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REDUCTION OF ARYL NITRO COMPOUNDS

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This invention relates to the catalytic hydrogen reduction of aryl nitro compounds in acid media, and more particularly to the reduction of aryl nitro compounds to form substituted aryl amines. Specifically it relates to the preparation of p-amino-phenol from nitrobenzene by catalytic hydrogen reduction in strong mineral acid.

Aminophenols have been made commercially from the corresponding nitrophenols by either iron or hydrogen reduction. However, such methods have proven extremely expensive in view of the high cost of nitrophenols. For this reason efforts have been made to produce aminophenols from aryl nitro compounds, for example, nitro-benzene, and it has been found that aminophenols have been so produced by electrolytic reduction while suspended in strong mineral acid. While the source of raw materials in such cases considerably reduced the expense of operation, electrolytic processes are of themselves necessarily more expensive and are only practical where there is a cheap source of electricity. The development of such processes, therefore, has not materially advanced the art with regard to the manufacture of aminophenols.

This invention has as an object the production of substituted amines by a commercially practical method. Another object is the production of substituted amines from aryl nitro compounds in which the substitute amine has at least one more substituent than the original nitro compound. A further object is the preparation of para-amino-phenol from nitrobenzene by a simple and practical method. Other objects will be apparent upon the reading of the description of the invention.

These objects are accomplished by the invention as indicated in the following description. Aryl nitro compounds, for example, nitrobenzene, are subjected to catalytic hydrogenation in the presence of an excess of a strong acid, especially a strong mineral acid. By this process a substantial amount of the corresponding substituted amine, e. g., aminophenol, is produced, the phenolic group usually becoming located in the para position to the amino group. It is therefore considered that the reaction is one of hydrogenating the aryl nitro compound to the corresponding aromatic hydroxyamine followed by the immediate rearrangement of said aromatic hydroxy amine to the substituted amine.

The rearrangement need not cause the hydroxy group to locate in the para position. Thus p-nitro diethyl aniline may yield the correspond-

ing ortho-aminophenol. Also in the case of para-nitrotoluene, the hydroxyl group may locate in the side chain, thus forming aminobenzyl-alcohol, which may then condense with unreduced para-nitrotoluene to form para-amino-phenyl-meta-nitro-ortho-tolyl methane.

It has further been found that by proper selection of starting materials certain other reactions of the hydroxy amines mentioned above can be caused to proceed apparently simultaneously that would otherwise require subsequent special treatment. For instance amino coumarin can be made from meta-nitrocinnamic acid, and likewise certain condensation products can be derived from para-nitro-benzaldehyde. Additional examples of aryl nitro compounds that may be treated in accordance with this process are ortho-nitrotoluene, ortho-nitrobenzene sulfonic acid, meta-bromnitrobenzene, alpha-nitro-naphthalene, meta-nitroaniline, ortho-nitrobenzoic acid and meta-nitro-benzaldehyde.

Chlorinated or carboxylated nitroaryl compounds (as well as other derivatives) may be treated in the same manner to form aryl hydroxyamine derivatives, but in case the additional substituent occupies the para position the reaction is altered somewhat. In these two particular cases, when the hydrogenation is carried out in sulfuric acid, a sulfonated hydroxy amine is produced while in other cases where the para position is blocked by groups other than the chlorine, carboxyl, and methyl, the reaction may not take place at all, in which instances the corresponding unhydroxylated amine is formed. In the case where the para position is blocked by a methyl group, the hydroxyl attaches to said methyl group thus forming an hydroxylated amine.

This application is not intended to cover the preparation of unsubstituted amines or substituted amines in which the substituent is carried over from the reactants and no substituent enters at the time of reduction. It is possible, as indicated, above, to prepare other than hydroxy-substituted amines by this process. For instance the use of concentrated HCl as the acid medium leads to the formation of chlor-substituted anilines, and the use of 100% sulfuric acid or oleum leads to the formation of sulfonated anilines. These reactions are included within the scope of the present invention.

The reduction reaction is carried out in an acid resistant vessel or autoclave and with hydrogenation catalysts such as platinum, palladi-

um, molybdenum sulfide, cobalt sulfide, tungsten sulfide, etc., that are active in the presence of strong acid.

In operating to produce high yields of the desired product, there should be used an acid which is strong enough to invert the aryl hydroxyl amine to the corresponding aminophenol, and temperatures that are ample both to activate the catalyst and to produce a high rearrangement speed. Sulfuric acid having a concentration of about 40%, and temperatures of 100° to 150° C. have been found preferable in converting phenylhydroxylamine to para-aminophenol at a rapid rate.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof, since many modifications may be made without departing from the spirit and scope of this invention.

Example 1

A 2½ liter gas-fired stirring autoclave was charged with:

(2.0 mols.) 246 parts nitrobenzene
(3.0 mols.) 300 parts 98% sulfuric acid
900 parts water
2 parts PtO₂·2H₂O

The autoclave was flushed out with hydrogen and the charge was heated to 100° to 110° C. while stirring. When this temperature was attained 500 lbs. of hydrogen pressure was applied, and the experiment was continued under these conditions until no more hydrogen was consumed. After cooling, the charge was removed from the autoclave, diluted slightly with water, and warmed to effect resolution of any crystals or precipitated material. Any unreacted nitrobenzene was removed at this point by steam distillation. To the hot charge in the steam-still an alkali was added to free the bases from their salts. Either sodium carbonate, sodium hydroxide or sodium sulfite are suitable (in amount equivalent to the sulfuric acid originally employed), and often a mixture of sodium hydroxide and sodium sulfite may be used to advantage. Steam distillation was then employed to remove by-product aniline, and para-aminophenol was separated from the resultant mother liquor by cooling. The mother liquor was adjusted to the "Brilliant-yellow" neutral point with sulfuric acid or sodium bicarbonate, which ever was necessary. In this way 124 parts para-aminophenol was obtained, which corresponds to a yield of about 57%.

Example 2

In an autoclave apparatus (such as described in Example 1) was placed the following charge:

	Parts
Ortho-nitrotoluene	411
98% sulfuric acid	300
Water	400
PdO ₂ ·2H ₂ O	1

The autoclave system was flushed out with hydrogen, the temperature raised to about 125° C., and hydrogenation was effected by applying 250 to 300 lbs. hydrogen pressure until no further absorption occurred. From the charge, treated as described in Example 1 to remove unreacted ortho-nitrotoluene and ortho-toluidine by steam distillation, was obtained a yield of 160 parts 3-methyl 4-aminophenol.

Example 3

The following charge was treated in the same manner as described in Examples 1 and 2:

	Parts
Nitrobenzene	369
37% hydrochloric acid	600
Water	600
PtO ₂ ·2H ₂ O	3.0

From the mother liquor was obtained 35 parts unreacted nitrobenzene, 220 parts aniline and 20 grams para-aminophenol.

Example 4

Using a procedure and apparatus similar to that described in Example 1, the following charge was hydrogenated:

	Parts
Nitrobenzene	369
85% phosphoric acid	350
Water	400
PtO ₂ ·2H ₂ O	3.0

The final product of this experiment was 203 parts aniline and 30 parts para-aminophenol.

Example 5

The following charge was hydrogenated in a pressure autoclave at 125° C. and 400 to 500 lbs. pressure:

	Parts
Nitrobenzene	369
Para-toluene sulfonic acid	1430
Water	1500
PtO ₂ ·2H ₂ O	3.0

After hydrogenating at 125° C. and 400 to 500 lbs. pressure, and working up the contents of the autoclave there was obtained 52 parts aniline and 160 parts para-aminophenol.

Example 6

The following charge was hydrogenated:

	Parts
Nitrobenzene	369
Para-toluene sulfonic acid	600
Sulfuric acid	150
Water	900
PtO ₂ ·2H ₂ O catalyst	1.0

After hydrogenating at 140° C. and 400 to 500 lbs. pressure for about 12 hours the charge was cooled and filtered. A solid compound was obtained in substantial amount which was characterized as the para-toluene sulfonic acid salt of the ester of para-toluene sulfonic acid and para-aminophenol, a compound which is described in Beilstein, Vol. XIII, page 441, ed. 4.

Example 7

A solution of (NH₄)₂ MoS₄ was prepared from commercial ammonium molybdate and H₂S gas. To this solution solid (NH₄)₂HPO₄ was added in the proportion of 1.3 part to 31.2 parts (NH₄)₂ MoS₄, the final volume being about 500 cc. This solution was then evaporated to dryness, and the residue heated in hydrogen at 400° C. for 16 hours before use. The catalyst so prepared was used in the following charge:

	Parts
Ortho-nitrochlorbenzene	472.5
Sulfuric acid	300
Water	450
Catalyst	5

This charge was placed in a pressure autoclave and hydrogenated for about 20 hours at

140° C. and 400 to 500 lbs. pressure. At the end of this time about 104 parts of nitro-compound was recovered unchanged, and after making alkaline 116 parts of ortho-aminochlorobenzene was steam distilled out. From the mother liquor was obtained 89 parts of product, a part of which was meta-chlor-para-aminophenol.

Example 8

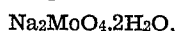
The following charge was hydrogenated to yield an appreciable quantity of para-aminophenol:

	Parts
Nitrobenzene	369
Sulfuric acid	310.4
Water	900
(NH ₄) ₂ MoS ₄	27

The sulfomolybdate was dissolved in the water, then acid, and finally nitrobenzene was added. From this charge, treated for 23 hours at 150° C. and 400 to 500 lbs. hydrogen pressure, there was obtained 100 parts aniline and 170 parts para-aminophenol.

Example 9

A solution of 13.5 parts commercial



containing 55.8% MoO₃, in 150 cc. water was prepared. H₂S was passed into this solution until it was saturated, and then enough acid was added to cause complete precipitation of the MoS₃ produced. The precipitate was washed on the filter and used in the following autoclave hydrogenation charge:

	Parts
Nitrobenzene	369
Sulfuric acid	300
Water	450
Catalyst paste	10

After hydrogenating for about 30 hours at 125° to 150° C., the product was worked up by steam-distilling, adding caustic-Na₂SO₃ solution, re-steam distilling and cooling to permit separation of para-aminophenol. In this manner 100 parts aniline and 175 parts para-aminophenol were obtained.

Example 10

A catalyst was prepared by dissolving 24.2 parts ammonium molybdate, 39 parts 60% fused sodium sulfide and 1.0 parts (NH₄)₂ HPO₄ in 500 cc. water. To this solution was added 20 parts Filtercel and then enough 40% sulfuric acid to cause complete precipitation of the molybdenum sulfide. After washing on the filter, a portion of this catalyst was used as follows in the usual hydrogenation autoclave:

	Parts
Nitrobenzene	369
Sulfuric acid	300
Water	450
Catalyst	10

This charge was hydrogenated at 400 to 500 lbs. for 20 hours at 150° C.

On working up the product it was found that 96 parts aniline and 170 parts para-aminophenol had been produced.

Example 11

A catalyst was prepared by treating with H₂S gas a solution of commercial sodium molybdate (containing 55.8% MoO₃) in 1200 cc. water and 20 cc. concentrated aqueous ammonia. At the end of about 4 hours' time the solution was ap-

parently saturated with H₂S, and it was acidified with sulfuric acid. The resultant precipitate was washed on the filter, and dried at ordinary temperature. A portion of this catalyst was heated for 5 hours in hydrogen at 400° C. and used in the following experiment.

Charge:

	Parts
Nitrobenzene	369
Sulfuric acid	600
Water	900
Catalyst	10

The hydrogenation was carried out at 400 to 500 lbs. pressure and 125° C. As products, after the usual method of working up the finished charge, 225 parts aniline and 12 parts para-aminophenol were obtained.

Example 12

A catalyst was prepared by treating pyrophoric finely divided metallic cobalt with hydrogen sulfide in benzene solution. The superficially sulfided cobalt so prepared was used in the following experiment:

	Parts
Nitrobenzene	369
Sulfuric acid	300
Water	450
Catalyst	10

After hydrogenating for 15 hours at 135° C. and 400 to 500 lbs., a yield of 189 parts aniline and 30 parts para-aminophenol was obtained.

Example 13

A catalyst was prepared by treating a solution of 24 parts CrO₃ (commercial, fused) and 49 parts ammonium molybdate in 1.0 liter of water with H₂S gas until reduction of CrO₃ to Cr₂O₃ was complete. H₂S flow was then continued until the molybdenum salt was completely sulfided. Dilute sulfuric acid was added until a filtered sample of the mother liquor was found to be colorless, thus showing the absence of MoS₄ ions. The whole slurry was filtered, washed, and dried by refluxing with benzene. In this manner it was possible to dry the catalyst at approximately 88° C. and in the absence of air. The catalyst was reduced in hydrogen at 400° C. for several hours before use.

In an autoclave the following charge was hydrogenated at 115° to 155° C. and 400 to 500 lbs. pressure:

	Parts
Nitrobenzene	369
H ₂ SO ₄	300
Water	450
Catalyst	25

After 15 hours treatment the charge was removed and only traces of nitrobenzene were found in it. A yield of 76 parts aniline and 181.5 parts para-aminophenol was obtained.

Example 14

A catalyst was prepared by adding 95 parts CoCl₂·6H₂O in 800 cc. water to a solution of 104 parts (NH₄)₂MoS₄ in 2.0 liters of water. The resulting precipitate was filtered, washed and dried by rinsing it several times in acetone. It was heated to 360° in hydrogen before use in the following charge:

	Parts
Sulfuric acid	300
Nitrobenzene	246
Water	900
Catalyst	10

After about 10 hours at 150° C. and 700 to 750 lbs. hydrogen pressure, the charge was removed and worked up for its aniline and para-aminophenol content. Yields of 60 parts aniline and 109 parts para-aminophenol were obtained.

Example 15

The following charge was hydrogenated in the usual equipment:

	Parts
Ortho-nitro-toluene.....	411
Concentrated HCl.....	800
PtO ₂ .2H ₂ O.....	3.0

On working up the products an appreciable yield of 4-chlor-2-methyl aniline was obtained.

Example 16

The following charge was subjected to high pressure hydrogenation:

	Parts
Nitrobenzene.....	369
Concentrated HCl.....	800
PtO ₂ .2H ₂ O.....	3.0

This charge yielded an appreciable amount of para-chloraniline.

Example 17

In a small glass-lined bomb was placed the following charge:

	Parts
Nitrobenzene.....	3.0
Sodium isopropyl-naphthalene sulfonic acid.....	3.0
25% H ₂ SO ₄	10.0
PtO ₂ .2H ₂ O catalyst.....	0.2

After hydrogenating at 135° and 500 lbs. hydrogen pressure, there was obtained both aniline and para-aminophenol as products.

Example 18

The following autoclave charge was hydrogenated at 135° to 145° C. and 400 to 500 lbs. pressure for a period of seven hours:

	Parts
Ortho-nitrophenol.....	139
H ₂ SO ₄	300
H ₂ O.....	700
MoS ₂ catalyst as described in Example 12.....	10

It was possible to isolate a sizeable quantity of 4-amino-resorcinol from this charge.

Example 19

In making 5-aminosalicylic acid from meta nitrobenzoic acid the following charge was hydrogenated:

	Parts
Meta-nitro-benzoic acid.....	167
H ₂ SO ₄	300
Water.....	450
PtO ₂ .2H ₂ O.....	2.0

After the consumption of hydrogen ceased at 114° to 147° and 400 to 500 lbs. pressure, the charge was withdrawn and neutralized. 5-Aminosalicylic acid separated and was filtered off.

Example 20

4-aminoresorcinol-3-methyl ether was prepared by hydrogenating the following charge:

	Parts
Ortho-nitroanisole.....	154
Sulfuric acid.....	300
Water.....	450
PtO ₂ .2H ₂ O.....	2

After heating for 3 hours at 123° to 150° C. the charge was neutralized and a product separated. This was washed free of amine with benzene. After recrystallization from toluene, crystals of 4-aminoresorcinol-3-methyl ether were obtained.

Example 21

The following charge was hydrogenated:

	Parts
Nitro-benzene.....	369
H ₂ SO ₄	300
Denatured alcohol.....	706
PtO ₂ .2H ₂ O catalyst.....	2

From the autoclave contents, after hydrogenation was found to be complete, there was obtained para-aminophenol, aniline and an appreciable amount of para-phenetidine.

Example 22

The following charge was hydrogenated in a small glass lined bomb:

	Parts
Nitrobenzene.....	3.0
Trifluoroacetic acid (3 mols.).....	8.34
Water.....	2.0
PtO ₂ .2H ₂ O catalyst.....	0.2

On completion of the reduction at 130° C. and 400 to 500 lbs. pressure, there was obtained aniline and an appreciable yield of para-aminophenol.

Example 23

An autoclave was loaded with the following materials:

	Parts
Metanitrobenzene-sulfonic acid.....	657
H ₂ SO ₄	300
H ₂ O.....	900
MoS ₂ catalyst.....	10

After hydrogenating this charge for about 17 hours at 140° to 150° C. and 400 to 500 lbs. pressure, crystals were evident in the liquor. On identification these turned out to be para-aminophenol ortho-sulfonic acid.

Example 24

The following charge was hydrogenated:

	Parts
Alpha-nitronaphthalene.....	174
Sulfuric acid.....	300
Water.....	450
MoS ₂ catalyst.....	10

After hydrogenating at temperatures up to 155° C. and at 400 to 500 lbs. pressure, the charge was cooled and made neutral by the addition of caustic soda solution. From the charge was obtained some 1-amino 4-oxy-naphthalene.

Although in the foregoing examples there has been indicated the use of certain definite conditions, it is to be understood that these conditions can be varied without departing from the scope of this invention. The following discussion will indicate the influence of variations in conditions on the course of the reaction.

Variations in the temperature and acid concentration have a great influence on the speed of rearrangement of phenylhydroxylamine to para-aminophenol. At low temperatures, for instance at 30° C., it may require weeks to rearrange phenylhydroxyl amine using 50% to 60% sulfuric acid. At 80° to 100° C., however, the rearrangement is complete in a few minutes. A comparatively long time is required with a dilute acid such as 5% to 10% H₂SO₄ even at 100° C., and

side reactions resulting in tar formation may occur.

On the other hand, with regard to the upper temperature limit at which the process can be operated, it has been found that carbonization is likely to occur at temperatures as high as 175° C., and such temperatures are not recommended. However, it has been possible to work at 175° C. using very dilute acid, but then the autoclave yields are diminished due to the necessity of maintaining a molar equivalent of acid over nitrobenzene. In general, it is preferred to operate at temperatures between about 100° C. and about 155° C.; however, when using sulfuric acid and a sulfide catalyst, best results have been obtained in working at temperatures between 135° and 155° C.

The preferred acid concentration depends upon the acid used, the temperature selected, and the results to be obtained. With hydrochloric acid, concentrations up to 20% to 25% may be used to produce hydroxylated amines. Higher concentrations tend to the production of chlorinated products in addition to the hydroxylated product. In the case of sulfuric acid, hydroxylated products are obtained with concentrations between 5% and 60%, while with acid concentrations in excess of 60% sulfonated products are obtained. Likewise it has been found that carbonization will occur at acid concentrations that are over 50%, especially if the temperatures are within the preferred range just indicated. In practice for the production of hydroxylated amines it has been convenient and effective to use sulfuric acid in concentrations of 25% and 50%, and preferably of about 40%.

In general, it may be said that an acid concentration is preferable at which the acid is most highly ionized.

In carrying out the reaction any acid insensitive hydrogenation catalyst may be used. By "acid insensitive hydrogenation catalyst" is meant the hydrogenation catalyst that is not rendered ineffective by the presence of a strong acid. The amount and kind of catalyst used is interrelated with the time, temperature and acid concentration. The exact definitions of such factors are well within the skill of any chemist having knowledge of this invention. With a palladium catalyst it is possible, for instance, to operate at from 80° to 100° C. due to its characteristically high activity. A relatively high acid concentration (50%) will then be chosen when working at so low a temperature.

With unreduced sulfide catalysts, however, it is necessary to approach 150° C. before they begin to display hydrogenation activity. With such systems it will be found best to use 25% to 40% sulfuric acid.

The hydrogen pressure, from the point of view of obtaining operative results, is not a critical factor. Pressures from atmospheric to the safety limits of the hydrogenation apparatus may be used. However, pressure somewhat influences the activity of the catalyst and also the availability of hydrogen in solution. High pressure will thus obviously favor aniline production. It therefore has been practical to operate within the pressure range of 200 to 750 pounds per square inch gauge, and preferably at a pressure of about 400 to about 500 pounds per square inch gauge. With the more active catalysts it has been found to be of advantage to withhold the hydrogenation reaction until conditions are right for the rapid rearrangement of the inter-

mediate hydrogenation product. This may be accomplished by postponing the application of pressure until the contents of the autoclave have been heated to the required temperature or by withholding the introduction of the catalyst until the proper temperature and pressure conditions have been established.

It has been pointed out that the temperature at which a catalyst becomes active regulates in a sense the temperature and concentration of acid employed in the experiment. Likewise the activity of individual samples of a particular kind of catalyst will influence these variables. Moist precipitated molybdenum sulfide (MoS₃) requires a temperature of 145° to 150° C. It is a mild catalyst and does not favor aniline production. High catalyst concentrations can be used.

Reduced molybdenum sulfide (MoS₂) is a much more active catalyst and works at temperatures down to 115° C. Less of this catalyst should be used in order to diminish aniline production.

There are numerous ways of producing either the sulfide or noble metal type of catalyst mentioned in the examples, and any other way may also be employed successfully, if the above factors are taken into consideration.

One of the main advantages of the invention is that a large quantity of material can be worked in one batch in a common type of pressure vessel or autoclave. This eliminates the necessity of operating and maintaining the complicated and costly apparatus used in electrolytic reductions.

This process is more economical than the method for preparing para-aminophenol by way of nitrophenol, in that nitrobenzene is considerably cheaper than nitrophenol.

Certain aminophenol or amine derivatives mentioned in the examples usually require a considerably involved method of procedure, and hence are made by the present process with advantage.

In summarizing the invention it may be said that it is now possible to manufacture on a large scale certain aminophenols and chlorinated or sulfonated amines by an economical process and from relatively inexpensive crude materials by means of a cheap, clean and efficient reducing agent. This is made possible by catalytic hydrogenation in strong acid media.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. The process for the production of substituted amines which comprises catalytically hydrogenating an aryl nitro compound in the liquid phase in the presence of a strong acid.

2. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature between 30° C. and 175° C.

3. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature of about 100° to about 155° C.

4. The process for the production of hydroxylated amines which comprises catalytically hydrogenating an aryl nitro compound in the liquid phase and in the presence of an aqueous sulfuric acid solution having an acid concentration between 5% and 60%.

5. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature of about 100° C. to about 155° C. and a pressure of about 400 to about 500 pounds per square inch gauge.

6. The process for the production of chlorinated amines which comprises catalytically hydrogenating an aryl nitro compound in the liquid phase in the presence of concentrated hydrochloric acid in excess of 20% to 25% hydrogen chloride. 5
7. The process for the preparation of sulfonated amines which comprises catalytically hydrogenating an aryl nitro compound in the liquid phase in the presence of sulfuric acid in solution in amount in excess of 60%. 10
8. The process for the production of substituted amines which comprises bringing under reaction conditions an aryl nitro compound, hydrogen, a strong acid, and an acid insensitive sulfide hydrogenation catalyst. 15
9. The process in accordance with claim 8 characterized in that the reaction is carried out at a temperature between 135° and 155° C.
10. The process for the production of substituted amines which comprises bringing under reaction conditions an aryl nitro compound, hydrogen, a strong acid and a molybdenum sulfide hydrogenation catalyst. 20
11. The process in accordance with claim 10 characterized in that the strong acid is sulfuric acid. 5
12. The process for the preparation of para-aminophenol which comprises catalytically hydrogenating nitrobenzene in the liquid phase in the presence of a strong acid.
13. The process in accordance with claim 1 characterized in that the hydrogenation reaction is withheld until conditions have been established that will provide for the rapid rearrangement of the product of hydrogenation. 10
14. The process in accordance with claim 1 characterized in that the temperature of reaction is established prior to the establishment of the hydrogen pressure under which the reaction is to be operated. 15

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