[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BOSTON UNIVERSITY]

# Configuration of Polybutadienes Prepared at High Temperatures[1]

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Solution polymerization of butadiene-1,3 was carried out at various temperatures, using propylene carbonate as solvent and di-*t*-butyl peroxide as initiator. The polymers were dissolved in carbon disulfide and analyzed for *cis*, *trans* and 1,2-addition by infrared absorption. The instrument was calibrated using reference standards of polybutadiene prepared at 5 and 97°. As the temperature was increased beyond 100°, the % *cis* increased very gradually and finally leveled off to a constant value, of about 36% *cis* over the temperature range 180 to 270°.

## Introduction

The stereochemical configuration of rubbery polymers containing double bonds has long been a subject of interest. It is generally accepted that in the case of natural Hevea rubber the isoprene units have all polymerized by 1,4-addition and are arranged in the *cis* configuration; while in the comparatively non-rubbery natural polymers *Balata* or *Gutta percha*, the arrangement is *trans*. In the case of the synthetic polybutadienes a further complication is introduced inasmuch as polymerization can and does yield a 1,2- as well as a 1,4-(*cis or trans*) product. By chemical analysis it has been shown that 1,2-addition accounts for approximately 20% of the free radical polymerized product (and up to 80% of the sodium polymerized product). Chemical analysis indicates that the total unsaturation approaches 100% and therefore about 80% of the free radical polymerized product has the 1,4-structure.

Measurement of the proportion of *cis* and *trans* configurations is readily carried out by infrared absorption, inasmuch as the *cis*, *trans* and vinyl groups have characteristic absorption bands at 724, 967 and 911 cm.$^{-1}$, respectively.[2a,b] Hart and Meyer[1] and Hampton[2] showed that in a series of polybutadienes polymerized at temperatures from $-19$ to $+97°$, the percentage of 1,2-addition remained fairly constant at 18 ± 2% while the percentage of *cis* addition varied from approximately 5% in the $-5°$ polymer to approximately 30% in the 97° polymer. On the basis of these results it appeared worthwhile to investigate the configuration of polybutadienes prepared at still higher temperatures.

**Preliminary Work.**—In order to work with as simple a system as possible it was decided to prepare the polymers by solution polymerization, using a solvent which would be liquid at room temperature and yet have a low vapor pressure at high temperatures. Polymerizations were carried out in sealed tubes with a number of solvents and initiators. From the results of these experiments it was decided to conduct most of the further polymerizations in propylene carbonate with di-*t*-butyl peroxide (DTBP) as the initiator.

**Preparation of Polymers: Apparatus and Techniques.**—For the present study a polymerization vessel was required which would contain the butadiene solutions at the high temperatures and pressures encountered, and which would permit rapid heat exchange between the contents and the heating bath so as to assure that the polymerization would take place at the desired temperature rather than during the period of warming up to this temperature. An apparatus was constructed in which the solution was contained in the annular space between two concentric stainless steel tubes (4 × 0.875 × 0.812", 4 × 0.750 × 0.687") which fitted between circular grooves in two steel end plates. Silicone gaskets were placed in the grooves and the plates were tightened together by means of $^1/_4$" bolts. In order to introduce the solution into the annular space after assembling the bomb, the top plate was provided with a threaded hole and removable screw plug. The bomb held approximately 4 g. of solution (equivalent to 1 g. of butadiene) and was most conveniently filled by chilling the bomb in an ice-bath and allowing the contents of a small vial to enter through a two-needle adapter, one needle extending through a hole and gasket in the vial cap, and the other through the gasketed opening in the bomb. The weight of the charge was determined by weighing the vial before and after transfer.

The polymerizations were carried out by immersing the bomb in a bath consisting of two gallons of high-temperature transformer oil heated by an immersion heater. The bath was mechanically stirred so that the bath liquid circulated through the inside of the smaller concentric tube as well as around the outside of the large one. After the required time of heating, the bomb was removed from the bath, immersed in kerosene to remove bath oil and then cooled under the water tap. In order to determine the yield of polymer the excess butadiene pressure was relieved and the liquid contents were transferred to a tared aluminum dish. Since some swollen polymer usually adhered to the wall of the tubes, the tubes as well as the dish were dried to a constant weight in the vacuum oven at 100° and the total weight of polymer obtained from the weights of the dried tubes and dish.

**Reagents Used.**—(1) Butadiene, Phillips "Pure" grade, distilled through silica gel and Ascarite prior to use; (2) propylene carbonate, supplied by Jefferson Chemical Co., Inc.; (3) DTBP, supplied by Buffalo Electro-Chemical Co; (4) Methyl Cellosolve, supplied by Carbide and Carbon Chemicals Corporation; (5) carbon disulfide, J. T. Baker C.P. grade.

**Preparation of Special Polymers.**—In order to have standards by which the infrared spectra of unknown and known polymers could be compared, emulsion polybutadienes were prepared at 5, 100 and 125°. The 5° polymer was prepared according to a standard polyamine-activated recipe with the usual bottle polymerization technique. The 100 and 125° emulsion polymers were prepared according to the persulfate-*t*-octyl mercaptan recipe of Rabjohn, *et al.*,[3] and Marvel and Lewis,[4] in sealed glass tubes of 5 mm. i.d. attached to the shaft of a slow speed stirrer and rotated end over end in the oil-bath.

For temperatures above 250° the oil-bath was no longer a suitable heating medium and so a salt-bath consisting of 55 parts of potassium nitrate to 45 parts of sodium nitrate was used. Since at these temperatures polymerization proceeded slowly with no initiator present, it was found convenient to use a smaller apparatus which was better adapted to withstand high pressures, even though it had somewhat poorer heat transfer than the concentric tube apparatus. The bomb used consisted of a heavy stainless steel tube (3 × $^7/_8$ × 1") threaded and capped at both ends and gasketed with lead washers. The bomb was filled by chilling in a Dry Ice-bath and pouring in the butadiene solution. It held approximately 5 ml. of solution and withstood the pressures involved without leaking at 285°.

**Analytical Preparation of Samples.**—Previous investigators[2a,b] have found that in the quantitative analysis of polybutadiene by infrared adsorption, best results are obtained

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[1] This research was supported by a grant from the General Latex and Chemical Corporation, Cambridge, Massachusetts.

[2] (a) E. J. Hart and A. W. Meyer, THIS JOURNAL, **71**, 1980 (1949); (b) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

[3] N. Rabjohn, *et al.*, *J. Polymer Sci.*, **2**, 488 (1947).

[4] C. S. Marvel and C. D. Lewis, *ibid.*, **3**, 354 (1948).

with a solution of the polymer in carbon disulfide. Preliminary experiments showed that with a 1-mm. cell, the concentration of the polymer should be between 4 and 10 mg./ml. for maximum general accuracy. In most cases the preparation of a clear solution was impossible due to the large proportion of insoluble gel in the polymers and so methods were developed for preparing stable dispersions. This was accomplished by transferring the desired amount of dried polymer into a vial containing the carbon disulfide and placing the vial on a shaker until it appeared that the polymer and solvent had equilibrated. In order to disperse the floating gel, the mixture was decanted and the gel ground thoroughly in a tissue macerator (Corning No. 7725). The suspension was then forced through a No. 27 hypodermic needle, the dispersion was allowed to "cream" and the cloudy solution was separated by syringe from any remaining large particles of gel. This technique gave a reasonably homogeneous dispersion which did not appreciably change over a limited time interval.

The concentration of the carbon disulfide solutions was determined by evaporation of 1-ml. aliquots, taken immediately after shaking the solution. Since the infrared determination took approximately 10 minutes it was important to make sure that the concentration remained constant during the duration of the run and, therefore, the solution was allowed to stand for 10 minutes and another 1-ml. sample was analyzed. As a final check, the solution was removed from the absorption cell after the run by rinsing the cell contents into a tared dish and the concentration again determined.

The results of a typical determination are: Sample no. 99: initial concn., 8.7 mg./ml.; concn. after 10 minutes, 8.7 mg./ml.; concn. after removal from cell, 8.9 mg./ml.

**Infrared Analysis.**—All the spectra were determined on a Baird automatic-recording double-beam infrared spectrophotometer. A 1-mm. sodium chloride cell filled with sample was placed in the path of one beam and a salt block in the path of the other. The solvent curve was run in a similar manner using the same (rinsed) cell. The spectra were recorded between 10 and 14 $\mu$ (1720–715 cm.$^{-1}$), in which region are located the three absorption bonds of interest. The curves were found to be reproducible within the expected experimental errors. Stray light corrections were determined since this particular instrument was not equipped with a filter for stray light.

**Interpretation of Spectra.**—In order to use the infrared absorption spectra quantitatively it is necessary to measure the extinction coefficients of the polymer at the wave lengths characteristic of the *cis*, *trans* and 1,2 absorption bands. The extinction coefficient, as used in this work, is defined as follows:

$$\text{extinction coefficient} = E = \log (I_0/I)/Cl$$

where

$I_0$ is the intensity of radiation transmitted by the pure solvent

$I$ is the intensity of radiation transmitted by the pure soln.

$C$ is the concentration in mg./ml.

$l$ is the length in cm. of the absorbing path (cell depth)

It is possible to use a molar extinction coefficient (defined as above but with $C$ in moles/l.), and previous investigators have shown that the molar $E$ of low molecular weight olefins containing (respectively) *cis*, *trans* or vinyl (1,2) groups is constant for a number of such olefins and is in fact characteristic of the group itself. Such molar $E$'s have been applied successfully in the analysis of polymers; however, in order to do this, the spectra of suitable monomers must be determined with the particular instrument and slit width employed in analyzing the polymer. In view of the work of Hart and Meyer and Hampton[2a,b] it appeared possible, and much simpler, to use polymers prepared in emulsion at various temperatures as standards, rather than low molecular weight olefins. As shown in Table I, extinction coefficients of polybutadienes prepared at 5 and 97° were determined, and by applying the data of Hampton[2b] on the composition of similar polymers, factors were derived which, when multiplied together with the calculated $E$ of an unknown polymer, give directly the percentage *cis*, *trans* and 1,2-composition of that polymer.

TABLE I

CALCULATION OF FACTORS

| | *E*'s | | | %[b] | | | Factors[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | *cis* | *trans* | 1,2 | *cis* | *trans* | 1,2 | *cis* | *trans* | 1,2 |
| 5° polymer[a] | 0.061 | 1.50 | 0.52 | 15 | 68 | 17 | 250 | 45 | 33 |
| 97° polymer | .13 | 1.24 | .62 | 34 | 48 | 18 | 254 | 39 | 29 |
| Mean | | | | | | | 252 | 42 | 31 |

[a] Average of 2 polymers. [b] According to Hampton.[2b] [c] Calculated by: factor = %/$E$.

The discrepancy between the factors calculated for the 5 and 97° polymers (of about 6% mean difference) is no greater than the mean deviation of Hampton's[2b] results. It is true that the accuracy of our results is limited by the accuracy of Hampton's[2b] data for the composition of the polymers which we used as standards; however, Hampton's[2b] careful work gives no grounds for expecting greater accuracy if we had used low molecular weight olefins as standards and corrected for absorption of other components at each characteristic frequency.

## Results

Table II gives the percentage of *cis*, *trans* and 1,2 calculated from the $E$'s and normalized to adjust the totals to 100%. The totals of *cis*, *trans* and 1,2 obtained *without* normalization are listed in the last column of Table II. Some support for the use of normalized values come from the results obtained from samples no. 47 and no. 47-d, which represent analyses of the same polymer in different concentrations. Further justification for the validity of the normalization procedure can be found in similar cases and in the fact that separate samples prepared at the same temperature give reasonable agreement on normalization. The normalized values of the % *cis* of polymers prepared at different temperatures, both in our work and in that of Hampton[2b] (including the recalculated data of Hart and Meyer[2a]), are plotted in Fig. 1.

TABLE II

| Sample number | Temp., of polymn., °C. | Time of polymn., min. | Yield, % | % *cis* | % *trans* | % 1,2 | Unnormalized |
|---|---|---|---|---|---|---|---|
| | | | | (normalized values) | | | |
| 63[a] | 125 | 45 | 12 | 33 | 48 | 19 | 99 |
| 62 | 125 | 5 hr. | 22 | 36 | 46 | 18 | 97 |
| 44 | 140 | 4.5 hr. | 12 | 35 | 47 | 18 | 98 |
| 31 | 150 | 30 | 13 | 34 | 47 | 19 | 101 |
| 47 | 168 | 15 | 23 | 34 | 47 | 19 | 98 |
| 47-d | 168 | 15 | 23 | 33 | 48 | 19 | 112 |
| 30 | 180 | 20 | 30 | 35 | 46 | 19 | 79 |
| 98 | 182[b] | 30 | 26 | 32 | 49 | 19 | 86 |
| 32 | 190 | 10 | 13 | 35 | 45 | 20 | 103 |
| 32-d | 190 | 10 | 13 | 35 | 46 | 19 | 101 |
| 41 | 199 | 20 | 20 | 42 | 41 | 17 | 76 |
| 41-d | 199 | 20 | 20 | 39 | 43 | 18 | 72 |
| 35 | 199 | 40 | 30 | 37 | 46 | 17 | 100 |
| 35-d | 199 | 40 | 30 | 39 | 43 | 18 | 102 |
| 28 | 225 | 15 | 18 | 34 | 46 | 20 | 83 |
| 83 | 233 | 10 | 23 | 32 | 48 | 20 | 92 |
| 85 | 233 | 35 | 26 | 31 | 49 | 20 | 73 |
| 86 | 233 | 120 | 28 | 32 | 48 | 20 | 60 |
| 72[c] | 270 | 10 | 4 | 34 | 46 | 20 | 68 |
| 71[c] | 270 | 50 | 8 | 36 | 46 | 18 | 63 |
| 73[c] | 270 | 120 | 7 | 40 | 43 | 17 | 42 |

[a] Polymerized in aqueous emulsion. [b] Methyl carbitol as solvent. [c] No initiator used.

## Discussion

Referring to the last column of Table II, the total unnormalized percentage composition would be expected to add up to 100% providing that (a) all the experimental errors are negligible, (b) the

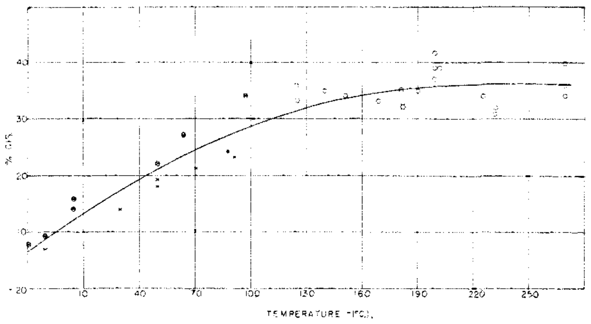

Fig. 1.—Percentage *cis vs.* temperature: ×, Hampton[2]; ⊗, Hart and Myer recalculated by Hampton[2]; O, present results in propylene carbonate; ꭓ, present results in methyl carbitol.

calculated factors are correct, and (c) the polymer has the theoretical total unsaturation, one double bond per butadiene unit. Inherent experimental difficulties of the infrared analysis of high polymers limit the probable accuracy of our experimental work to about 6%. We have shown that two possible sources of error in our technique do not give rise to inaccuracies greater than this amount. These include (i) absorption by other components at frequencies considered characteristic of the components sought, and (ii) possible light scattering by dispersed gel. The agreement between the calculated factors (Table I) for the 5 and 97° polymers appears to justify neglect of the first source of error. With regard to light scattering, we have established that the background "nose" of the infrared spectra of our gel dispersions was no greater than normally encountered with clear solutions of polybutadiene; and furthermore we have obtained good agreement between individual samples which gave clear solutions (samples 32 and 28 of Table II) and samples prepared at similar temperatures which gave gel dispersions (samples 35 and 83, respectively). The accuracy of the calculated factors is limited by the assumption that the configuration of free radical polymers is influenced only by the temperature and not the method or recipe of polymerization. That this is justified is shown in a further section.

The last condition (c) remains a subject of speculation. It has been shown that in emulsion polybutadiene prepared at ordinary temperatures the theoretical unsaturation, as determined by chemical methods, approaches 98%.[5] Reference to Table II shows that 9 out of 13 polymers prepared at temperatures below 200° yield a total of 100 ± 3% for the sum of the *cis*, *trans* and 1,2. Of the remaining four that give totals significantly different from 100%, there is reason to suspect the accuracy of the concentration of at least two, which were prepared in the early stages of this investigation. The low totals obtained from polymers prepared above 200° will be further discussed below.

The question may be raised as to whether the polymers were actually formed at the indicated (bath) temperatures, or at lower temperatures during gradual warming of the solution. To obtain evidence on this point, we have placed melting point capillaries containing anthracene (m.p. 217°) inside the empty annular space of the bomb, and immersed the bomb in the bath at 222° for various lengths of time. The anthracene was found to melt after 1.5 minutes of immersion. Since the anthracene was separated from the wall of the bomb by air and glass, we feel that this sets an upper limit on the time which would be required for a solution in direct contact with the walls to come to bath temperature. A study of the yields obtained from runs at 230° for 3, 10, 25 and 120 minutes, show that the yields are 4, 23, 26 and 28%, respectively. Therefore, we are justified in assuming that the major part of our samples were formed at the temperatures indicated.

It is generally assumed that the configuration of a polymer prepared by free-radical polymerization is dependent on the temperature alone and not on the nature of the solvent or emulsion. This assumption is confirmed in the composition of two polymers prepared at 125° in emulsion and in propylene carbonate solution (samples no. 63 and 62, respectively). Further confirmation comes from results obtained with a polymer prepared at 182° in methyl carbitol (diethylene glycol monomethyl ether) (sample no. 98). Most of the polymers were prepared with di-*t*-butyl peroxide as initiator; however, the polymers prepared at 270° were polymerized without initiator and were of substantially the same composition as those prepared with di-*t*-butyl peroxide at lower temperatures.

## Conclusions

Inspection of Table II and Fig. 1 shows that the percentage of *cis* polymer increases gradually from −20 to +130° and then slowly levels off to a constant value of about 36% at higher temperatures. It did not seem worthwhile to continue this study up to higher temperatures, particularly since depolymerization would become important above about 320°.

As found by others[2a-4] at temperatures below 125°, the percentage of 1,2 remains approximately constant at 19 ± 2% from 100 to 270°.

An unexplained feature of this work involves the low totals of *cis*, *trans* and 1,2 obtained from samples polymerized above 200°. The techniques used in determining both the yields and concentrations (of polymer in carbon disulfide) leave little doubt as to the accuracy of these data, and we are therefore led to the conclusion that the total unsaturation has somehow decreased from the theoretical value of one double bond per butadiene unit. Moreover, an examination of the totals and yields obtained from samples no. 71–73 and samples no. 83–86 shows that as the time of polymerization was increased, the totals decreased while the yields remained approximately constant. This would seem to indicate that the saturation of the double bonds increases with the time and temperature of polymerization and that the effect is purely a statistical one, the ratio of *cis*:*trans*:1,2 remaining unaffected. Further work along these lines is needed before an explanation can be given.

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[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING DEPARTMENT, UNIVERSITY OF CALIFORNIA, BERKELEY]

# The Principal Electronic Absorption Bands of the Vinylogous Series Derived from Benzylaldehyde and Benzophenone

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The spectra of the vinylogous series $C_6H_5(CH{=}CH)_nCHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ were measured over the range from $n = 0$ to $n = 6$. The measurements were made in methanol, acetic acid and benzene solutions, and also in acetic acid containing enough sulfuric acid to obtain the principal bands of the ions of all of them except benzaldehyde and benzophenone. With the exception of benzophenone the neutral series obeyed the equation $\lambda^2_{\max} = a + bn$ up to $n = 5$ for the aldehydes and $n = 4$ for the ketones. The ionic series obeyed the equation $\lambda_{\max} = a + bn$. The wave numbers of the principal bands of the ions were smaller than those of the corresponding neutral compound whether the aldehydes or ketones were considered. The wave numbers of the principal bands of the ketones were found to be smaller than those of the corresponding aldehydes whether the neutral compounds or the ions were considered. The wave numbers of the principal bands of all four series were found to decrease with each interpolation of a vinyl group by amounts that decreased with every interpolation. Assuming that these decreases followed geometric progressions, empirical equations have been written for all four series. The same common factors were used for aldehydes and ketones. These equations were applicable as far as the measurements were made ($n = 6$). The equation for the ketonic series did not fit benzophenone. From the spectra, approximate values for the ratio of ion to base were made at a fixed acidity. The logarithms of these ratios were larger for ketones than for the corresponding aldehydes by approximately constant amounts. In both aldehydic and ketonic series these logarithms increase with each interpolation of a vinyl group by increments that decreased approximately by a geometric progression with the same common factor for both series. The logarithms, which are proportional to base strengths, therefore obeyed an equation similar to those obeyed by the wave numbers. It is pointed out that these equations are empirical and their accuracy must be largely fortuitous. However, they show that the effect on the energy of a reaction of interpolating vinyl groups in a conjugate system decreases with the length of the conjugate system.

## Introduction

A compound and its vinylogs, $R(CH{=}CH)_nR'$ with $n = 0, 1, 2\ldots$, form a series that is homologous with respect to $CH{=}CH$. Such series can be called vinylogous series. In the spectra of a vinylogous series there generally are certain bands that show such a close relationship from member to member that they can be considered as a class common to the series. Often these bands are more intense or of longer wave lengths than the others and are called the principal bands of the series. The peaks of these bands move in a regular way toward the red as $n$ increases.

The relationship between the position of the principal band and $n$ varies with the series, but often can be expressed by a simple mathematical equation. For many series of the type $R_2\overset{+}{N}{=}CH(CH{=}CH)_nNR_2$, $\lambda_{\max}$ of the principal band is very nearly a linear function of $n$ up to as large a value of $n$ as have been obtained and including the first member ($n = 0$).[1] For the series $C_6H_5(CH{=}CH)_2C_6H_5$ the square of $\lambda_{\max}$ is linear with $n$, except for $n = 0$.[2] This square law is moderately applicable to several series in which the conjugate system is attached to a $C{=}O$ or $C{=}N$ group, but the measurements do not extend to values of $n > 4$.[3]

Our measurements of the spectra of the series $C_6H_5(CH{=}CH)CHO$ and $C_6H_5(CH{=}CH)_nCOC_6H_5$ are of interest because (1) measurements have been made up to $n = 6$, which allows the breakdown of the square law to be observed, (2) the first member of the ketonic series has a different symmetry to the other ketones and so does not conform to the series, and (3) the aldehydes and ketones are basic and form the new series $C_6H_5(CH{=}CH)_nCH\overset{+}{O}H$ and $C_6H_5(CH{-}CH)_nC\overset{+}{O}HC_6H_5$ in which a positive charge can be carried along the conjugate system without the separation of opposite charges necessary for the aldehydes and ketones.

A conjugate system allows the possibility of many stereoisomers. However a glance at Figs. 1 and 6 will convince the reader that such regularity could result only if all the compounds have the same stereo pattern.

Since the names and formulas of these compounds are long, we shall indicate each compound by a letter with a subscript. The letter A or K shows that it belongs to the aldehydic or ketonic series. The subscript number shows the number of vinyl groups. Thus $A_2$ is 5-phenylpentadienal and $K_0$ is benzophenone.

## Materials and Methods

**$A_3$,$A_4$,$A_5$,$A_6$.**—These aldehydes were prepared by condensing crotonaldehyde with cinnamaldehyde or 5-phenylpentadienal in alcohol using piperidine acetate as the catalyst.[4] $A_3$ and $A_5$ were obtained from $A_1$, and were separated with toluene in which $A_5$ is insoluble in the cold. $A_4$ and $A_6$ were obtained from $A_2$ and were separated with ethyl acetate in which $A_6$ is insoluble. After recrystallizations these aldehydes were sublimed in vacuum. The freshly prepared final products were beautiful colored crystals. The yields were always less than 10% and sometimes less than 5%.

**$A_2$.**—Cinnamaldehyde and cyanacetic acid were condensed and the product was decarboxylated by heating with copper powder.[5] The resulting nitrile was reduced with $SnCl_2$ and HCl in dioxane.[6] After hydrolysis of the stannic complex compound the aldehyde was treated with

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