

ORGANOSILICON COMPOUNDS

XXXIV*. THE REARRANGEMENT OF ARYLDIMETHYL(CHLOROMETHYL)-SILANES CATALYSED BY ALUMINIUM CHLORIDE. WITH A NOTE ON SILICONIUM IONS

R. W. BOTT**, C. EABORN**, AND B. M. RUSHTON

Department of Chemistry, The University, Leicester (Great Britain)

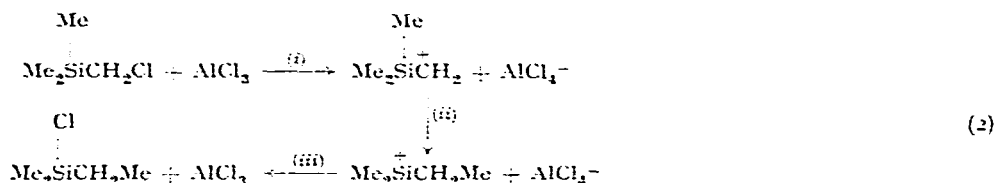
(Received December 14th, 1964)

INTRODUCTION

Whitmore, Sommer and Gold¹ found that trimethyl(chloromethyl)silane undergoes rearrangement to ethyldimethylchlorosilane in presence of aluminium chloride (eqn. 1). They estimated that 79% of rearrangement took place, but were able to isolate the product in only 53% yield because of secondary reactions. They suggested



that the mechanism of the reaction was similar to that of analogous Wagner-Meerwein rearrangements, as shown in (2).



Subsequently, related rearrangements involving migration of alkyl^{2,3} or trimethylsilyl groups³ from silicon to carbon were noted, and Eaborn and Jeffrey observed that a phenyl group migrated (with formation of benzyldimethylfluorosilane) when phenyldimethylethoxysilane was treated with aqueous-alcoholic hydrogen fluoride⁴. The object of the present work was to see whether aluminium chloride-catalysed rearrangement of $\text{ArMe}_2\text{SiCH}_2\text{Cl}$ compounds (eqn. 3) could be carried out satisfactorily, and, if so, to study the characteristics of the reaction, including dependence of the ease of rearrangement on the nature of the aryl group.



* For Part XXXIII see ref. 24.

** Present address: The Chemical Laboratory, University of Sussex, Brighton (Great Britain).

RESULTS AND DISCUSSION

Phenyldimethyl(chloromethyl)silane was found to undergo rearrangement readily in presence of a catalytic amount of aluminium chloride, and benzylchlorodimethylsilane was obtained in 94% yield. Rate studies were carried out on the reaction in solution, 1,2-dichloroethane at -20° being used as solvent after a large number of others had been tried and rejected*. Perhaps not surprisingly, we encountered the difficulties often associated with rate studies of catalysis by Friedel-Crafts catalysts in solution (see for example, refs. 5), and could not obtain really satisfactory kinetics; in our case the difficulties were more serious than usual because of the small amounts of catalyst involved. With phenyldimethyl(chloromethyl)silane the reaction as judged by the formation of hydrolysable chlorine (presumably $\equiv\text{Si-Cl}$) usually occurred to some 93-98% of the theoretical, and within a run a first-order plot was linear for about 60-70% of reaction but subsequently curved over in the direction indicating a speeding-up of the reaction, before tailing off in the last stages (a typical plot is shown in the Fig. 1). The rates varied as much as two-fold from one batch of solvent to another (probably, we suspect, because of varying water, olefin, and/or hydrogen chloride content), but could be reproduced reasonably well (to within ca. $\pm 10\%$) within one batch of solvent, except that occasional runs gave

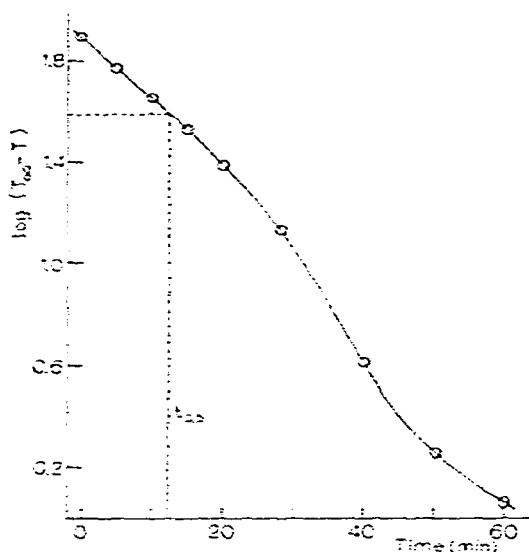


Fig. 1. Plot of $\log(T_\infty - T)$ versus time for the aluminium chloride-catalysed rearrangement of $\text{PhMe}_2\text{SiCH}_2\text{Cl}$.

quite anomalous results. The initial rate and the shape of the first-order plot were unaffected by doubling the initial concentration of phenyldimethyl(chloromethyl)silane, indicating that reaction was of first order in the chloride, as expected. The order with respect to aluminium chloride could not be determined. Addition of the reaction product, $\text{PhCH}_2\text{SiMe}_2\text{Cl}$, in amount equivalent to the reactant taken, appeared to

* The rearrangement also seemed to take place normally, as judged by formation of hydrolysable chlorine, in benzene, toluene, and methylene chloride.

reduce the initial rate by about 20–30 %, but did not alter the shape of the reaction curve, indicating that the increase in rate after 60 % of reaction in a normal run was not due to the accumulation of the product. Bubbling argon through the solvent immediately before the reaction, in the hope of removing any traces of hydrogen chloride, had no detectable effect. When hydrogen chloride was bubbled through the solvent beforehand, the subsequent reaction was roughly of first-order throughout, and about twice as fast as usual, but hydrolysable chlorine formed in this case was only 43 % of the theoretical, probably because rapid acid cleavage (by the acid HAlCl_4) of the Si-Ph bond occurred (*cf.* ref. 6). Addition of some moist solvent reduced the rate greatly, probably by destroying the aluminium chloride.

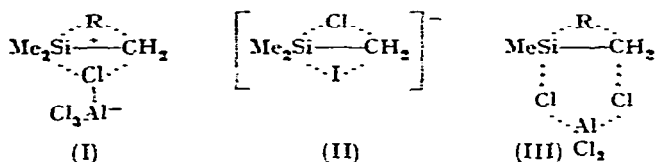
Although the formation of hydrolysable chlorine indicated, as noted, that over 90 % of rearrangement occurred, benzylchlorodimethylsilane could not be isolated in more than 72 % yield. It is possible that secondary reactions take place along with the rearrangement (for example, Friedel-Crafts alkylation of aryl groups, particularly in $\equiv \text{Si}-\text{CH}_2\text{Ar}$ systems) but the low yield is probably a result of reactions during the working-up, for benzylchlorodimethylsilane could be recovered in only 73 % yield after being dissolved in 1,2-dichloroethane containing aluminium chloride.

The first-order plots for rearrangement of *p*-tolyl- and (*p*-chlorophenyl)-dimethyl(chloromethyl)silane at -20° were generally similar to those for the phenyl compound, although the departure from first-order behaviour seemed to occur rather earlier with the *p*-chlorophenyl compound (at *ca.* 50 % reaction) and rather later with the *p*-tolyl compound (at $> 80\%$ reaction). For the $\text{XC}_6\text{H}_4\text{Me}_2\text{SiCH}_2\text{Cl}$ compounds, half-lives under conditions as far as possible identical, with 0.020 *M* aluminium chloride, were as follows: (X =) *p*-Me, 7; H, 12; *p*-Cl, 54 min (no reliance can be placed, of course, on the absolute values of the half-lives). It will be seen that the relative reactivities of the compounds are (X =) *p*-Me:H:*p*-Cl = 1.7:1:0.022, so that electron-releasing substituents assist and electron-withdrawing groups retard reaction*. Trimethyl(chloromethyl)silane is much less reactive, and the reaction at -20° was too slow to study; reaction at 25° , in presence of 0.040 *M* aluminium chloride (*i.e.* with twice as much catalyst as was used at -20° for aryl compounds) gave a first-order plot similar to those for the aryl compounds at -20° (being linear up to about 60 % completion of reaction); the half-life was 200 min.

The relative ease of rearrangement of the various $\text{RSiMe}_2\text{CH}_2\text{Cl}$ compounds, *viz.* (R =) *p*-MeC₆H₄ > C₆H₅ > *p*-ClC₆H₄ \gg Me, is reminiscent of the relative migratory aptitudes of the various R groups in Wagner-Meerwein rearrangements⁷. The quite large differences in ease of rearrangement indicate that the R groups participate directly in the rate-determining step of the rearrangement, which cannot thus be the simple ionization of the CH₂-Cl bond. (Indeed, not only would the differences in stability of the classical ions $\text{RMe}_2\text{SiCH}_2^+$ be very small, but the ion $\text{PhMe}_2\text{SiCH}_2^+$ would probably be *less* easily formed than the ion $\text{Me}_3\text{SiCH}_2^+$, since the phenyl withdraws electrons more strongly from silicon than the methyl group.) The effects are consistent with the mechanism (2) if steps (i) and (ii) are synchronous, and migration of the R group assists ionization, but they do not, of course, prove the existence of this mechanism. In particular, it is unnecessary (and undesirable in view

* The deactivating effect of the *p*-chloro substituent is, in our opinion, rather large in comparison with the activating effect of the *p*-methyl group.

of the lack of evidence, discussed below, for the existence of siliconium ions) to postulate the intermediate existence of a siliconium ion. An alternative termolecular mechanism, involving synchronous nucleophilic attack on silicon, migration of the group R, and separation of chloride ion from carbon under electrophilic attack has been suggested⁸, but we now favour a transition state of the type shown in (I). It is reasonable to write such a transition state [which bears analogy to that, (II), postulated



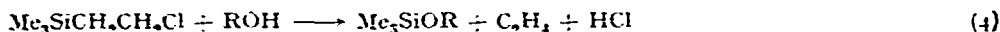
for attack of iodide ion on (chloromethyl)silanes^{9,10}; in view of the known ease of uncatalysed migration of halogen atoms, notably fluorine atoms¹¹, to silicon from a neighbouring carbon atom. The availability of vacant *d*-orbitals on the silicon atom makes this a much more acceptable process than it would be for an analogous rearrangement from carbon to carbon; there is, indeed, some evidence that in (halomethyl)-silicon compounds interaction between the π -electrons of the halogen and the *d*-orbitals of the silicon atom is present even in the unactivated molecule¹².

The somewhat more complicated process (III) is equally consistent with the facts.

A note on siliconium ions

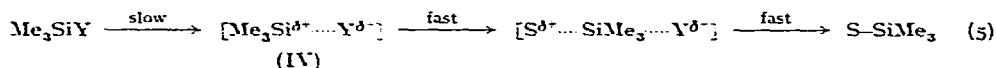
Although there was no evidence that siliconium ions, R_2Si^+ , exist in solution, even as reaction intermediates, under conditions in which the analogous carbonium ions, R_2C^+ , are formed, one of us previously pointed out that this did not mean that the ions H_3Si^+ or Me_3Si^+ , for example, are necessarily less stable (relative to their precursors) than the ions H_3C^+ and Me_3C^+ , respectively, since the absence of ionization mechanisms for silicon compounds could be simply the result of the great ease of reaction by other mechanisms not available for carbon compounds¹³. Mass spectrometric studies¹⁵ have now shown that in the gas phase the ion Me_3Si^+ is formed about as readily from several precursors Me_3SiX as is the ion Me_3C^+ from Me_3CX . (An exception is provided by the Me_3MCl compounds; in this case, because of the high bond dissociation energy of the silicon compound, markedly more energy is needed to form the Me_3Si^+ ion¹⁵.) In solution, the formation of the Me_3Si^+ ion will probably be less favoured, because of the more effective solvation of the smaller Me_3C^+ ion, but it seems likely, nevertheless, that siliconium-ion mechanisms will be observed. So far, however, the existence of such a mechanism has not, in our opinion, been demonstrated.

Results held, reasonably, to indicate the existence of a siliconium-ion mechanism were obtained by Sommer and Baughman in a study of the solvolysis of (β -chloroethyl)trimethylsilane (eqn. 4, $\text{R} = \text{Et}$ or H)¹⁴.



* These arguments have been endorsed by Sommer and Baughman¹⁴.

They showed that the rate-determining step does not involve an external nucleophile (since the reaction was not base-catalysed), that excess positive charge develops on the silicon atom in the transition state, and that the transition state has about the same amount of polar character as that in the solvolysis of *tert*-butyl chloride, and thus they proposed that a "limiting siliconium-ion mechanism" (eqn. 5, Y = CH₂CH₂Cl, S = solvent) was operating, involving the ionized intermediate (IV).



Although the mechanism is entirely consistent with the results for this reaction in isolation, we regard the evidence as inconclusive for the following reasons*:

(i) The rate-determining step suggested involves a simple ionization of the Si-CH₂CH₂Cl bond. There is no reason to believe that the carbanion ClCH₂CH₂⁻ would be particularly stable, and solvolytic cleavages of C-Si bonds involving formation of carbanions which are probably much more stable (e.g. cleavage of the compounds Me₃SiC≡CPh¹⁶ and 9-fluorenyl-SiMe₃¹⁷) not only take place much more slowly than the decomposition of the compound Me₃SiCH₂CH₂Cl in neutral solution but are also strongly base-catalysed.

(ii) The proposed mechanism implies that the chlorine atom does not participate directly in the rate-determining step, and thus that the rapid rate of solvolysis is only coincidentally connected with the well-known ease of decomposition of (*β*-chloroalkyl)silicon compounds under a variety of conditions^{18,19}, including the thermal decomposition in the gas phase (see below).

(iii) The Me₃C⁻ ion is a common reaction intermediate. Since Me₃C-alkyl bonds undergo ionization in the gas phase about as readily as Me₃Si-alkyl bonds¹⁵, and probably more readily than the latter in solution, then if mechanism (5) is correct for the decomposition of the compound Me₃SiCH₂CH₂Cl, the carbon analogue Me₃CCH₂CH₂Cl should react in a similar way at least as readily. By similar reasoning the compound Ph₃CCH₂CH₂Cl should be very much more reactive.

We cannot find any reports of the solvolysis of the compound Me₃CCH₂CH₂Cl, but it seems unlikely to undergo the ready fragmentation observed for the silicon compound since, for example, it can be made from a reaction which is, in effect, the reverse of the fragmentation, namely from *tert*-butyl chloride and ethylene in presence of aluminium chloride²⁰. (In the presence of aluminium chloride, the compound Et₃SiCH₂CH₂Cl decomposes rapidly to ethylene and triethylchlorosilane¹⁹.) Again, the corresponding bromide can be made from the alcohol, Me₃CCH₂CH₂OH, and hydrogen bromide²¹.

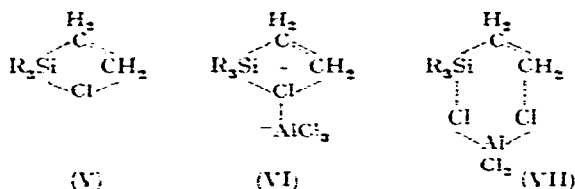
More impressively, the compound Ph₃CCH₂CH₂Cl reacts only slowly even with ethanolic ethoxide at 95° (ref. 22).

In our view then, Sommer and Baughman's results do not provide unambiguous evidence for the mechanism they propose, which means that there is still no firm evidence for the existence of a siliconium ion as a reaction intermediate.

We think it likely that the ready unimolecular solvolysis of the compound Me₃SiCH₂CH₂Cl is related to the ease of thermal decomposition of (*β*-chloroalkyl)-

* A mechanism involving a synchronous rate-determining unimolecular fragmentation to the entities Me₃Si⁻, C₂H₄, and Cl⁻ would avoid objections (i) and (ii), but not (iii).

silicon compounds and to the tendency for intramolecular transfer of halogen from carbon to silicon (see above). The gas-phase decomposition of (β -chloroalkyl)silicon compounds apparently involves a four-centre, unimolecular process (V)²³, and the operation of such a process in solution (followed by rapid solvolysis of the chlorotrimethylsilane) would, provided there were charge-separation in the transition state, be consistent with Sommer and Baughman's results. The related decomposition of the compound $\text{Et}_2\text{SiCH}_2\text{CH}_2\text{Cl}$ by aluminium chloride¹⁹ may involve a process such as (VI) [or, less attractive, (VII)] analogous to that suggested above for the rearrangement of $\text{RMe}_2\text{SiCH}_2\text{Cl}$.



EXPERIMENTAL

Aryldimethyl(chloromethyl)silanes

These compounds, $\text{XC}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{Cl}$, were made as described previously⁹, and had the following properties. (X =) H, b.p. $85^\circ/5$ mm, n_D^{20} 1.5212; *p*-Cl, b.p. $101\text{--}102^\circ/2$ mm, n_D^{20} 1.5345; *p*-Me, b.p. $80^\circ/1$ mm, n_D^{20} 1.5184.

Rearrangement of phenyldimethyl(chloromethyl)silane

(i) To the chloride (71 g, 0.38 mole) at room temperature was added freshly sublimed aluminium chloride (0.7 g). An explosion shattered the apparatus.

(ii) To the chloride (10 g, 0.054 mole), in a flask fitted with a reflux condenser, and cooled to -50° , was added aluminium chloride (0.053 g) with stirring and exclusion of moisture. The temperature was slowly raised to 35° , when vigorous reaction set in. When this had subsided, the mixture was heated under reflux for 2.5 h, and then fractionally distilled to give benzylchlorodimethylsilane (9.4 g, 94%), b.p. $29\text{--}32^\circ/0.3\text{--}0.4$ mm, $210.5^\circ/770$ mm. (Found: C, 58.7; H, 7.3; acid equivalent, 185. $\text{C}_9\text{H}_{13}\text{ClSi}$ calcd.: C, 58.9; H, 7.1%; acid equivalent, 184.8.)

The product was (a) treated with methylmagnesium iodide in ether to give benzyltrimethylsilane (64%), b.p. 190° , n_D^{20} 1.4922 (infrared spectrum was identical with that of an authentic specimen), and (b) hydrolysed to give *sym*-dibenzyltetramethyldisiloxane*, b.p. $127^\circ/0.15$ mm, n_D^{20} 1.5157. (Found: C, 68.9; H, 8.1. $\text{C}_{18}\text{H}_{26}\text{OSi}_2$ calcd.: C, 68.8; H, 8.3%.)

(iii) A solution of aluminium chloride (0.83 g) in 1,2-dichloroethane (250 g) was cooled to -20° , with exclusion of moisture, and phenyldimethyl(chloromethyl)silane (18 g) in 1,2-dichloroethane (50 ml) was added with stirring. The mixture was kept at -20° for 15 h, then the solvent was removed under reduced pressure in a rotary evaporator, and light petroleum (b.p. $< 40^\circ$, 250 ml) was added. The mixture was kept at 0° for some hours and the precipitated aluminium chloride was removed by

* New compound.

filtration. The filtrate was fractionated to give benzylchlorodimethylsilane (13.0 g, 72%), b.p. 75–76°/5 mm. (Acid equivalent, 185.5. Calcd.: 184.8.) and several small higher-boiling fractions and a black residue, none of which could be identified.

(Unsuccessful attempts were made to increase the yield of benzylchlorodimethylsilane, mainly by use of complexing reagents to precipitate the aluminium chloride from the 1,2-dichloroethane solution before the work-up.)

Recovery of benzylchlorodimethylsilane

Benzylchlorodimethylsilane (9.7 g) was dissolved in 1,2-dichloroethane (170 ml) containing aluminium chloride (0.50 g). Removal of the solvent in a rotary evaporator, followed by fractionation gave unchanged benzylchlorodimethylsilane (7.1 g, 73%).

From a similar experiment in which the aluminium chloride was omitted, 96% of the benzylchlorodimethylsilane was recovered.

*Rearrangement of *p*-tolyl(dimethyl(chloromethyl)silane*

The chloride (20.8 g) was added with stirring to a solution of aluminium chloride (0.9 g) in 1,2-dichloroethane (250 ml) at room temperature, the mixture becoming hot. Solvent was removed at reduced pressure, and the residue was quickly distilled at reduced pressure and then fractionated to give chlorodimethyl(*p*-methylbenzyl)silane* (12.3 g, 59%), b.p. 85°/4 mm. (Found: C, 60.6; H, 7.5; hydrolysable Cl, 17.8. C₁₀H₁₃ClSi calcd.: C, 60.5; H, 7.6; hydrolysable Cl, 17.9%.)

Kinetic studies

Purification of aluminium chloride. A good grade of aluminium chloride was sublimed at 0.5 mm. The sublimate was resublimed, and was then placed in a Carius tube with "AnalaR" aluminium wire (AlCl₃/Al = 5/1 by wt.). The tube was sealed at 0.5 mm and heated at 240° for 9 h. The aluminium chloride was transferred in a dry box under nitrogen to a sublimation apparatus, and resublimed to give pure-white material, which was 99.9% pure by analysis. The chloride was stored in the dry-box.

Purification of 1,2-dichloroethane. The chloride (1 l) was washed successively with oleum (20% SO₃, 2 × 250 ml), water (2 × 1 l), aqueous sodium bicarbonate (1 l), and water and then dried (Na₂SO₄). It was fractionated through a 100 plate Dixon gauze column, the first 150 ml (which contained any water-solvent azeotrope) being discarded, to give material of b.p. 83.8°/761 mm, n_D^{25} 1.4430. Only one peak could be detected in vapour phase chromatography.

Rate measurements. A sample of aluminium chloride was weighed into a small tube in the dry-box, and the tube was then quickly put into a 50 ml flask, containing 1,2-dichloroethane (25.0 ml) under argon, fitted with a magnetic stirrer. The mixture was heated to 50° with stirring to aid dissolution and quickly cooled to room temperature. A portion (10.0 ml) was transferred by syringe to a weighed dry reaction flask fitted with serum cap and pre-flushed with argon, and the flask and its contents were weighed to show the exact amount of solution, and then placed in a thermostat at $-20 \pm 0.05^\circ$. The rough volume of organosilane required was added from a syringe, the amount added being determined by weighing of the syringe and contents before

* New compound.

and after the addition. Samples were withdrawn with 1 ml syringes at appropriate times and added to 30 vol.-% aqueous alcohol (25 ml) containing 0.5 *M* sodium hydroxide (1 ml) in a stoppered conical flask. Weighing before and after the addition gave the amount of reaction mixture taken. A fresh syringe was used for each withdrawal, and it was found that a reasonably constant amount (*ca.* 1 g) of reaction mixture could be transferred each time. After withdrawal of every 3 samples, argon was injected into the reaction vessel to counteract the reduced pressure, which made sampling difficult. "Infinity" samples were taken after 10 times the half-life, and zero-time samples were taken just before the organosilane was added, allowance being made for the subsequent volume change.

The aqueous-alcoholic sample was acidified with 6 *N* nitric acid (*ca.* 6 ml), 25 ml of 0.020 *N* silver nitrate was added, followed by 2 ml of nitrobenzene, and the usual Volhard titration was conducted using 0.05 *N* potassium thiocyanate.

In the following typical run, 0.597 g of phenyldimethyl(chloromethyl)silane was added to 13.00 g of 0.0212 *M* solution of aluminium chloride in 1,2-dichloroethane. The volume (*T*) of 0.0200 *N* silver nitrate required for the reaction samples (corrected to 1.00 g) at various times, *t*, are shown. The "infinity" titration figure corresponds with 92.4% of expected reaction.

<i>t</i> (min)	0	5	10	15	20	30	40	50	70	80	∞
<i>T</i> (ml)	3.01	4.87	6.21	7.39	8.49	10.54	12.02	12.88	13.58	13.68	13.97

ACKNOWLEDGEMENTS

This work was supported by a grant from the Office of Aerospace Research, United States Air Force, through its European Office. We thank Dr. L. SPALTER, of the Chemistry Research Laboratory, Aerospace Research Laboratories, Wright Patterson Air Force Base, for his interest and encouragement.

SUMMARY

The compounds $\text{NC}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{Cl}$ ($\text{X} = \text{H}$, *p*-Me, and *p*-Cl) readily rearrange to the compounds $\text{ClMe}_2\text{SiCH}_2\text{C}_6\text{H}_4\text{X}$ in presence of aluminium chloride. In solution in 1,2-dichloroethane the ease of rearrangement falls in the order ($\text{X} =$) *p*-Me > H > *p*-Cl, and in all three cases is much faster than that of the compound $\text{Me}_2\text{SiCH}_2\text{Cl}$. A mechanism involving synchronous intramolecular migration of the organic group and the chlorine atom is proposed.

Evidence in the literature for the existence of siliconium ions as reaction intermediates is discussed.

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