

Reduction of poly(vinyl chloride) with tri-*n*-butyltin hydride

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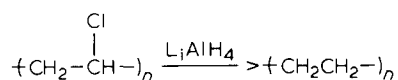
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Reduction of PVC with tributyl-tin-hydride (Bu_3SnH) was studied in order to optimize the method. The reactions were carried out in mixtures of xylene and tetrahydrofuran, chlorine content was determined by ^1H n.m.r. spectroscopy, and the melting behaviour by d.s.c. It was possible to obtain a product with less than 0.1% chlorine in less than 6 h. The ^{13}C n.m.r. spectrum showed that the product contained about 4 methyl branches per 1000 monomer units and gave no evidence of chlorinated structures.

Keywords Poly(vinyl chloride); reduction; tri-*n*-butyltin hydride; ^1H nuclear magnetic resonance spectroscopy; differential scanning calorimetry

INTRODUCTION

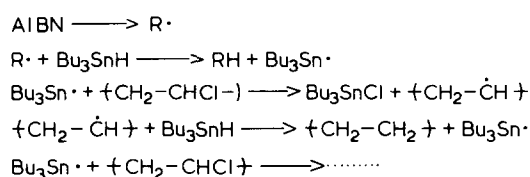
Reductive dehalogenation of poly(vinyl chloride) (PVC) to the corresponding hydrocarbon offers the possibility of studying irregular structures in the original PVC, in particular branching. A method of reduction was described in the 1950's by Cotman¹⁻³ who used lithium aluminium hydride as a reducing agent.



This method has been used by many workers to determine the number of branches in the reduced polymer, and, consequently, in the original PVC. Earlier, i.r. spectroscopy was used⁴ but recently Abbäs⁵, Bovey⁶ and their coworkers have used ^{13}C n.m.r. spectroscopy. They showed that the short chain branches in PVC are mainly CH_2Cl groups and not butyl groups which earlier were believed to be the most frequent.

Although valuable, the reduction of PVC with LiAlH_4 has several disadvantages. Problems with incomplete chlorine removal^{1-3,5,7} and lack of reproducibility^{5,8} have been reported. By both i.r.⁹ and ^{13}C n.m.r.⁵ the presence of *trans*-alkene bonds have been demonstrated, but this structure is considered to be a result of side reactions^{10,11}. Practical drawbacks are long reaction times, ranging from one week^{8,12} to one month¹³, and the risk of explosions⁸.

Recently, Starnes *et al.*^{10,11} reported on a new reduction method for PVC which overcomes these problems. In this procedure tri-*n*-butyltin hydride (Bu_3SnH) is used as reducing agent together with a small amount of radical initiator (azobisisobutyronitrile, AIBN):



To obtain almost complete removal of chlorine the reaction was effected in two steps. First, 2-methyltetrahydrofuran (Me-THF) was used as solvent and the solution was heated under reflux (about 80°C) for 24 h. The product precipitated with a chlorine content of 2-4%. Almost complete chlorine removal (0-0.4%) was then obtained in a second step with a xylene solution of the initial 'one-pass' product heated to 90°C for 24 h. The ^{13}C n.m.r. spectrum of the product showed that this method does not result in double bonds as does the reduction with LiAlH_4 . Thus, $\text{Bu}_3\text{Sn}_3\text{H}$ seems, in many respects, superior to LiAlH_4 for the reduction of PVC.

In connection with our studies^{14,15} on polymerization of vinyl chloride at pressures below the saturation pressure of the monomer (subsaturated polymerization) we wished to investigate how the degree of subsaturation influenced the branching structure. The Bu_3SnH method as described by Starnes *et al.* could be advantageous compared with our earlier LiAlH_4 method¹². However, it was desirable to improve the method in two respects. The first improvement would be to avoid using Me-THF, which is rather expensive, as the solvent. The second, and more important, should be to obtain complete chlorine removal in one step only. In that way the work-up between the two reaction steps is avoided and the total reaction time should decrease. In this paper we will describe a procedure for obtaining almost complete removal in a single stage reduction with Bu_3SnH_4 with a reaction time of 5-6 hours.

EXPERIMENTAL

Materials

Tributyltinhydride was prepared from polymethylhydrosiloxane (Aldrich) and tributyltin oxide (Aldrich)¹⁶. The siloxane (40 g) and tributyltin oxide (170 g) were allowed to react for 30 min under a stream of nitrogen. The hydride was then recovered by distillation (84°-86°C, 2 mm Hg) and was redistilled (86°C, 2 mm Hg) once before use.

Methanol (Merck, p.a.), *p*-xylene (Fluda, puriss. p.a.) and AIBN (Aldrich) were used as received.

Tetrahydrofuran (Merck) was distilled under nitrogen immediately before use. The PVC sample used throughout this investigation was a commercial suspension PVC (S687, KemaNord AB, Sweden) with $M_n = 48\,000$ and $M_w = 105\,000$.

Reductions

The reductions were effected in a three-necked round-bottomed flask equipped with an inlet tube for nitrogen, dropping funnel, reflux condenser and Teflon-coated magnetic stirring bar. The flask was immersed in a thermostatically controlled oil bath.

Temperatures and concentrations of the different components were varied in order to obtain an optimum procedure. The final version for the reduction of 1 g PVC was as follows: the polymer was suspended in xylene (10 ml), THF (30 ml) was added and the temperature was raised to 50°C. After complete dissolution xylene (30 ml) was added and the temperature was increased to 80°C. Then, a solution of Bu_3SnH (5 ml) and AIBN (60 mg) in xylene (20 ml) was added and the dropping funnel was rinsed with xylene (10 ml). After 1 hour the reflux condenser was removed and THF was allowed to evaporate off. A solution of Bu_3SnH (1 ml) and AIBN (30 g) in xylene (5 ml) (rinsing with xylene (5 ml)) was added after a reaction time of 2 h. At the same time the temperature was increased to 90°C. After a total reaction time of 5–6 h the solution was slowly added with vigorous agitation to cold methanol (500 ml) to precipitate the polymer. The precipitate was recovered by suction filtration and washed with methanol. The final purification was effected by reprecipitation in xylene-methanol and the product was dried under vacuum for 40 h.

Analysis

To determine the residual chlorine content ^1H n.m.r. was used. Spectra were obtained at 200 MHz with a Varian XL 200 from 5% (w/v) solutions in 1,2,4-trichlorobenzene-benzene- d_6 (3:1) at 120°C. To obtain the signal-to-noise ratio shown in Figure 4 for samples with low chlorine content, about 2000 scans were accumulated. To avoid overflow, accumulation in double precession (32 bits word length) was used. The Fourier transformation was performed with floating point arithmetic to avoid the introduction of round-off errors.

The ^{13}C spectrum given below was obtained at 50.3 MHz with a 15% solution in 1,2,4-trichlorobenzene-benzene- d_6 at 120°C. The flip angle was 65°, the pulse interval 10 s and the free induction decays with spectra windows of 8000 Hz were stored in 16 K computer locations. The number of scans accumulated was 8000.

The melting behaviour of the reduced samples were determined by calorimetry using a Perkin Elmer DSC-2. About 5 mg sample was used and the heating rate was 10 K min^{-1} . All runs were performed in a nitrogen atmosphere. Before analysis all samples were given the same thermal treatment by rapid heating to 150°C and cooling down to room temperature in a controlled manner.

RESULTS AND DISCUSSION

As mentioned, Me-THF (bp = 80°C) was used by Starnes *et al.* in the first step of the reduction^{10,11}. The most widely used solvent for PVC is, however, THF (bp = 64°–65°C). The higher boiling point should give a faster reaction

when using Me-THF but this solvent is rather expensive. The decomposition rate of AIBN at 80°C is about 7 times higher than at 65°C¹⁷. By increasing the initiator concentration it should be possible to use THF in the first step without any change in reaction rate. The use of THF in the reduction of PVC with Bu_3SnH has been reported¹⁸.

However, the most serious disadvantage with both solvents is that precipitation occurs at a chlorine content of about 2–5% which halts the reaction. It is possible that the higher temperature obtained with Me-THF results in a somewhat lower chlorine content before precipitation. If a lower chlorine concentration is desirable a second reduction step must be performed with a solvent capable of dissolving the polyethylene-like product. Starnes *et al.* used xylene at 90°C which is a good solvent for polyethylene. Naturally, the ideal solvent should dissolve both PVC and polyethylene under the applied experimental conditions. Mixtures of THF and xylene could be of interest in this respect.

The boiling point in the THF–xylene system is given in Figure 1. This figure gives an idea of which concentration range might be of interest. To obtain boiling point temperatures higher than 90°C, which is necessary to dissolve polyethylene, mixtures with xylene concentrations higher than ~65% (v/v) must be employed.

The solubility of the PVC sample in mixtures with 60–80% xylene under reflux was tested. With 60% xylene dissolution took place and no precipitation occurred when the concentration of xylene was increased to 75%. No turbidity could be observed even when the solution was cooled to room temperature. However, a mixture with 80% xylene did not dissolve PVC in a reasonable time.

For the beginning of the reduction a mixture of THF and xylene with 70% xylene could be of interest. This mixture did also dissolve, under reflux, a high density polyethylene with a narrow molecular weight distribution ($M_n = 17\,000$, $M_w = 58\,000$). The time to obtain complete dissolution was rather long, but in the reduction

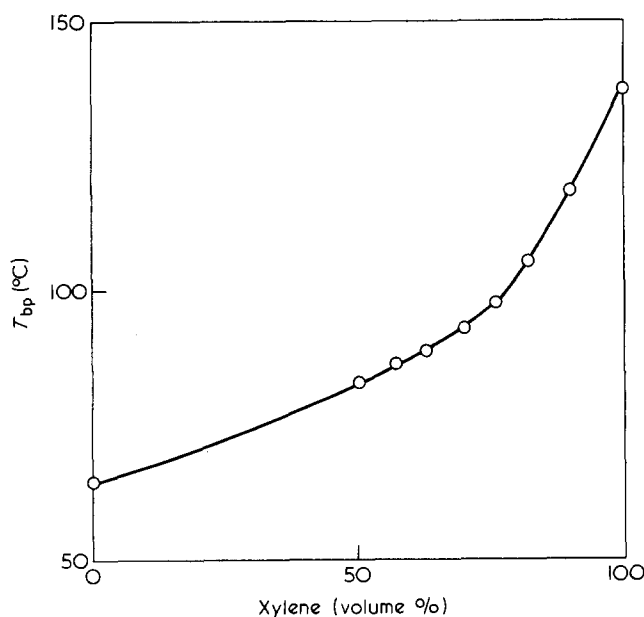


Figure 1 Boiling point, T_{bp} , of the xylene–THF system. The composition is given as volume % of the pure components

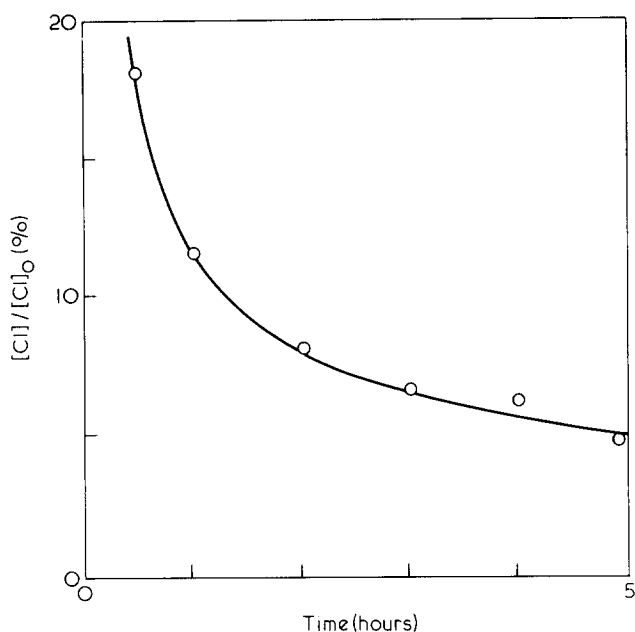


Figure 2 Chlorine content, in percent, of the original as a function of reaction time in reduction performed in xylene: THF (70 : 30) at 80°C, see text

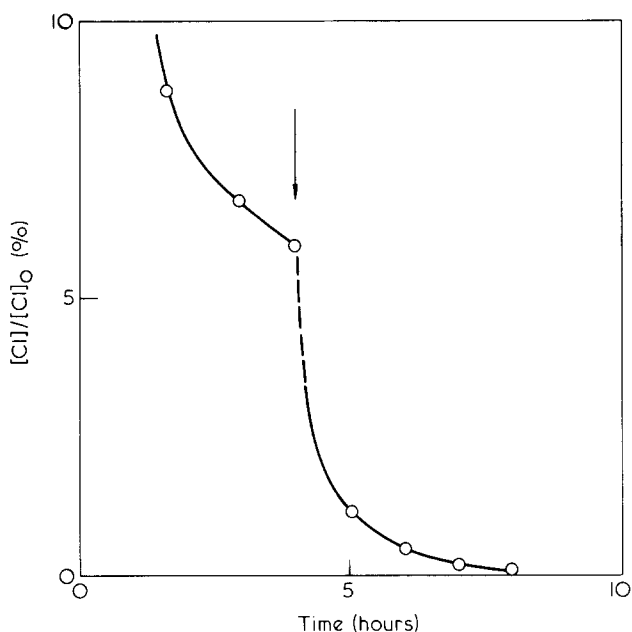


Figure 3 Chlorine content as a function of reaction time in a reduction performed in xylene: THF. After 4 h a second addition of Bu_3SnH , AIBN and xylene was made, see text

experiment the solution properties of polyethylene are obtained with the polymer already in solution. To dissolve PVC quickly a higher concentration of THF can be used in the beginning, correcting the xylene concentration to 70% after complete dissolution.

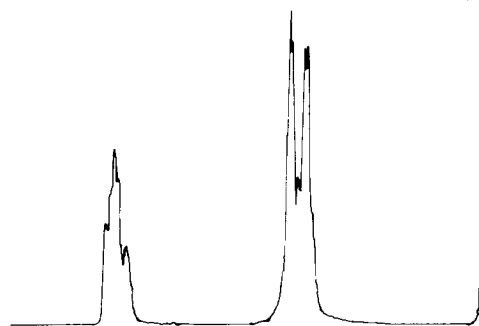
In Figure 2 the result of a reduction performed in THF/xylene (30:70) at 80°C is given. The molar ratio between Bu_3SnH and PVC (monomer unit) was 1:2. As shown the chlorine content drops very quickly in the beginning and thereafter the reaction rate decreases without any sign of precipitation. At 80°C the half-life of AIBN is only 1 h which explains the decreasing rate.

In the next experiment, therefore, a second addition of

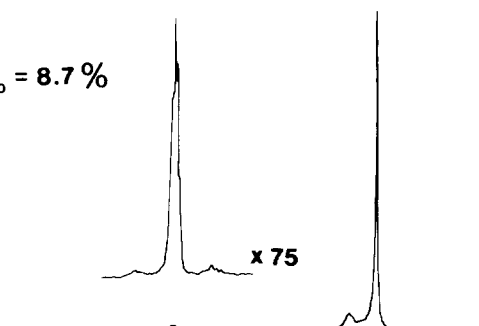
initiator and hydride was made after 4 h. The molar ratio between hydride and the estimated chlorine content at this point (~5% from Figure 2) was 1.25. To prevent precipitation, the xylene concentration was increased to 75% and the temperature to 90°C. As shown in Figure 3, the second addition resulted in the same behaviour as the first addition. The chlorine content after 8 h was about 0.1% and at this stage a slight turbidity could be seen.

The analysis of chlorine content was made by ^1H n.m.r.

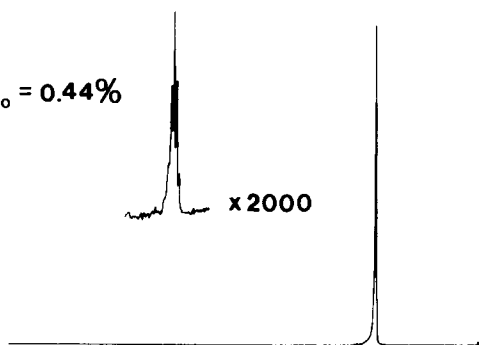
PVC



$[\text{Cl}]/[\text{Cl}]_0 = 8.7\%$



$[\text{Cl}]/[\text{Cl}]_0 = 0.44\%$



$[\text{Cl}]/[\text{Cl}]_0 = 0.05\%$

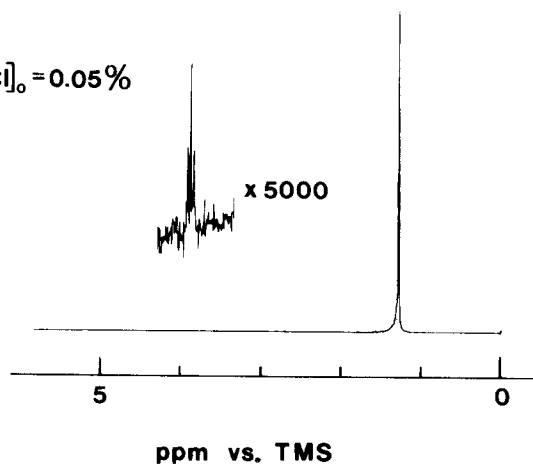


Figure 4 200 MHz ^1H n.m.r. spectra of the original PVC sample and three reduced samples with different degrees of reduction. TMS: tetramethylsilane (internal standard)

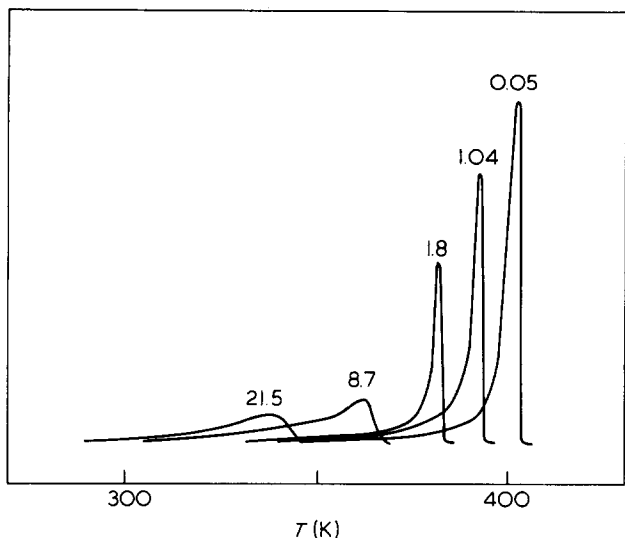


Figure 5 D.s.c. traces of some reduced samples with different degrees of reduction. The chlorine contents (%) as determined by ¹H n.m.r. are given at each peak

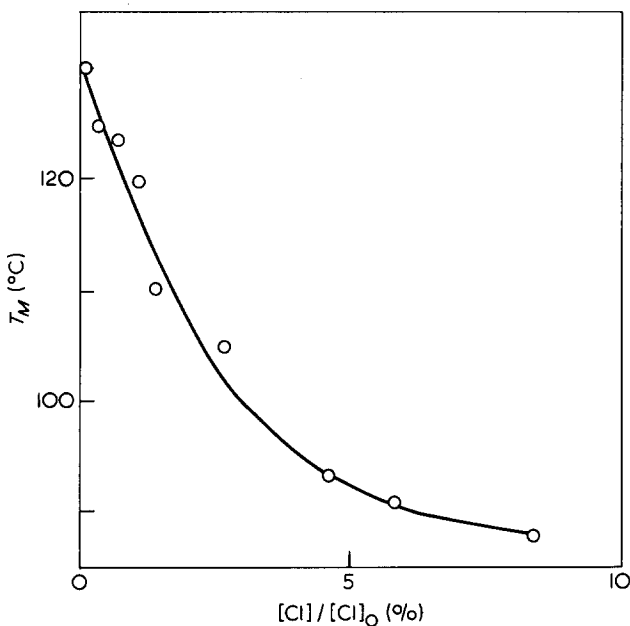


Figure 6 Melting point, T_M , of reduced PVC as a function of the chlorine content

The spectra of some samples are shown in Figure 4. With decreasing chlorine content the signal for CHCl -protons (4–4.5 ppm) decreases while the signal for CH^2 -protons increases. The chlorine content is calculated from the relation between these two main signals and the eventual influence of chlorine at end groups is not taken into account.

To obtain the signal-to-noise ratio shown in Figure 4, for the sample with 0.05% chlorine, about 2000 scans were accumulated with a 5% solution. It was necessary to use double precision (32 bits word length) during data accumulation and floating point transformation.

It should also be possible to use the melting behaviour as a test of the completeness of the reduction. In Figure 5 the d.s.c. traces obtained for some samples are given. Due to the increased possibility of ordering at reduced chlorine

content the glass transition of PVC disappears and crystallinity is introduced. The melting peak becomes larger and shifts to higher temperatures when the chlorine content decreases. The peak temperature is related to the concentration of chlorine according to Figure 6. Determination of the melting point can thus be used as a rapid test for the degree of dehalogenation. However, this implies that the degree of branching is about the same in all samples. This requirement is fulfilled for ordinary PVC. In polymers prepared at subsaturation conditions the content of branches is higher. In such polymers, both long chain branches^{15,16,19,20} and butyl branches^{19,20} are present to much higher degrees than in ordinary PVC. These branches will naturally decrease the melting point as well as the crystallinity.

Based on the experience of several similar reduction experiments, the experimental conditions described in the experimental section were found to be suitable for the reduction of PVC with Bu_3SnH . Firstly, the sample is slurried in a small amount of xylene and then THF is added. The dissolution is promoted by increasing the temperature. After complete dissolution the xylene concentration is increased to 70%, the temperature is adjusted to 80°C and the reagents are added. To decrease the THF concentration the reflux condenser is removed after a reaction time of 1 hour and THF is allowed to evaporate. After 2 h more reagents are added together with xylene and the temperature is increased to 90°C. Normally, the reduction is completed in a total reaction time of 6 h. At this stage a slight turbidity can sometimes be seen. The chlorine content in the recovered product is normally 0.1% or less of that in PVC.

The ¹³C n.m.r. spectrum of an ordinary suspension PVC reduced according to this procedure is shown in Figure 7. The assignments are those given by Randall²¹. Besides the main peak representing $-(\text{CH}_2)_n-$ some small peaks, associated with end groups and methyl side groups, can be observed. The latter emanate from CH_2Cl branches in the original PVC^{5,6}. The content of such groups is 4.2 per 1000 monomer units which is similar to that reported by others^{5,6,10,11}.

Starnes *et al.*²² have shown that incomplete reduction with LiAlH_4 gives both isolated and pairs of chlorine

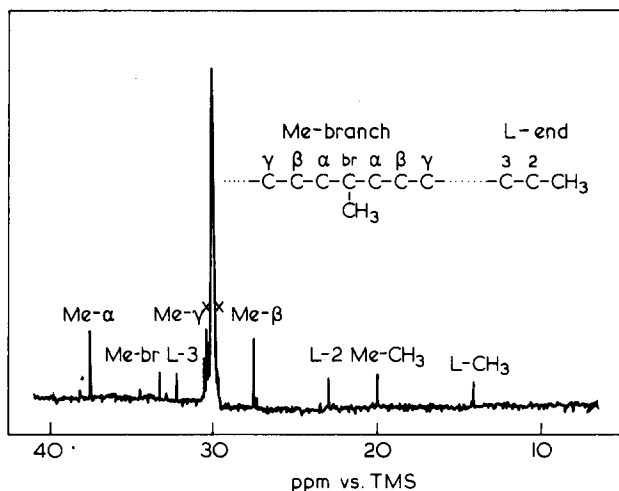


Figure 7 50.3 MHz ¹³C n.m.r. spectrum of PVC reduced with Bu_3SnH to chlorine content of 0.05%. TMS: tetramethylsilane (internal standard)

whereas Bu_3SnH gives only isolated chlorine. The spectral positions for this structure are:

	C-Cl	Cl α	Cl β	Carbon δ , ppm
-C - C - C - C - C - C - C - C -				63.7
				Cl- α 39.1
	Cl			Cl- β 26.7

In the spectrum in *Figure 7* there are no signs of peaks for the C-Cl (not shown), Cl- α and Cl- β carbons which is a confirmation of the completeness of the reduction.

CONCLUSION

The method for reduction of PVC with Bu_3SnH introduced by Starnes and his coworkers has been improved. Instead of employing a two-step procedure with a 24 h reaction time for each step, a chlorine content less than 0.1% can be obtained within 6 h by a one-step method. This is effected by using mixtures of THF and xylene as solvent. This improved method will be used for our investigations on structural defects in PVC and their influence on the thermal stability which are reported separately^{19,20}.

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