the first-order rate coefficients, sensibly constant throughout a run, refer to the solvolysis of the tertiary chloride. Total hydrolysis of the mixture and titration with standard silver nitrate solution gave Cl, 32·9 (calc. for C_4H_9OCl : Cl, 32·7%).

Time (min.)	0	5	10	20·1	30·0	40·0	60·0	112·0	∞
Titre (c.c.)	0·62	1·22	1·76	2·77	3·72	4·89	5·98	8·56	12·41
10^3k_1 (min.$^{-1}$)	—	10·3	10·1	10·1	10·1	10·0	10·1	10·0	—

*iso*Butyraldehyde was estimated throughout the kinetic runs by the polarographic method described in Part I. 2-Methylpropane-1 : 2-diol could be determined only at complete reaction since unchanged tertiary chloride was hydrolysed under the conditions of the estimation. An example of the results obtained is given in the results section.

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[10] Bunton, Hadwick, Llewellyn, and Pocker, *Chem. and Ind.*, 1956, 547.

[11] Quoted by Long and Paul, see ref. 6.

The rate of reaction of 2-methylallyl alcohol was investigated by sealing into ampoules portions (12 c.c.) of solutions containing known concentrations of substrate (*ca.* 0·03M) and of perchloric acid. The ampoules were heated at 44·6° in a thermostat, withdrawn at intervals, and stored in alcohol–carbon dioxide until required. Portions (5 c.c.) were analysed for glycol (G) by periodate titration as described in Part I. Other portions were diluted so as to give a perchloric acid concentration of 1·08N and analysed for *iso*butyraldehyde (A). The ratio A/(A + G) was constant for at least 70% reaction and then slowly increased in value. From the initial values of A/(A + G) and the initial substrate concentration, infinity values for (A) and (G) were found and used to calculate first-order rate coefficients; an example is given in the results section.

Product Analysis.—Products from the hydrolysis of the oxide were investigated by placing solutions of it in water and of perchloric acid of appropriate concentration in the separate limbs of an inverted U-tube. The tube was heated to the required temperature and the solutions were then mixed by inverting the tube. Analysis of the resultant solution for glycol and for *iso*butyraldehyde was made by the standard procedures.

A large-scale analysis of the products of solvolysis of 2-chloro-2-methylpropan-1-ol was carried out with 140 g. of a mixture of this substance (55·6%) and its isomer. Separation of the products by extraction, after saturation with sodium chloride, of the reaction mixture with ether, followed by distillation, gave the following fractions: (i) b. p. 62—64° (12 g.), *iso*butyraldehyde; (ii) b. p. 128—130° (60 g.), 1-chloro-2-methylpropan-2-ol, (iii) b. p. 67—74°/10 mm. (10 g.), 2-methylpropane-1 : 2-diol. The intermediate fraction (b. p. 64—128°) was small (*ca.* 1 g.) and there was no sign of a fraction of b. p. 114°. Trials with artificial mixtures indicated that if 2 g. of 2-methylallyl alcohol (*ca.* 4%) had been present in the mixture it would have been detected.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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