258. *The Mechanism of Elimination Reactions. Part I. Unimolecular Olefin Formation from Alkyl Halides in Sulphur Dioxide and Formic Acid.*

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Substitution and elimination so often occur together that the duality of homogeneous mechanism established for substitution suggested the possibility of a similar duality for elimination: in substitution we have the bimolecular and unimolecular mechanisms already many times illustrated (*e.g.*, this vol., p. 1177), and thus the hitherto known bimolecular elimination (Hanhart and Ingold), *e.g.*,

$$OH^- + H\cdot CR_2\cdot CR_2\cdot X \longrightarrow H_2O + CR_2{:}CR_2 + X^-$$

might have a unimolecular counterpart, depending on the slow formation of an organic cation and the rapid liberation of a proton from the latter:

$$\begin{cases} H\cdot CR_2\cdot CR_2\cdot X \xrightarrow[\text{(slow)}]{} H\cdot CR_2\cdot CR_2^+ + X^- \\ H\cdot CR_2\cdot CR_2^+ \xrightarrow[\text{(fast)}]{} H^+ + CR_2{:}CR_2 \end{cases}$$

In this initial search for such a reaction, we avoided competition from unimolecular substitution by operating in the non-basic solvents sulphur dioxide and formic acid, both of which can ionise alkyl halides. The halides used were α-phenylethyl chloride and *tert.*-butyl chloride, which undergo unimolecular substitution in basic solvents, and have hydrogen in such a position that the cation if formed could eliminate it.

It is shown that in both solvents both halides come spontaneously into equilibrium with the appropriate olefin and hydrogen chloride. For α-phenylethyl chloride in formic acid the rate of the forward reaction agrees with the rate of racemisation sufficiently to suggest that the two experiments measure the same process. For *tert.*-butyl chloride the forward rate in dry formic acid is of the same order of magnitude as the rate of unimolecular hydrolysis in wet formic acid, and again the suggestion is that the process measured is the same, *viz.*, the rate of ionisation.

REPLACEMENT and elimination reactions in substitution products of paraffins so often occur side by side that it is difficult to make any close study of one process without taking stock of the other, and for this reason the series of papers now commenced represents only a continuation of a theme already partly developed. In a group of researches commenced 9 years ago and published mainly under the title " The Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions " we established a general mechanism of elimination (Hanhart and Ingold, J., 1927, 997) and traced its consequences in many fields of application. In the course of this work we found ourselves inevitably studying aliphatic substitution, and 3 years ago we made this subject the principal aim of the continued investigations, which are described chiefly in papers entitled " The Mechanism of Substitution at a Saturated Carbon Atom." In this field we have established multiplicity of mechanism (Hughes, Ingold, and Patel, J., 1933, 526), set up a general framework of theory (Hughes and Ingold, J., 1935, 244), and indicated or contributed numerous applications. During these investigations on substitution our knowledge concerning elimination has automatically grown, and now it seems opportune again to concentrate on that subject. The difference between the new attack and the old is this : instead of adding detail to the study of the one elimination mechanism the principal laws of which are already known, we now set ourselves to discover what mechanisms are possible and what factors control them, thus to prepare the way for a theory of eliminations as broad as that which has been established for substitutions.

In Hanhart and Ingold's mechanism of elimination, a reagent possessing basic properties extracts the protonic part of a combined hydrogen atom, whilst an electron-attracting group simultaneously separates in possession of an extra electron; it is necessary that the hydrogen atom and the electron-attractor shall be bound to adjacent carbon atoms in the original molecule in order that the atomic electron shells shall remain complete throughout the change. Two bonds are thus broken, but the reaction does not go in two stages : each bond-fission assists the other, the two comprising a single synchronised act. In the equation

$$\mathrm{X} + \mathrm{H}\vdots\!-\!\mathrm{CR_2{\cdot}CR_2}\vdots\!-\!\mathrm{Y} \longrightarrow \mathrm{XH} + \mathrm{CR_2{:}CR_2} + \mathrm{Y} \quad .\;\;.\;\;.\;\;. \quad (\mathrm{E2})$$

the vertical lines indicate the direction of the electron transfers; the basic reagent X may be negatively charged or neutral, and the electron-attracting group Y may be formally neutral or positive; but after reaction the formal charge of X will be more positive by one unit, and that of Y more negative by one unit, than before.

The reaction is bimolecular, and hence we label it E2. In general it is experimentally of the second order. This has been established for $\mathrm{X} = \overset{-}{\mathrm{O}}\mathrm{H}$ in the case of ammonium, sulphonium, and halogen compounds, $\mathrm{Y} = \overset{+}{\mathrm{N}}\mathrm{R_3}, \overset{+}{\mathrm{S}}\mathrm{R_2}$, Hal. (Hughes and Ingold, J., 1933, 523, *et seq.*), *e.g.*,

$$\overset{-}{\mathrm{O}}\mathrm{H} + \mathrm{H{\cdot}CHPh{\cdot}CH_2{\cdot}}\overset{+}{\mathrm{N}}\mathrm{Me_3} \longrightarrow \mathrm{H_2O} + \mathrm{CHPh{:}CH_2} + \mathrm{NMe_3} \text{ (2nd Order; E2)}$$

We must point out, however, that mechanism E2 is not of necessity associated with second-order kinetics. In the above example a rather strongly basic reagent is employed, but, if the hydrogen atom of the organic molecule is rendered sufficiently vulnerable by constitutional influences, a much weaker base will suffice, for instance, a solvent molecule. Introducing a *p*-nitro-group into the above ammonium cation, Hughes and Ingold (*loc. cit.*) observed the reaction :

$$H_2O + H\cdot CH(C_6H_4\cdot NO_2)\cdot CH_2\cdot \overset{+}{N}Me_3 \longrightarrow H_3\overset{+}{O} + CH(C_6H_4\cdot NO_2){:}CH_2 + NMe_3 \qquad \text{(1st order; E2)}$$

which is of the first order in aqueous solution. (The reaction $H_3\overset{+}{O} + NMe_3 \longrightarrow H_2O + H\overset{+}{N}Me_3$ immediately removes NMe_3, and thus prevents its incursion into the elimination process as an additional basic reagent.) In spite of its kinetic order this reaction almost certainly pursues the bimolecular mechanism, E2, as is indicated, for instance, by the large increases of speed which are observed when small amounts of some stronger base than water, *e.g.*, trimethylamine, are added initially.

There are, however, many elimination reactions which cannot pursue mechanism E2. For instance, αα-diphenylethyl chloride decomposes into diphenylethylene and hydrogen chloride in the absence of any substance likely to act as a basic reagent (Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021).

One mechanism which we imagine to be rather generally available would consist in the slow ionisation of the paraffin derivative (the negative charge going to the electron-attracting group) followed by the rapid ejection of a proton from the hydrocarbon cation :

$$\left.\begin{array}{l} H\cdot CR_2\cdot CR_2 \vdots\!-\!Y \xrightarrow[\text{slow}]{} H\cdot CR_2\cdot \overset{+}{C}R_2 + Y \\ H \vdots\!-\!CR_2\cdot \overset{+}{C}R_2 \xrightarrow[\text{fast}]{} \overset{+}{H} + CR_2{:}CR_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad (E1)$$

This reaction, which we label E1, may be described as unimolecular, and should be of the first order in dilute solution. Its rate-controlling stage is the preliminary ionisation exactly as in unimolecular nucleophilic substitution (S_N1). It should be available to any paraffin derivative which is sufficiently easily ionised to undergo this form of substitution, and which also possesses the hydrogen atom necessary for the elimination, *e.g.*, to most secondary and tertiary alkyl halides.

We have attempted to obtain evidence of the operation of this mechanism in more easily controllable examples than that of αα-diphenylethyl chloride, *viz.*, α-phenylethyl chloride, and, to some extent, *tert.*-butyl chloride. Both these compounds undergo unimolecular nucleophilic substitution (S_N1) at speeds convenient for measurement, and both have hydrogen in the right position for elimination. Our choice of solvents was guided by the following considerations. It was necessary that the solvents should be good ionising media for alkyl halides. Water at first suggested itself, and it will be shown in Part II that unimolecular elimination (mechanism E1) can in fact be demonstrated in aqueous solvents; but in this first investigation it seemed desirable to avoid water, since any such basic solvent might, as illustrated above, promote bimolecular elimination (mechanism E2) as a pseudo-first-order reaction, which it would be difficult kinetically to distinguish from the mechanism we wished to study. The solvents actually employed were sulphur dioxide and formic acid. Neither is perceptibly basic, and both are supposed to have the ability to ionise certain alkyl halides, including α-phenylethyl chloride.

The most important previous experiment on α-phenylethyl chloride in sulphur dioxide solution is that of Bergmann and Polanyi (*Naturwiss.*, 1933, **21**, 378), who showed that the rate of racemisation of the optically active compound was substantially unaffected by added chloride ions. We have tried to determine whether this unimolecular racemisation can be accounted for by the reversible formation of styrene, but all that can be said is that we have established the possibility of this explanation. There certainly is an equilibrium

$$CHPhMeCl \rightleftharpoons CHPh{:}CH_2 + HCl \quad . \quad . \quad . \quad . \quad (I)$$

in which the principal component is that on the left. The evidence of this is as follows. When α-phenylethyl chloride was kept for some time at 0° in solution in sulphur dioxide, the material remaining after removal of the solvent yielded, along with much unchanged chloride, a small proportion (order 10^{-3}) of styrene, or, in some experiments, polystyrene. When, on the other hand, styrene and a slight excess of hydrogen chloride were together dissolved in sulphur dioxide the subsequently isolated materials were α-phenylethyl chloride together with a similarly small quantity of styrene and/or polystyrene. The addition of bromine to a solution of α-phenylethyl chloride in sulphur dioxide resulted in the complete conversion of the chloride partly into crystalline styrene dibromide and partly into an oil which was probably styrene chlorobromide. In order to eliminate the complication arising from halogen interchange between the added bromine and the liberated hydrogen chloride, the same experiment was repeated with α-phenylethyl bromide and bromine; the yield of crystalline styrene dibromide was now quantitative. Having thus demonstrated the equilibrium formulated above, the next step should have been to measure the rate of the forward reaction for comparison with the rate of racemisation; but this we could not do owing to the one-sidedness of the equilibrium. The electrical conduction of dry hydrogen chloride in " conductivity " sulphur dioxide is too slight to enable such measurements to be used for this purpose. It may be mentioned, in view of the reported conductivity of some alkyl halides in sulphur dioxide, that pure α-phenylethyl chloride in freshly prepared solution in pure sulphur dioxide has no measurable conductivity.

The reaction in formic acid is in some respects more amenable to treatment. Bodendorf and Böhme had shown (*Annalen*, 1935, **516**, 1) that optically active α-phenylethyl chloride undergoes unimolecular racemisation in this solvent more rapidly than in sulphur dioxide. The occurrence of the elimination in formic acid can most easily be demonstrated in the following way. Although α-phenylethyl chloride and styrene are miscible with formic acid, polystyrene has only a limited solubility; therefore, if a solution of α-phenylethyl chloride of more than a certain concentration (10% suffices) is kept, a layer of polystyrene * begins to separate, and this layer continues to accumulate for a considerable time. Its formation may be assisted by the passage of nitrogen which aspirates away a good deal of the eliminated hydrogen chloride. In more dilute solution (*e.g.*, 5%) no polystyrene separates, and for such solutions our qualitative investigation of the forward and reverse reactions followed the lines already described for sulphur dioxide. No matter whether the starting materials consisted of α-phenylethyl chloride or of styrene and hydrogen chloride, the most abundant product was always α-phenylethyl chloride. However, polystyrene was obtained in considerably greater amounts than from the sulphur dioxide solutions, although styrene itself could be found only occasionally and in small quantity. Inasmuch as the formic acid employed was not completely free from water, a small amount of α-phenylethyl alcohol was produced; and this substance when dissolved along with an equivalent of hydrogen chloride in formic acid gave mixtures entirely similar to those obtained from α-phenylethyl chloride or from styrene and hydrogen chloride. At this point we proceeded to a more quantitative study.

A 0·15*M*-solution of α-phenylethyl chloride in formic acid came into a nearly steady state with 34% of the chlorine present in the form of free hydrogen chloride. A slightly higher figure was obtained when the starting materials were styrene and hydrogen chloride. Clearly, therefore, this was a case in which we could estimate the initial rate of production of chloride ions, *i.e.*, the rate of the forward reaction in the absence of disturbances due to reversibility. The extrapolated initial rate at 16·9° was 0·0009 sec.^{-1}. The rate of racemisation, interpolated to 16·9° from Bodendorf and Böhme's rates at 0° and 25°, is 0·0013 sec.^{-1}. Considering the errors and the difference of method, the agreement is striking, and may be taken to indicate the identity of the process the rate of which is measured by these two types of experiment.

In the case of *tert.*-butyl chloride, the equilibrium $CMe_3{\cdot}Cl \rightleftharpoons CMe_2{:}CH_2 + HCl$ in sulphur dioxide strongly favours the left-hand component, and our evidence of the

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* It contains some α-phenylethyl chloride, which, when the solution become inhomogeneous, is partitioned between the two phases.

forward reaction consists simply in the fact that the addition of bromine causes complete decomposition of the alkyl chloride with the formation of *iso*butylene dibromide in high yield. The behaviour of *tert.*-butyl chloride in solution in anhydrous formic acid is described in an accompanying paper (Bateman and Hughes, this vol., p. 1187). *iso*Butylene and hydrogen chloride were formed, and, at the concentrations used, 7% of hydrogen chloride was present at equilibrium. Furthermore, the initial rate of development of hydrogen chloride in this reaction, although difficult to estimate, was at least roughly the same as in the process in which the alkyl chloride undergoes unimolecular hydrolysis in formic acid as the solvent. Again we may assume the identity of the rate-controlling process in these two reactions.

Our opinion is that the mechanism of olefin elimination in the cases cited is that in which the rate-controlling stage is halogen-ionisation (E1), but we do not claim that the evidence advanced in this paper constitutes a flawless proof of this. The simplest alternatives are, first, that the mechanism depends on the prior transfer of a proton to the solvent (E2); and second, that it consists in a single-stage intramolecular elimination of hydrogen chloride (Ei). The former possibility can be almost certainly excluded because the solvents employed have practically no affinity for protons (witness, *e.g.*, the negligible conductivity of hydrogen chloride in sulphur dioxide); and because we can show (following papers) that, even in aqueous solvents, which have a strong affinity for protons, the mechanism remains dependent on halogen-ionisation, and not on proton-transfer. All we can say of the intramolecular alternative is that it seems to provide too slight and indirect a rôle for the solvent, which obviously plays a fundamental part in the reactions described. Our preferred hypothesis (Ei) agrees with the views of Bergmann and Polanyi and of Bodendorf and Böhme to the effect that their observations on racemisation measure the rate of ionisation of the halide, even although we now know that racemisation arises in a regeneration of the halide from a non-asymmetric olefin: in mechanism E1 the instability of an alkyl cation containing a labile proton is made responsible for the production of the olefin.

EXPERIMENTAL.

α-Phenylethyl Chloride and Bromide in Sulphur Dioxide.—The chloride was prepared from α-phenylethyl alcohol and thionyl chloride. It could not be dried by means of phosphoric oxide as this brought about decomposition, and the material was found to undergo decomposition slowly if any hydrogen chloride remained in it. It was therefore dried with potassium carbonate, and finally distilled from a small amount of this reagent in a good vacuum (Found: C, 68·3; H, 6·4; Cl, 25·2. Calc.: C, 68·3; H, 6·4; Cl, 25·3%). If required for conductivity work it was subjected to a non-ebullient distillation in a vacuum, in order to eliminate the traces of saline material which get carried over in any ordinary distillation.

The bromide was prepared from the alcohol and hydrogen bromide, and purified by similar methods, except that no experiments on conductivity were done with it.

The sulphur dioxide, drawn from a syphon, was dried in the gas phase by passage over phosphoric oxide, and then distilled from one to another of a row of bulbs on an exhausted all-glass gas-line. Three bulbs, each containing phosphoric oxide, were used to dry the reagent in the liquid phase, and in each bulb contact for two days was allowed. One of the other bulbs contained the alkyl halide, and this could be made to receive the sulphur dioxide (10—20 parts) by cooling in liquid air whilst the drying bulb containing the solvent was immersed in solid carbon dioxide. When sulphur dioxide was required for tests of conductivity the same process of purification was gone through, with the addition that, before the first drying, the gas from the syphon was bubbled through acidified dilute barium chloride solution in order to remove sulphur trioxide.

In the experiments on the products of the spontaneous reaction in solution, styrene was obtained in the first runnings of distillation, and the polystyrene, if at all, in the least volatile portion. The styrene was finally isolated and identified always as its dibromide (mixed m. p.). The main central fraction in these distillations was always the α-phenylethyl halide, which was identified by its b. p. and analytical data. In the experiments in which bromine was added to solutions of α-phenylethyl chloride or bromide, crystalline styrene dibromide separated during evaporation of the sulphur dioxide. The material thus obtained from α-phenylethyl chloride contained a little oil, and only had the correct m. p. after being washed with light petroleum.

The product obtained from α-phenylethyl bromide, on the other hand, had the right m. p. without purification.*

The sulphur dioxide used for the tests of conductivity had itself a specific conductivity of about 6×10^{-7} mho-cm.$^{-1}$. The resistance of the cell filled with this sulphur dioxide was slightly increased when pure α-phenylethyl chloride (about 5%) was added. The conductivity of a solution $0{\cdot}015M$ with respect to hydrogen chloride was 10×10^{-7} mho-cm.$^{-1}$, which leaves a balance of 4×10^{-7} mho-cm.$^{-1}$ for the dissolved hydrogen chloride. The hydrogen chloride used in this experiment and others of a similar kind was dried in the gas phase with phosphoric oxide, with which it was enclosed in a tube for some days, to be subsequently swept into the cooled conductivity cell with a little " conductivity " sulphur dioxide. The concentration was determined by noting the volume of the solution in the cell which had been calibrated for volume, and, after the resistance measurement, distilling the whole contents of the cell into chloride-free potassium hydroxide; the chloride was then estimated gravimetrically. When a small amount of water is added to a solution of α-phenylethyl chloride in sulphur dioxide, the conductivity undergoes a rapid and marked increase, owing presumably to hydrolysis and the formation of hydroxonium chloride.

The rate of racemisation of *l*-α-phenylethyl chloride in dry liquid sulphur dioxide was measured at 26·5°. The reaction followed a first-order law, the rate constant being $1{\cdot}15 \times 10^{-4}$ sec.$^{-1}$, a figure which agrees sufficiently well with Bergmann and Polanyi's, having regard to the difference of temperature between their experiment and ours. A parallel experiment was carried out in which water (0·7% by vol.) was added to the solvent. The rate constant was now $1{\cdot}08 \times 10^{-4}$ sec.$^{-1}$.

tert.-*Butyl Chloride in Sulphur Dioxide.*—A solution of the chloride (10 c.c.) and bromine (4 c.c.) in sulphur dioxide (60 c.c.) was kept at room temperature for 14 hours. It was then nearly colourless. The sulphur dioxide was removed by distillation along with a considerable amount of hydrogen chloride. No *tert.*-butyl chloride was recovered, but the residual oil on distillation yielded a liquid of constant b. p. 42°/16 mm., which is proved by analysis to be *iso*butylene dibromide (Found: C, 22·9; H, 3·6; Br, 73·7. Calc.: C, 22·2; H, 3·7; Br, 74·1%).

α-*Phenylethyl Chloride in Formic Acid.*—The experiments of Bodendorf and Böhme, with whose results we wished to compare our own, were conducted with Kahlbaum's " anhydrous " formic acid, the freezing point of which they specified, and therefore we used similar material; as mentioned by Bateman and Hughes (this vol., p. 1190), it is not in fact perfectly anhydrous.

A few details may be added to the description, given in the introduction, of the qualitative experiments. A 10% solution of α-phenylethyl chloride in formic acid became heterogeneous in about 0·5 hour at the room temperature, and the polystyrene layer which rose to the surface increased in size over a period of one week. The experiment was then stopped and the yield of polystyrene, b. p. about 275°/16 mm. was 65% (Found: C, 90·7; H, 7·7. Calc.: C, 92·3; H, 7·7%), and a fraction was obtained the b. p. and analysis of which suggested a mixture of α-phenylethyl chloride and alcohol. During the experiment a stream of nitrogen, saturated with formic acid vapour, was passed through the solution, and hydrogen chloride was carried away and caught in alkali. In the experiments with the more dilute solutions, which remained homogeneous, the solutes were isolated by extraction with carbon tetrachloride after addition of water. Styrene and polystyrene were obtained from the head and tail portions of the subsequent distillation and the former identified as its dibromide. The centre fractions, although essentially α-phenylethyl chloride, always contained oxygen. The proportion of chloride was estimated by taking advantage of the rapid unimolecular hydrolysis of this substance: the α-phenylethyl chloride fraction was shaken with water, and the chloride ion determined. The proportion of α-phenylethyl alcohol was measured by treating the fraction with thionyl chloride, and then estimating the rapidly hydrolysable chloride as just described. The compositions were in the neighbourhood: α-phenylethyl chloride, 80%; α-phenylethyl alcohol, 10%; unidentified, 10%.

Kinetic and Equilibrium Measurements.—α-Phenylethyl chloride (2 c.c.) was dissolved in formic acid (100 c.c.) at 16·90° ± 0·02°. At intervals, portions of 5 c.c. were withdrawn and

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* A crystalline *dimeride* of styrene was obtained in one experiment, in which α-phenylethyl bromide was allowed spontaneously to decompose in sulphur dioxide. A mixture of α-phenylethyl bromide and polystyrene was isolated, which on keeping deposited a crystalline substance. After crystallisation from light petroleum this had m. p. 105° (Found: M, 214, 216; C, 91·9; H, 7·6. $C_{16}H_{16}$ requires M, 208; C, 92·3; H, 7·7%).

run into carbon tetrachloride (50 c.c.). The carbon tetrachloride was extracted with water (total of 60 c.c.) and the chloride-ion content of the aqueous extract was estimated by Volhard's method. The total halide concentration was also determined by a Volhard titration, after running 5 c.c. of the reaction mixture into alcohol : α-phenylethyl chloride reacts quantitatively with silver nitrate under these conditions. In the table, a is the initial concentration of α-phenylethyl chloride, x the concentration of hydrogen chloride after reaction for t seconds, x_∞ the equilibrium concentration of hydrogen chloride, k_1' the first order " constant " calculated from the formula $k_1' = (1/t) . \log_e \{a/(a - x)\}$, which neglects reversibility, and k_1 the constant obtained from the integrated rate equation of a first-order reaction with second-order reversal (A $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ B + C) :

$$k_1 = x_\infty/t(2a - x_\infty) . \log_e[\{ax_\infty + x(a - x_\infty)\}/\{a(x_\infty - x)\}].$$

The quantities a, x, and x_∞ are expressed as equivalent c.c of 0·0295N-ammonium thiocyanate per 5 c.c. of the reaction mixture.

$a = 25{\cdot}14$; $x_\infty = 8{\cdot}20$.

....	62	98	132	180	240	300	365	420	480	600
x	1·40	2·02	2·72	3·32	4·28	5·02	5·68	6·10	6·75	7·20
$10^4k_1'$	9·25	8·53	8·65	7·87	7·76	7·44	7·02	6·61	6·52	5·62
10^4k_1	9·31	8·68	8·92	8·22	8·23	8·38	8·33	8·20	8·89	8·33

Solutions of (*a*) styrene and (*b*) α-phenylethyl alcohol in " Kahlbaum " formic acid containing hydrogen chloride were kept in a thermostat at 16·9°. The concentration of chloride ions at equilibrium, and the total halide concentration, were determined in each case by the methods described for the kinetic measurements. The results were as follows :

(*a*).

$[\text{Styrene}]_{\text{initial}} = 0{\cdot}155M$
$[\text{Cl}]_{\text{total}} = 0{\cdot}126M$
$[\text{Cl}]_{\text{equilibrium}} = 0{\cdot}0503M$

(*b*).

$[\alpha\text{-Phenylethyl alcohol}]_{\text{initial}} = 0{\cdot}145M$
$[\text{Cl}]_{\text{total}} = 0{\cdot}126M$
$[\text{Cl}]_{\text{equilibrium}} = 0{\cdot}049M$

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