Pentaphenylpropylene (0.5 g.) is reduced when its solution in butyl alcohol (40 ml.) is treated with sodium (1.8 g.). The resulting **α,α,γ,γ,γ-pentaphenylpropane** (0.4 g.) crystallizes from acetic acid in the form of small needles that melt at 158–159°.

Anal. Calcd. for $C_{35}H_{28}$: C, 93.34; H, 6.66. Found: C, 93.22; H, 6.97.

Action of Sodium Amalgam on the Propylene.—The red solution obtained by shaking pentaphenylpropylene in ether with 40% sodium amalgam for seven days is decolorized by the addition of alcohol. After washing the solution with water and evaporating the ether, there is obtained 0.8 g. of a crystalline product which melts at 131–133° alone or mixed with the starting material.

Action of Lithium on the Propylene.—A solution of the propylene (1 g.) in ether (50 ml.) usually becomes red after shaking for twenty-four hours with finely-cut lithium (0.4 g.). To ensure complete reaction, shaking should be continued for seven days.

Such a solution treated with alcohol yields an oil after removal of the lithium hydroxide and the ether. This oil when dissolved in acetic acid deposits 0.2 g. of **α,α,δ,δ-tetraphenylbutene-β** (m. p. 139–140°, literature,[7] 140.5), while from the acetic acid mother liquor is obtained a small amount of triphenylmethane (m. p. 92° from petroleum ether). There are no indications of the presence of a third product, but the difficulty of separating these two hydrocarbons prevents their quantitative isolation.

(7) Schlenk and Bergmann, *Ann.*, **463**, 106 (1928).

A solution of the lithium compounds from pentaphenylpropylene (1 g.) is decolorized when carbon dioxide is passed into it. From the resulting mixture there is obtained a solid (1 g.) soluble in dilute sodium carbonate. By fractional crystallization from ethyl alcohol this solid may be separated into the less soluble triphenylacetic acid (0.3 g.), which melts at 264–266° alone or mixed with an authentic sample, and tetraphenylbutenedicarboxylic acid (0.22 g.). The latter product gives benzophenone on oxidation with aqueous potassium permanganate and melts at 255–257° alone or mixed with a sample prepared according to the method of Schlenk and Bergmann[7] (p. 102).

Action of Lithium on 1-Biphenylene-3-phenylindene.—An ethereal solution of 1-biphenylene-3-phenylindene (0.5 g.) is shaken for three days with an excess of lithium and then treated with alcohol. Crystallization of the product from acetic acid yields 0.4 g. of 1,2,3,4-dibenzo-9-phenylfluorene which melts at 209° alone or mixed with a known sample.[8]

Summary

α,α,γ,γ,γ-Pentaphenylpropylene is cleaved by lithium, yielding triphenylmethyl-lithium and, through dimerization of the other product, α,α,δ,δ-tetraphenylbutenedilithium.

(8) Koelsch, THIS JOURNAL, **56**, 480 (1934).

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[A COMMUNICATION FROM THE LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Use of Polarographs in Determining Ketones

BY GERALD T. BORCHERDT, VILLIERS W. MELOCHE AND HOMER ADKINS

The solution of a number of problems in organic chemistry depends upon obtaining a method of analysis for small amounts of ketones and aldehydes in mixtures containing two or more such compounds. The present paper is concerned with the development of procedures for the use of the polarograph for the accurate determination of acetophenone and *p*-chlorobenzophenone separately and in mixtures with each other. A subsequent paper illustrates the value of the procedures in following a tautomeric change.

Two different polarographs have been used in this study, the one a Heyrovsky instrument and the other a product of Leeds and Northrup. The former makes its record on photographic paper which must be developed, while the latter instrument draws a line in ink similar to that made by the well-known Leeds and Northrup potentiometer temperature recorder.[1,2]

A polarograph is an instrument which continuously increases the potential across a cell, at the same time making a record of the amount of current passing through the cell. The cell is a small glass vessel containing 0.01 to 5.00 ml. of a solution to be analyzed. A stream of fine drops of mercury flows from a capillary (cathode) through the solution to the floor of the cell, which is covered with mercury (anode).

Current flows through the cell after the potential across it has reached a value characteristic of the most readily reducible compound in the cell. The amount of current flowing then increases rapidly with a small increase in potential across the cell. During this time is drawn the "A" portion of the curve, as indicated in Fig. 1. This

(1) For references on Heyrovsky polarograph see review paper by Winkel and Proske, *Angew. Chem.*, **50**, 18 (1937). See also "Chemische Analysen mit dem Polarographen," by Dr. Hans Hohn, Verlag von Julius Springer, Berlin, 1937.

(2) Funds for the purchase of the instruments used in this investigation were provided by the Graduate Research Committee of the University of Wisconsin.

portion of the curve is terminated when the amount of current passing through the cell no longer materially increases with increase in potential. When the potential across the cell has reached a value characteristic of the second most readily reducible compound, again the amount of current rapidly increases with increase in potential and the "B" portion of the curve is drawn. The "B" portion of the curve is terminated when the amount of current passing through the cell no longer increases with increase in potential. There is then no considerable increase in current with increase in potential until the potential characteristic of the third most readily reducible compound is reached and the "C" portion of the curve is drawn. In the work reported herewith the most readily reducible compound (A) is *p*-chlorobenzophenone, the next is acetophenone (B) and the next is ammonium chloride (C), the supporting electrolyte in the cell.

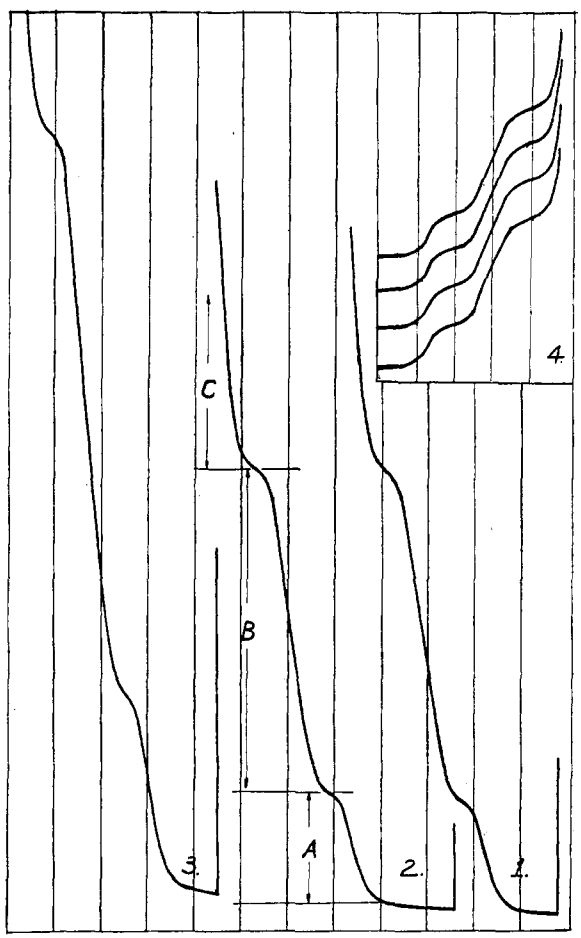

Fig. 1.—Polarograms: The above is a reproduction of a photograph of polarograms. Curves 1 and 2 are duplicate polarograms made on the same sample, while curve 3 is on the same sample at increased sensitivity, using the Leeds and Northrup instrument. The polarograms marked 4 were quadruplicate determinations made with a Heyrovsky instrument. The A portion of polarogram 2 was due to *p*-chlorobenzophenone, the B portion to acetophenone, and the C portion to ammonium chloride. The length of A in the original was about three centimeters.

The more important factors in determining the height of the "A" portion of the curve are (1) the characteristics and concentration of "A;" (2) the characteristics of other compounds in the cell, including other "reducible" compounds such as "B" and "C" and "inert" compounds such as organic solvents and electrolytes; (3) the diameter, shape and surface of the orifice from which the mercury flows into the cell; (4) the temperature; and (5) the "sensitivity" of the recording device. The "sensitivity" is dependent upon the portion of the current that is shunted through the measuring device and may be readily changed by means of an Ayrton shunt or rheostat.

It will thus be apparent that in order to use the polarograph as an instrument for determining the concentration of a ketone or the ratio of two ketones in a solution, it is necessary to standardize the instrument against solutions containing known amounts of them.[3] Since the use of the polarograph for quantitative work depends upon the measurement of distances upon a chart, it is desirable to obtain curves which "break" sharply, as otherwise there may be a good deal of uncertainty as to the measurements. The more important variables determining the sharpness of the break between the A and B portions of the curve, for example, are, first, the actual and relative concentrations of A and B and, second, the characteristics and concentrations of the solvent and electrolytes. The sharpness of the break is also a function of the "sensitivity" of the measuring device as defined in the last paragraph and may also be modified in the Leeds and Northrup instrument by the introduction of a shunt circuit around the galvanometer of the recorder.

Five different methods of measuring the curves have been used, as illustrated in Fig. 2, since the preferred method was not apparent to us. (a) In the first, the heights were taken as the distances between the points located at the change of direc-

(3) Shikata is apparently the only investigator who has attempted to use the polarograph for the determination of ketones. He claims to have determined the solubility in water of a number of ketones (*Mem. Coll. Kyoto University*, Vol. VIII, for 1930). He apparently does not consider the variables affecting wave height noted above. It seems to us difficult to make a quantitative determination on the basis of such polarograms as he has published.

tion of curvature. (b) In the second, the heights were taken as the distances between the points at the greatest curvatures; the portion of the curve drawn during the "break" from one compound to another being disregarded. (c) In the third method, the heights were measured between the intersection of projections of the straight portions of the curves. (d) The fourth method was like the third, except that one-half of the distance during the "break" was added to each height. A fifth method, which bore the same relationship to the second as the fourth does to the third, was also used, but, since it seemed to have no advantages over other methods, no data on it are given.

No matter how the curves are measured the heights are apparently not precisely proportional to the concentration of ketones. This fact makes it necessary either to prepare standard solution having approximately the same composition as the solution to be analyzed, or else to determine a correction which may be applied to the measured wave heights. The first alternative necessitates preparing several different standard solutions if accurate analyses are to be made on solutions containing widely different amounts and ratios of ketones.

Four different methods of applying corrections have been made using each of the five different methods of measuring wave heights. It is unnecessary to go into the results in detail, but it will suffice to give the method of correction which has been found to be most satisfactory.

The preferred method of correction of wave heights involves the preparation of two standard solutions, in one of which the ratio of A to B was less than, and in one greater than, in any of the solutions to be analyzed. It has been found to lead to more accurate results if the concentration of *one* of the ketones is approximately the same in the two standard solutions and in the 'unknown," while the other is varied sufficiently in concentration to give the desired ratio of ketones in solution. This is readily done since it involves merely diluting the solutions in such a way that the wave heights for one of the ketones is approximately the same in the various solutions. Polarograms are then made for each of the two solutions and the wave heights measured.

If A and A′ are the wave heights for *p*-chlorobenzophenone, B and B′ the wave heights for acetophenone, and R and R′ the ratio of the ketones in the two standard solutions, then

$$\frac{A + X}{B + Y} = R \text{ and } \frac{A' + X}{B' + Y} = R'$$

where X and Y are the corrections to be added to the wave heights in order to make the ratios calculated from the wave heights equal to the known ratios of ketones in the standard solutions. The values of X and Y may be calculated readily from these two equations, since A, A', B, B', R and R' are known.

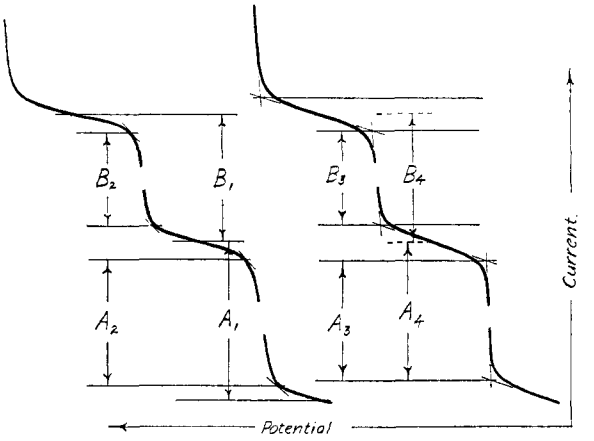

Fig. 2.—Methods of measuring polarograms. The a, b, c and d methods of measurement referred to in the text correspond with the A_1B_1, A_2B_2, A_3B_3, and A_4B_4 of the figure. In the figure, the portion of the curve drawn during the "break" has been idealized and greatly magnified, as compared with the A and B portions of the curve shown from a photograph in Fig. 1.

In practice it has been found to be better to express A in terms of B (or *vice versa*) rather than to express each in terms of the measured wave heights. That is, if the measured wave height of A is 2.53 cm., and of B is 2.83 cm., the height of A is considered as 0.897 and of B as 1.000. Thus wave heights on different polarograms on the same sample or different samples from the same solution may be averaged, thereby minimizing errors of measurement. The supporting electrolyte need not be measured into the cell exactly and the sensitivity of the polarograph may be varied without modifying the relative wave heights, although both of these change the actual heights of the waves. Small losses of solvent as the result of bubbling nitrogen or hydrogen through the cell may affect wave height but not relative wave heights.

The correction may be made more simply by plotting for each of the standards the observed ratio of wave heights against the known ratio of ketones. A line drawn through these points makes it possible to read the ratio of ketones

in an unknown upon the basis of the relative wave heights.

There are recorded in Tables I and II, certain results obtained in applying the methods discussed above to the determination of the ratio of ketones in solutions containing known amounts of acetophenone and *p*-chlorobenzophenone. The first column of each table contains the ratios of ketones placed in the cell; the second column the ratio of ketones calculated from the wave heights of the polarograms as determined on a Heyrovsky polarograph. The first eight lines in the third column, of each of the tables, give the values of X and Y calculated from the ratios and wave heights of the two standard solutions. In subsequent lines of column 3 are given the ratios of the ketones calculated to be present on the basis of the measured wave heights (column 2) and the values of X and Y given above. A comparison of the figures in column 3 with those in column 1 indicates the accuracy of the polarographic determination. In column 4 are given in per cent. the differences between the figures in columns 1 and 3. Four different methods of measuring the polarograms have been used and are indicated as a, b, c and d, corresponding to the methods illustrated in Fig. 2.

TABLE I

ANALYSIS FOR RATIOS OF KETONES IN STANDARD SOLUTIONS

The cells contained 27 mg. of ammonium chloride, 0.74 mg. of *p*-chlorobenzophenone (A) and from 0.04 to 0.40 mg. of acetophenone (B) made up to 5 ml. in 80% alcohol–20% water.

Actual	Ratio of ketones $\left(\frac{B+Y}{A+X}=R\right)$ Detn.	Corr. detn.	% error
0.968	1.048 a	$X = -0.086$	
.097	0.182 a	$Y = -.007$	
.968	1.016 b	$X = -.033$	
.097	0.131 b	$Y = +.015$	
.968	1.044 c	$X = -.063$	
.097	0.161 c	$Y = -.012$	
.968	1.079 d	$X = -.113$	
.097	0.210 d	$Y = -.003$	
.776	.876 a	0.795	2.5
	.820 b	.776	0.0
	.860 c	.786	1.0
	.910 d	.799	2.7
.582	.653 a	.573	1.6
	.625 b	.583	0.2
	.630 c	.560	3.7
	.665 d	.555	4.6
.388	.474 a	.391	0.8
	.419 b	.382	1.5
	.416 c	.350	7.7
	.477 d	.366	5.6
.194	2.74 a	.190	2.0
	.233 b	.197	1.5
	.243 c	.178	8.0
	.286 d	.174	10.3

TABLE II

ANALYSIS FOR RATIOS OF KETONES IN STANDARD SOLUTIONS

The cells contained 27 mg. ammonium chloride, 0.39 mg. acetophenone (B) and from 0.073 to 0.734 mg. *p*-chlorobenzophenone (A) made up to 5 ml. in 80% alcohol–20% water.

Actual	Ratio of ketones $\left(\frac{A+X}{B+Y}=R\right)$ Detn.	Corr. detn.	% error
1.032	0.940 a	$X = -0.188$	
0.103	.187 a	$Y = -.102$	
1.032	.926 b	$X = -.124$	
0.103	.111 b	$Y = -.020$	
1.032	.918 c	$X = -.157$	
0.103	.134 c	$Y = -.047$	
1.032	.897 d	$X = -.193$	
0.103	.148 d	$Y = -0.64$	
.826	.768 a	0.822	0.5
	.746 b	.828	.3
	.765 c	.849	2.8
	.734 d	.828	0.3
.619	.577 a	.586	5.3
	.555 b	.610	1.4
	.583 c	.636	2.7
	.556 d	.609	1.6
.413	.416 a	.388	6.3
	.377 b	.407	1.4
	.401 c	.419	1.5
	.396 d	.410	0.7
.206	.265 a	.201	2.4
	.197 b	.202	1.9
	.239 c	.228	10.7
	.244 d	.222	7.5

Measurements similar to those recorded in Tables I and II were also made with the Leeds and Northrup instrument. Two solutions of 2.5 ml. each containing 0.119 mg. of acetophenone and 0.206 mg. of *p*-chloroacetophenone, and 0.0297 mg. of acetophenone and 0.206 mg. of *p*-chlorobenzophenone, respectively, were used as standards. From a measurement of the polarograms on these solutions the values of B and B' were found to be 0.963 and 0.321, where A and A' were 1.000, and R and R' were 0.839 and 0.209. The values of X and Y calculated from these figures are -0.108 and $+0.019$.

Two solutions were then analyzed, and found to contain the ketones in the ratios of 0.65 and 0.43, respectively, while the ratios of the ketones actually present were 0.63 and 0.42. Standard

solutions and "unknowns" were also used, which differed from those described above in that one drop of a 10% solution of sodium hydroxide was added to each cell. This resulted in sharper "breaks" in the polarograms, so that the discrepancy between the found and calculated ratio of ketones was about half that shown above.

An inspection of the data in Tables I and II will show that the ratio of ketones in eight mixtures of acetophenone and *p*-chlorobenzophenone was determined within 1.5% using the second or "b" method of measurement. Even in the case of the measurement showing the largest error (10.7%) the found ratio was 0.228, when the actual ratio was 0.206. There are few, if any, other analytical methods that would give a more accurate indication of the ratio of two ketones in a solution, especially when one is in such a large excess. The amounts of a single ketone may be determined with an error of less than 2%, as shown in Table III. In the most inaccurate determination the error was 0.025 mg. in a solution containing 0.881 mg.

TABLE III

ANALYSIS OF SOLUTIONS CONTAINING A SINGLE KETONE

Measured wave height, cm.	Value of X	Ketone, mg. Present	Found	% error
	p-Chlorobenzophenone			
3.120 a	−0.252	0.881	0.900	2.1
2.930 b	− .089	.881	.885	0.5
3.070 c	− .256	.881	.896	1.7
3.155 d	− .308	.881	.906	2.8
	Acetophenone			
4.500 a	−0.340	0.628	0.628	0.0
4.190 b	− .117	.628	.625	.5
4.285 c	− .272	.628	.616	1.9
4.505 d	− .445	.628	.621	1.1
3.460 a	− .340	.471	.471	0.0
3.135 b	− .117	.471	.463	1.7
3.325 c	− .272	.471	.469	0.4
3.480 d	− .445	.471	.464	1.5
2.460 a	− .340	.314	.320	1.9
2.175 b	− .117	.314	.315	0.3
2.325 c	− .272	.314	.315	.3
2.495 d	− .445	.314	.314	.0

The value of the correction factor to be used with polarograms on solutions containing a single ketone was determined as follows. Polarograms were made on two solutions of acetophenone, one of which contained 0.785 mg. and the other 0.157 mg. of the ketone. If the height of the wave of the first polarogram is B and of the second B', then $(B + X)/(B' + X) = 0.785/0.157$. The calculated values of X are given in Table III. Similarly, polarograms were made for 5 ml. of solutions containing 1.468 mg. and 0.293 mg. of *p*-chorobenzophenone. The values of X calculated from $(A + X)/(A' + X) = 1.468/0.293$ are also given in Table III.

The result of applying these corrections to the measured wave heights of four different solutions containing various amounts of *p*-chlorobenzophenone or acetophenone is given in Table III. The calculation of the amount of ketone reported as "found" was made as follows. The corrected wave heights (in cm.) for 0.785 mg. of acetophenone were for the various methods of measurement 5.200 a, 5.125 b, 5.120 c, and 5.130 d, and for 1.468 mg. of *p*-chlorobenzophenone 4.685 a, 4.710 b, 4.610 c, and 4.610 d. These values are the measured wave heights less the values of X. The corrected wave height for the first analysis given in Table III is (3.120–0.252) or 2.868. If the amount of ketone present is Y, then, 1.468 : 4.685 :: Y : 2.868, or Y equals 0.900 mg. as given in the fourth column of Table III.

It should be noted that, within wide limits, reduction in the amount or concentration of the ketone in the cell does not decrease the accuracy of the determination. However, the determination of the ratio of ketones is less accurate if the concentration of one ketone is five or ten times as great as that of the other ketone. The amounts of ketone present in the cell were usually from 0.04 to 0.74 mg. in 5 ml. of solution. Since equally good polarograms can be made on 1 ml. of solution, the amounts of ketone needed would be 0.01 to 0.15 mg. There is no difficulty in making good polarograms on solutions one-tenth as concentrated as those actually used. Thus, accurate determinations can be made readily upon solutions containing one-millionth of a gram of acetophenone, for example. The above depends upon essentially macro methods of manipulation. Heyrovsky, using micro methods, has reported analyses upon 0.000000001 g. of material.[4]

The concentration of the ketone in the cell is not affected appreciably during the process of making a polarogram, so that repeated determinations may be made. Each determination reported in Tables I and II is an average of the measurements made upon four polarograms from a single sample. Four such curves are shown in the upper right-hand corner of Fig. 1.

(4) Heyrovsky, *Mikrochemie*, **12**, 25 (1932); Majer, *ibid.*, **18**, 74 (1935).

Procedure for Analysis.—The sample to be analyzed was placed in a cell of the design described elsewhere.[4] The cell was placed in a thermostat maintained at 25 ± 0.1°. Hydrogen or, better, oxygen-free nitrogen was allowed to bubble through the solution for several minutes. It is advisable to bubble the gas through a solution of the same composition as that in the cell, in order to avoid changes in concentration due to loss of volatile constituents in the cell. Carefully prepared mercury, from a reservoir whose upper level was about 55 cm. above the tip of the capillary, was then allowed to drop through the solution. The flow of gas through the solution was stopped and the gas merely allowed to flow through the cell. After a few minutes, the polarograph was set to 0.8 volt and started. After one polarogram was made, the instrument was reset and the process repeated.

The greatest source of difficulty in the actual use of a polarograph is in the capillary from which the mercury flows into the cell. The tips used in this study were drawn from thermometer tubing and broken back to give the desired drop rate. They were kept under water during the intervals between use. The capillary should be of such a size that the flow is about one drop per second in the electrolyte. If the drop rate is more than three drops per second, there is a good probability that the mercury will flow in a stream when the potential across the cell becomes greater than 1.5 volts. A slow drop rate (one drop in two or three seconds) is not unsatisfactory with the Heyrovsky instrument, but gives very poor curves with a Leeds and Northrup polarograph. This difference between the instruments results from the fact that the former gives a continuous record while the latter takes a reading every two seconds. The irregularities on the Leeds and Northrup curves with a slow drop rate may be minimized by putting a shunt of 1000 to 3000 ohms across the galvanometer on the recorder. The difficulty with this procedure is that, though it produces smooth curves, it greatly reduces the sharpness of the breaks. The sharpness of the break may be increased by the addition of a little base, such as phenethylamine or sodium hydroxide. Benzene as a solvent results in poor curves. Alcohol in any concentration or ether up to 20% does not greatly affect the sharpness of the breaks. Chloroform appeared to be entirely unsatisfactory as a solvent for the sample while making a polarogram.

Summary

Procedures have been described for determining with a polarograph the ratio and (or) amounts of acetophenone and (or) *p*-chlorobenzophenone in samples containing from 0.000001 to 0.001 g. The method involves the comparison of wave heights made on standard solutions with those made upon solutions containing unknown amounts and ratios of ketones. It appears practical to determine the ratio or amounts of ketones by this method with an error of less than 2%.

Some of the factors which affect a polarographic determination have been considered and a comparison made between four different methods of measuring polarograms. One method, designated as "b" in Fig. 2, appears to be the most satisfactory with a Heyrovsky polarograph, while another method, designated as "d," is more satisfactory for the polarograms made by the Leeds and Northrup instrument.

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