[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Mechanism of the Alkaline Cleavage of Silicon–Hydrogen Bonds: Temperature Coefficients of the Rate of Cleavage of Several Trialkylsilanes

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The alkaline cleavage of silicon–hydrogen bonds[1] presents an interesting problem from the viewpoint of mechanism in that nothing exactly like it exists in carbon chemistry. Furthermore, it is rather unique in that presumably a hydride ion is split off. From a preparative viewpoint it offers the possibility of preparing the highly reactive silanols under rather mild conditions.

The reaction can be expressed stoichiometrically by the equation

$$OH^- + R_3SiH + R'OH = R_3SiOH + OR'^- + H_2 \quad (1)$$

Evidence for the conversion of hydroxyl to alkoxyl is presented below.

Previous qualitative results obtained in this Laboratory[2] indicate that the substituent effects in this reaction are similar to those of carbon compounds undergoing nucleophilic attack, *i.e.*, the bulkier the substituents the slower the reaction. The work described in this paper is an attempt to put these observations on a more quantitative basis and to determine, if possible, what type of phenomenon produces them.

Experimental

Materials.—Ethyl alcohol, 5% water by volume, produced by the U. S. Industrial Chemicals Co., was used as the solvent in most of these experiments. The density was 0.807^{25}_4. This corresponds to a water content of 7.0% by weight or 3.46 *M*. Where indicated more water was added.

J. T. Baker Analyzed C. P. potassium hydroxide was used as the alkali. Some of the alcoholic solutions of this compound were initially slightly cloudy due to the presence of carbonate and had to be filtered to clarify them. All the alkali solutions were standardized against standard hydrochloric acid using methyl orange as an indicator.

The several trialkylsilanes used in this investigation were prepared by addition of the appropriate chlorosilane to Grignard reagents. The reaction mixtures were treated with ice acidulated with hydrochloric acid and then dried over Drierite. After stripping off the ether the product was distilled through a column having about ten theoretical plates. The details of the preparations and the results of their analysis are listed in Table I.

For the kinetic runs the silanes were dissolved in alcohol and the concentration determined by measuring the gas evolved from a 2.00-cc. aliquot of approximately 0.5 *M* silane in contact with five or six pellets of potassium hydroxide.

Methods and Apparatus.—The kinetic runs were made as follows. Into a 50-cc. Erlenmeyer flask equipped with a side bulb was pipetted an aliquot of standard alcoholic potassium hydroxide together with enough alcohol to give the desired final concentration, and into the side bulb was placed an aliquot of standard alcoholic silane solution. The flask was placed in a thermostat of conventional design and was connected to a jacketed gas buret by rubber tubing. After allowing about fifteen minutes for temperature equilibration, the pressure was brought to atmospheric in the flask-buret system and the excess gas removed from the buret. The run was started by removing the flask from the bath, inverting, shaking a few times and replacing in a shaking machine in the bath. The shaker was started and the volume of evolved gas read at intervals. The thermostat maintained constant temperature to within 0.05° and the timing was done with an electric clock equipped with a second sweep. The error in the buret reading was about 0.03 cc. and in the timing about two to three seconds.

In this investigation it was necessary to prove the identity of the gas evolved. This was done by connecting a 200-cc. flask containing freshly distilled solvent and base to a vacuum line. After the solvent had boiled *in vacuo* for ten minutes, the line to the vacuum was closed and the silane was admitted through a stopcock, care being taken to admit a minimum of air. When evolution of gas had brought the pressure in the system to atmospheric, it was opened to a displacement bulb where the remainder of the evolved gas was collected over water. The gas was then withdrawn into sampling pipets and analyzed by conventional gas combustion methods.

The alcohol vapor which was always present in the samples was removed by passing the gas through fuming sulfuric acid and then through potassium hydroxide solution. The contraction in the volume due to this procedure was never more than 1%.

TABLE I

PREPARATION OF TRIALKYLSILANES

Prepn.	Grignard	Chlorosilane	Product: Yield, g. (%)	B. p., °C. Obs.	B. p., °C. Calcd.[a]	Hydrogen, % Obs.	Hydrogen, % Theo.[b]
(*n*-Pr)$_3$SiH	*n*-PrBr 185 g. (1.51 moles)	SiHCl$_3$ 87 g. (0.65 mole)	45 (43)	169.5–169.8[c]	...	0.63	0.63
(*n*-Pr)$_2$MeSiH	*n*-PrBr 100 g. (0.82 mole)	MeSiHCl$_2$ 44 g. (0.39 mole)	25 (49)	126.8–127.2	126	.76	.77
n-PrMe$_2$SiH	*n*-PrBr 106 g. (0.86 mole), MeBr 166 g. (1.75 moles)[d]	SiHCl$_3$ 115 g. (0.86 mole)	10 (12)	73–74	79	.99	.98
Et$_3$SiH	EtBr 220 g. (2.02 moles)	SiHCl$_3$ 82 g. (0.61 mole)	50 (71)	106.8–107.2[e]	...	.84	.86
Et$_2$MeSiH	EtBr 170 g. (1.56 moles)	MeSiHCl$_2$ 84 g. (0.74 mole)	15 (20)	77.2–77.6	77	.96	.98

[a] For method of calculation see Lewis and Newkirk, THIS JOURNAL, 69, 701 (1947). [b] Hydrogen determined by adding weighed amount of product to several pellets of potassium hydroxide dissolved in 3 cc. of ethanol and measuring volume of evolved gas. One mole of hydrogen liberated for each Si-H. [c] B. p. 170–171°, Pape, *Ber.*, 14, 1872 (1881). [d] In this case Grignard reagents were added to chlorosilane. [e] B. p. 107°, Ladenburg, *Ann.*, 164, 300 (1872).

Results and Discussion

Determination of Products.—Most previous investigations[1] were done with aqueous alkali or when done in alcoholic media the product gases were not analyzed. Since it is possible that the reaction could proceed in alcohol either as

(1) For general reviews of this subject see A. Stock, *Ber.*, **50**, 170 (1917); *Z. Elektrochem.*, **32**, 341 (1926).

(2) Private communication from S. D. Brewer of this Laboratory.

$$R_3SiH + OR'^- \xrightarrow{HOR} H_2 + R_3SiOR' + OR^- \quad (2)$$

or

$$R_3SiH + OR'^- \longrightarrow R_3SiO^- + HR' \quad (3)$$

evolving in one case hydrogen and in the other hydrocarbon, a series of experiments were made to determine the reaction products.

Triethylsilane was used in the identification of the evolved gases. The gas produced by the reaction of 0.1 mole of base with 0.05 mole of silane in 100 cc. of solvent was collected and analyzed as described above. The results are given in Table II.

TABLE II

COMPOSITION OF GASES EVOLVED FROM THE REACTION OF TRIETHYLSILANE AND BASIC REAGENTS

Basic reagent	Medium	% H_2	% Ethane	% Butane
NaOEt	Abs. EtOH[a]	98.8	0.10	..
KOH	Abs. EtOH	98.6	.72	..
KOH	EtOH 95% by vol.[b]	99.8	.05	..
KOH	*n*-Butyl alc.	98.8	..	.05
NaOBu	*n*-Butyl alc.	98.5	..	.05

[a] Distilled from magnesium ethoxide directly into reaction flask immediately before using. [b] Alcohol distilled from magnesium ethoxide and water added.

In addition, samples of these gases were analyzed on a General Electric mass spectrometer. This indicated that no gas, other than hydrogen, was present in more than 5% concentration.

All these facts show that hydrogen is the major product of the reaction and, hence, it must proceed according to equation 2. Even the experiment with absolute alcohol and potassium hydroxide gave so small an amount of hydrocarbon that here also the dominant reaction must be that of equation 2.

Previous work in this field[3] shows that the particle split from the silane is probably a hydride ion. The evidence presented in Table I and discussed above also points in that direction for if a proton were ejected it is difficult to see how the reaction could proceed other than by equation 3. Thus a negative hydroxyl or alkoxyl must be the attacking reagent. It is improbable that the hydride ion ever exists as such in solution, but, as results presented below show, is probably neutralized at the instant of reaction by a proton from the hydroxyl of the solvent.

When an alkali metal salt of the solvent is used, the base (hydroxyl or alkoxyl) is regenerated. With potassium hydroxide in aqueous alcohol there is usually enough water present to regenerate completely the hydroxyl ion. However, in the case of potassium hydroxide in absolute alcohol, since predominantly hydrogen is given off, there must be a conversion of hydroxyl ions to alkoxyl as the reaction proceeds, *cf.* equation 1.

Determination of Order.—Diethylmethylsilane was selected as a model for the determination of the order of the reaction. This was done principally because its rate of reaction is in a convenient range. The results of the rate of gas evolution could be expressed by the equation

$$k_1 t = \ln[V_F/(V_F - V)] \quad (4)$$

where k_1 = first order rate constant
t = time
V = volume of evolved gas at time, t
V_F = volume of gas evolved at infinite time

Since the function of the variable, V, appears as a ratio of volumes a correction for the volume occupied by the solvent vapors is unnecessary.

The curves obtained by plotting the logarithmic function of equation 4 against the time were good straight lines up to about 70–80% reaction. Beyond this point there was some curvature, indicating a slightly higher order of reaction. However, the linear part of the curves were so straight and the curvature so slight as to leave no doubt that the dominant reaction was first order.

The results of these runs are given in Table III.

TABLE III

RATE CONSTANTS, k_1, AND HALF TIMES, $t_{1/2}$, FOR Si–H CLEAVAGE OF DIETHYLMETHYLSILANE IN AQUEOUS ALCOHOL AT 34.40°, H_2O = 3.46 *M*

[Silane]	[KOH]	k_1 (min.$^{-1}$)	$t_{1/2}$ (min.)
0.0822	0.297M	0.0464	13.5[a]
.0822	.297	.0464	13.5[a]
.0822	.297	.0463	14.1[a]
.0576	.297	.0460	14.0
.0411	.297	.0512	12.8
.0411	.297	.0502	12.9
.0822	.178	.0314	20.0
.0822	.119	.0209	29.2
.0822	.0594	.0113	55.5
.0576	.208	.0341	18.9
.0411	.149	.0299	21.3

[a] The first three lines of the table give an estimate of the reproducibility of the method.

The half times are quite constant when the potassium hydroxide concentration is fixed regardless of the silane concentration. This is added proof of the first order character of this reaction, since for a second order reaction the half time should double over the same concentration range. Furthermore, since the alkali is capable of being regenerated, the first order character must apply to the silane.

It can be seen that the first order constants, k_1, in Table II vary with alkali concentration. If no alkali is tied up as a salt of the silanol produced and if the base is continually being regenerated, then the general catalysis law should hold. Also, since the silane is stable under neutral conditions, the intercept should be at the origin. Hence

$$k_1 = k_2[OH^-] \quad (5)$$

where k_2 = specific rate constant for OH^-. This was found to be true. A least squares plot of the constants, k_1, against the potassium hydroxide concentration gave a straight line whose slope, k_2,

(3) Gilman, THIS JOURNAL, **68**, 1128 (1946); Kraus and Nelson, *ibid.*, **56**, 195 (1934).

was 0.157 ± 0.005 (1 mole^{-1} min.$^{-1}$) and an intercept of 0.001 ± 0.001 (min.$^{-1}$).

Therefore, this reaction is first order in both silane and hydroxide, and the rate expression can be written

$$-\text{d[silane]}/dt = k_2\,[\text{silane}][\text{OH}^-] \qquad (6)$$

Effect of Water.—More than just a silane and hydroxide must be involved in the critical complex, for a free hydride ion is an extremely potent reducing agent and would not give the clean reaction observed. It is probable that this hydride ion is neutralized at the instant of reaction by a proton from the hydroxyl of the solvent. To check this hypothesis, a series of experiments were made with water added to the 95% ethanol. These were performed at two different temperatures and on a number of different silanes. The specific rate constants for hydroxyl ion, k_2, were obtained by dividing the first order constants, k_1, by the concentration of the potassium hydroxide. This procedure is valid since the k_1 *vs.* potassium hydroxide plots go through the origin. The results of this investigation are given in Table IV.

TABLE IV

SPECIFIC RATE CONSTANTS FOR HYDROXYL ION SHOWING EFFECT OF WATER ON Si-H CLEAVAGE

Silane concn. about 0.1 *M*
Potassium hydroxide concn. about 0.2 *M*

Silane	Temp., °C.	[H₂O] 3.46 *M*	8.61 *M*	13.86 *M*	19.07 *M*
Diethylmethyl	34.45	0.164	0.234	0.318	0.352
	44.73	.349	.422	.529	.601
Dimethylpropyl	35.05	.352	.521	.634	.775
	44.44	.794	.955	1.13	1.31
Triethyl	34.45	.097	.147	0.176	0.196
	44.70	.227	.315	.356	.391
Dipropylmethyl	34.45	.109	.149	.169	.184
	44.67	.241	.348	.374	.401

The plots of the rate constants for triethylsilane and dipropylmethylsilane against water concentration showed a distinct downward curvature. These compounds, because of their higher hydrocarbon content, are presumably the least soluble in the aqueous alcohol solvents. Even though no opalescence was ever observed at the start of reaction, it is possible that the presence of the added water produced an increasing incipient insolubility which led to the observed deviation from linearity. Tripropylsilane, although completely miscible in 3.46 *M* water, showed opalescence in 8.61 *M* water and hence was not used in this series of experiment.

On the other hand, diethylmethylsilane and dimethylpropylsilane gave good straight lines with the exception that the point for diethylmethylsilane at 34.5° and 19.07 *M* water was slightly below the line defined by the other points. These are the conditions under which one would expect least solubility. The curves for these two silanes obviously can be represented by equations of the type

$$k_2 = a + b[\text{H}_2\text{O}] \qquad (7)$$

the constants of which are given in Table V. This linearity between k_2 and the water concentration means that a molecule of water must be tied up in the activated complex. Furthermore, since the intercept, a, is not zero, the reaction must proceed in dry alcohol. As the following arguments show, a molecule of alcohol can substitute for the water in the activated complex.

If the solvent is a reactant and hence is present in very great excess and its concentration is not appreciably changed during the course of the reaction, then it will not appear in the rate expression and will have no effect on the order of the reaction. However, if the composition of the reacting solvent is greatly changed, then this change should be observable in a changed rate constant, the effect being similar to that described for the influence of the alkali concentration upon the rate. Now consider the equation

$$k_2 = k'[\text{EtOH}] + k''[\text{H}_2\text{O}] \qquad (8)$$

where k' and k'' are the specific rate constants for ethanol and water, respectively.

Assuming that there is no volume change on mixing ethanol and water, an assumption which is valid to within ±3%, and assuming the density of water to be 1 and the density of alcohol to be 0.8, it can be shown that

$$[\text{EtOH}] = 17.4 - 0.294[\text{H}_2\text{O}] \qquad (9)$$

Substituting this back in equation (8) and rearranging gives

$$k_2 = 17.4k' + (k'' - 0.294k')[\text{H}_2\text{O}] \qquad (10)$$

Thus comparing a and b of equation (7) with the coefficients of equation (10)

$$a = 17.4k'$$
$$b = k'' - 0.294k'$$

These equations were used to prepare the following table.

TABLE V

RATE CONSTANTS FOR THE SOLVENT EFFECT ON ALKALINE Si-H CLEAVAGE

Silane	Temp., °C.	a	b	k'	k''	R'	R''
Diethylmethyl-	34.45	0.109	0.0150	0.0063	0.0168		
	44.73	.292	.0168	.0168	.0217	2.7	1.3
Dimethylpropyl	35.05	.274	.0266	.0157	.0312		
	44.44	.673	.0335	.0387	.0449	2.5	1.4

Also included in Table V are the ratios R' and R''. These are the ratios of the rate constant at the higher temperature to the rate constant at the lower for the alcohol, k', and water, k'', reactions, respectively. The approximations introduced into the values of the rate constants make it impossible to place too much reliance in the values in the energies of activation that could be calculated from R' and R''. However, difference between the energies would account for a rate of re-

action with water several orders of magnitude higher than that with alcohol. From the expression which compares the rates of the water reaction with the alcohol one

$$k''/k' = e^{(\Delta S''^{\pm} - \Delta S'^{\pm})/R} e^{-(E''_a - E'_a)/RT}$$

where

$\Delta S''^{\pm} - \Delta S'^{\pm}$ = difference between entropies of activation of water and alcohol reactions (relative entropy)

$E''_a - E'_a$ = difference between the energies of activation of water and alcohol reactions (relative energy or heat)

the relative rates depend not only upon the energies but also upon the entropies of activation. Since the rates, k' and k'', differ only by a factor of about three and not by orders of magnitude, this must be the result of a much more negative entropy of activation in the water reaction. These results are explicable on the basis that the water molecule is smaller than the ethanol molecule, and can get into the requisite position for reaction with greater facility. In other words, the force fields and hence the potential energies opposing reaction are less the smaller the neutralizing solvent particle. This energy effect is largely offset by a more negative entropy term. The decrease in entropy could be due to a higher frequency of vibration in the activated state for an H–OH bond undergoing rupture than for a H–OEt bond in the same situation. The higher frequency results in a more negative entropy of the activated state for the water reaction. That the vibration should have a shorter period in the water case than in the ethanol is reasonable for the force constants of the H–O bonds are probably reduced by comparable amounts and the heavier ethyl group would then produce a lower frequency.

The results given in Table V and the foregoing arguments show that a molecule of the hydroxylated solvent enters into the activated complex to give up a proton which neutralizes the hydride split from the silane.

Effect of Silane Structure.—An investigation was next undertaken to determine the effect of varying silane structure upon the rate. To this end a series of experiments was made at two different temperatures in 95% alcohol (3.46 M in water). The results of this investigation are given in Table VI.

The average specific rate constants for hydroxyl were treated in the usual manner to obtain the relative thermodynamic functions of activation for the various silanes.[4] Diethylmethylsilane was taken as the reference compound as the greatest amount of work had been done with it and hence its behavior was best characterized.

The errors of 2–3% in the values of k_2 lead to errors of ±0.5 kcal. in the relative energies of activation and to ±1 e.u. in the entropies.

The rates given in Table VI show the same general variation of magnitude with structure as is found in carbon chemistry in compounds undergoing nucleophilic attack.[5] It is therefore probable that this reaction proceeds by a nucleophilic attack by hydroxyl upon silane, *i. e.*, the approach of the hydroxyl is along the line of the Si–H bond but on the side of the silicon opposite from the hydrogen.

Table VII shows a marked parallelism between the bulk of the substituent groups, and the heat and entropy of activation. In general, increasing

(4) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 118 ff.

(5) Hughes and Ingold, *J. Chem. Soc.*, 244 (1935); Hughes, Ingold, *et al.*, *ibid.*, 1196, 1201, 1208 (1937).

TABLE VI[a]

RATE CONSTANTS FOR Si–H CLEAVAGE BY POTASSIUM HYDROXIDE IN 95% ETHANOL

Time in minutes, $k_2 = k_1/[KOH]$

Silane	k_1	[KOH]	k_2	k_1	[KOH]	k_2
		34.40°			44.73°	
Diethylmethyl				0.0943	0.297	0.317
				.0726	.208	.348
	See Table II			.0620	.178	.347
				.0386	.119	.324
					Av. k_2	.329
		34.45°			44.70°	
Triethyl	0.0266	0.297	0.0895	0.0630	0.304	0.207
	.0201	.208	.0964	.0482	.213	.227
	.0163	.178	.0915	.0382	.182	.204
	.0111	.119	.0930	.0286	.121	.236
		Av. k_2	.093		Av. k_2	.219
		35.05°			44.44°	
Dimethylpropyl	0.0775	0.304	0.255[b]	0.178	0.304	0.585[b]
	.0748	.213	.354	.169	.213	.793
	.0643	.182	.386	.140	.182	.769
	.0467	.121	.352	.094	.121	.776
		Av. k_2	.364		Av. k_2	.779
		34.45°			44.67°	
Dipropylmethyl	0.0291	0.297	0.098	0.0706	0.304	0.252
	.0227	.208	.108	.0513	.213	.241
	.0193	.178	.107	.0424	.182	.233
	.0127	.119	.109	.0313	.121	.258
		Av. k_2	.106		Av. k_2	.241
		35.10°			44.44°	
Tripropyl	0.0121	0.304	0.0396	0.0285	0.304	0.0935
	.0089	.213	.0418	.0200	.213	.0938
	.0077	.182	.0424	.0171	.182	.0938
	.0048	.121	.0397	.0124	.121	.1032
		Av. k_2	.0409		Av. k_2	.096

[a] In all cases the silane concentration was about 0.1 M. [b] This figure for k_2 was omitted from the average. This is permissible under the usual conventions for omitting data so far out of line.

TABLE VII

RELATIVE HEATS, ENTROPIES AND FREE ENERGIES OF ACTIVATION FOR Si–H CLEAVAGE BY OH^- AT 40.0° IN 95% ETHANOL

$\Delta H_0^{\pm} = 13.3$ kcal.

	$\Delta H^{\pm} - \Delta H_0^{\pm}$, kcal.	$\Delta S^{\pm} - \Delta S_0^{\pm}$	$\Delta F^{\pm} - \Delta F_0^{\pm}$, kcal.
Diethylmethyl	0.0	0	0.0
Dimethylpropyl	1.8	7	− .4
Dipropylmethyl	1.7	4	.5
Triethyl	2.4	6	.5
Tripropyl	4.2	9	1.4

the bulk of the groups produces both a more positive heat and a more positive entropy of activation.

That the heat of activation should increase with increasing size of substituent is reasonable. The larger groups give greater force fields for the attacking reagent to penetrate, and hence higher energy barriers for it to surmount.

The increasing entropy of activation with larger substituents, however, is surprising for in a rearward attack one would expect the most highly hindered compounds to have the greatest restriction of approach and hence to have the lowest entropies. This is definitely not the case. The observed variation of the entropies with increasing bulk of alkyl substitution is explicable on the basis advanced above for the relative effect of water and alcohol upon the rate, that is, by a varying frequency of vibration in the activated state. It is known that alkali will break silicon–carbon bonds, particularly if they are activated by halogen attached to nearby carbon.[6] Therefore, when silicon is under nucleophilic attack by hydroxyl, all the bonds between the silicon and its neighbors must be weakened. This means lowered force constants for all these bonds and since the frequencies will depend upon the bulk of the groups, the heavier groups will produce greater reductions in frequency and hence more positive entropies. Thus the bulkier the group the more positive is the entropy of activation.

If all the bonds are weakened, then the one that is weakened most will be the one to be broken. The prediction of which bond will break will depend upon a knowledge of the electronegativities of the atoms involved, upon the bond strengths, and upon the bond polarizabilities. Unfortunately it is impossible to combine the available values of these quantities[7] to account for the observed facts.

Dimethylpropylsilane constitutes an exception to these generalizations. It is not at all obvious in view of the foregoing arguments why both the heat and entropy of activation should be out of line. Suffice it to say that it is not a smaller heat of activation which makes this compound react faster than diethylmethylsilane. It is a more positive entropy term which overwhelms the larger heat term to give a more negative free energy of activation and make it react faster. This is not a state of affairs which could have been predicted from a knowledge of the rates at one temperature only. It constitutes another illustration of the pitfalls to be encountered in attempts to account for effect of structure upon rate from a knowledge of the free energies of activation alone.

(6) Krieble and Elliott, THIS JOURNAL, **68**, 2291 (1946); Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946).

(7) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 53–60.

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Summary

A number of trialkylsilanes have been subjected to cleavage by alcoholic alkali and the rates of reaction measured. This has been done at two temperatures and the relative energies and entropies of activation calculated.

The reaction is first order in silane, first order in hydroxide and probably first order in the hydroxylated solvent. The alkaline cleavage of hydrogen from trialkylsilanes in alcohol was shown to proceed by way of a nucleophilic attack of hydroxyl upon silicon. The hydride ion ejected is simultaneously accepted by a proton of the solvent.

The reaction is impeded by increasing bulk of alkyl groups attached to silicon and by increasing size of the group attached to the hydroxyl of the solvent.

Increasing the bulk and number of silicon-alkyl groups produces both a more positive energy and a more positive entropy of activation. A theory is proposed to account for these effects.

The preparation of three new silanes, diethylmethyl, dipropylmethyl and dimethylpropyl, is described.

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