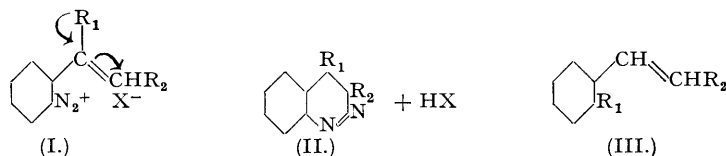


### 138. Cinnolines. Part VII. Further Observations on the Widman-Stoermer Reaction.

By J. C. E. SIMPSON.

Production of 4-aryl-3-alkyl-(or aryl)-cinnolines from appropriate diazotised *o*-aminoarylethylenes is independent of the steric configuration of the latter. Formation of cinnolines from (III;  $R_1 = \text{NH}_2$ ;  $R_2 = \alpha$ -pyridyl or  $\alpha$ -quinolyl) was not observed. These facts support the ionic mechanism suggested (*J.*, 1945, 520) for the cinnoline synthesis.

PARTS II and IV of this series (Simpson, *J.*, 1943, 447; Schofield and Simpson, *J.*, 1945, 520) have dealt with the factual and theoretical aspects of the Widman-Stoermer reaction, which is a general method for the synthesis of 4-aryl-, 4-aryl-3-alkyl-, 4-aryl-3-aryl-, and 3 : 4-diaryl-cinnolines. In Part IV this reaction (I  $\rightarrow$  II) was represented as proceeding *via* a polarised form of a diazotised *o*-aminoarylethylene containing a suitable  $\alpha$ -substituent, *i.e.*, one which reinforces the ethylenic polarisation depicted in (I) ( $R_1 = \text{OH}$  or aryl), and it was pointed out that the rapid formation of 3 : 4-diphenylcinnoline from each of the two possible geometrical forms



of the aminoethylene supported the suggested mechanism to the extent that it indicated that the cyclisation must be more or less ionic in character. It has now been found that the production of other 3-substituted 4-arylcinnolines is likewise independent of the steric configuration of the parent aminoethylenes, the most striking example being that of 4-phenyl-3-methylcinnoline (II;  $R_1 = \text{Ph}$ ;  $R_2 = \text{Me}$ ). Stoermer and Fincke (*Ber.*, 1909, 42, 3115), who first prepared this substance, obtained a crystalline aminoethylene by dehydration of the carbinol prepared from *o*-aminobenzophenone and ethylmagnesium iodide. The present author, on the other hand, obtained an oily ethylene, which was converted into two crystalline stereoisomeric hydrochlorides. One of these, m. p. 205°, was probably identical with the salt, m. p. 208°, prepared by Stoermer and Fincke from their crystalline aminoethylene, and the other, m. p. 185—198°, was evidently a mixture. However, each salt on diazotisation gave an almost quantitative yield of the cinnoline, clearly proving the irrelevance of steric configuration. In agreement with these observations, oily ethylenes, undoubtedly mixtures of stereoisomers, were encountered in the preparation of 4-*p*-anisyl-3-methylcinnoline (II;  $R_1 = p\text{-MeOC}_6\text{H}_4$ ;  $R_2 = \text{Me}$ ), carried out by Mr. C. M. Atkinson in this laboratory, and 3-phenyl-4-*p*-anisylcinnoline (II;  $R_1 = p\text{-MeOC}_6\text{H}_4$ ;  $R_2 = \text{Ph}$ ). On the other hand, the ethylene which gives rise to 4-*p*-anisylcinnoline, and in which geometrical isomerism is impossible, crystallises readily as observed by Stoermer and Gaus (*Ber.*, 1912, 45, 3104) and confirmed in the present work.

Before the suggestion that the Widman-Stoermer reaction involves a polarised molecule of type (I), it was pointed out (Part II) that compounds of type (I) in which  $R_1$  is hydrogen or carboxyl and  $R_2$  is aryl do not yield cinnoline derivatives, and this behaviour is readily understood if reinforcement by  $R_1$  of the  $C_\alpha$ - $C_\beta$  polarisation is essential to the formation of the cinnoline nucleus, as the requisite "T" effect could not be developed when  $R_1 = \text{H}$  or  $\text{CO}_2\text{H}$ . In order more fully to investigate this point, an examination has been made of the behaviour of two diazonium salts of type (I), in which  $R_1 = \text{H}$  and  $R_2 = \alpha$ -pyridyl and  $\alpha$ -quinolyl respectively.

2-(2'-Aminostyryl)pyridine (III;  $R_1 = \text{NH}_2$ ;  $R_2 = \alpha\text{-C}_5\text{H}_4\text{N}$ ) was prepared by R ath and Lehmann (*Ber.*, 1925, 58, 342) on a small scale, and apparently in varying yield, by reduction of the nitro-compound with zinc dust "in strongly acid solution"; it is however readily obtained in consistently good yield by reduction with iron and acetic acid, a method which is very successful in the preparation of numerous *o*-amino-acetophenones and -benzophenones (*J.*, 1945, 646). The base was readily diazotised; the diazonium salt coupled with  $\beta$ -naphthol, but no cinnoline formation could be observed at room temperature. When the solution was heated, nitrogen was readily evolved and 2-(2'-hydroxystyryl)pyridine (III;  $R_1 = \text{OH}$ ;  $R_2 = \alpha\text{-C}_5\text{H}_4\text{N}$ ) was formed as main product. Treatment of the diazonium solution with cuprous chloride gave a crystalline covalent copper compound, which was not obtained pure, but on decomposition yielded 2-(2'-chlorostyryl)pyridine (III;  $R_1 = \text{Cl}$ ;  $R_2 = \alpha\text{-C}_5\text{H}_4\text{N}$ ). The diazotised aminostilbazole thus shows the normal reactions of a diazonium salt, with no appreciable tendency towards any well-defined ring-closure.

In some respects the behaviour of 2-(2'-aminostyryl)quinoline (III;  $R_1 = \text{NH}_2$ ;  $R_2 = \alpha\text{-C}_9\text{H}_6\text{N}$ ) resembled that of the pyridine derivative. Thus diazotisation of the amine was again facile, and 2-(2'-chlorostyryl)quinoline (III;  $R_1 = \text{Cl}$ ;  $R_2 = \alpha\text{-C}_9\text{H}_6\text{N}$ ) was readily formed in the Sandmeyer reaction, again, apparently, *via* a covalent copper compound. The diazonium salt (in hydrochloric acid) was stable at 5°; when the solution was heated, the main product was 2-(2'-hydroxystyryl)quinoline (III;  $R_1 = \text{OH}$ ;  $R_2 = \alpha\text{-C}_9\text{H}_6\text{N}$ ), but a noteworthy feature of this reaction was the simultaneous production of considerable amounts of 2-(2'-chlorostyryl)quinoline. The chloro- and hydroxy-styrylquinolines accounted for the bulk of the material used, and there was no evidence of the formation of any cinnoline derivative or other product.

The extent to which the salts (I;  $R_1 = \text{H}$ ;  $R_2 = \alpha$ -pyridyl or  $\alpha$ -quinolyl) will yield pyridinium or quino-

linium ions under the reaction conditions used is uncertain, but it is improbable that such ions would favour cinnoline formation, because a strongly kationoid centre in  $R_2$  could compete with the diazonium grouping for any available electrons on  $C_\beta$  and thus diminish the extent of cinnoline formation [cf. the production of 2-phenylchrysene as a concomitant of 4-phenyl-3-(1'-naphthyl)cinnoline (*J.*, 1943, 447; 1945, 520)]. It is not considered likely that this effect would entirely inhibit the cinnoline synthesis, the failure of which in the present work is believed to support the mechanism previously advanced (*loc. cit.*), and, in particular, to confirm that the *sine qua non* of the reaction is the attachment to  $C_\alpha$  of an electron-donating substituent.

The application of the reaction to the synthesis of 4-methylcinnolines will be discussed in a subsequent paper.

#### EXPERIMENTAL.

(Melting points are uncorrected.)

**4-Phenyl-3-methylcinnoline.**—Phenyl-*o*-aminophenylethylcarbinol, m. p. 102—103° (15.6 g.), was obtained from *o*-aminobenzophenone (14 g.) by the method of Stoermer and Fincke (*loc. cit.*). In contrast to the experience of these authors, dehydration of the carbinol [with 15 vols. of a mixture of concentrated sulphuric acid and water (1 : 6, v/v) for  $\frac{1}{2}$  hour at 100°] gave a mixture of aminoethylenes which could not be crystallised. Conversion into the hydrochlorides and fractional crystallisation of the mixture from 2*N*-hydrochloric acid gave a number of fractions of which the least soluble had m. p. 204—205° and was probably identical with the product, m. p. 208°, described by Stoermer and Fincke (Found: C, 73.55; H, 6.4; N, 6.2; Cl, 14.25. Calc. for  $C_{15}H_{16}NCl$ : C, 73.3; H, 6.55; N, 5.7; Cl, 14.45%). One of the most soluble fractions had m. p. 185—198° (Found: C, 73.65; H, 6.65; N, 6.1; Cl, 14.35%) and was clearly a stereoisomeric mixture. Small-scale experiments showed that each fraction gave a high yield of cinnoline on diazotisation; consequently the total hydrochloride mixture was dissolved in 2*N*-hydrochloric acid (250 c.c.), cooled in ice, and treated with 10% sodium nitrite (70 c.c.). The crude product obtained by basification of the solution with ammonia contained a little non-basic material; this was removed, either by filtration of a solution of the crude material in hot 2*N*-hydrochloric acid or by dissolving the crude substance in ether and extracting the cinnoline with dilute hydrochloric acid. The purified cinnoline was crystallised from aqueous alcohol; it formed yellow parallelograms (12.8 g.), m. p. 134—136° (lit., 135—136°) (Found: C, 82.1; H, 5.4; N, 12.7. Calc. for  $C_{15}H_{16}N_2$ : C, 81.8; H, 5.5; N, 12.7%).

**3-Phenyl-4-*p*-anisylcinnoline.**—A Grignard solution from magnesium (7.5 g.), benzyl chloride (44 c.c.), and ether (60 c.c.) was treated with a solution of 2-amino-4'-methoxybenzophenone (15 g.) in ether (150 c.c.), added during 10 minutes at room temperature; heat was evolved, and the mixture refluxed gently. After being refluxed for a further 1½ hours, the product was treated with iced ammoniacal ammonium chloride solution. 2-Aminophenylanisylbenzylcarbinol readily crystallised (18.3 g., very sparingly soluble in ether); it separated from aqueous alcohol or benzene-ligroin (b. p. 40—60°) in nodules of small soft needles, m. p. 133—134.5° (Found: N, 4.95.  $C_{21}H_{21}O_2N$  requires N, 4.4%). Treatment of the carbinol (17.8 g.) with a mixture of concentrated sulphuric acid (50 c.c.) and water (300 c.c.) at 100° for 1 hour, followed by basification with ammonia, yielded the ethylene as a viscous reddish-yellow resin, which was dissolved in acetic acid (50 c.c.). After addition of concentrated hydrochloric acid (30 c.c.) and water (30 c.c.), the clear solution was diazotised at 5° with 10% aqueous sodium nitrite (65 c.c.). The ochre-coloured crystalline hydrochloride which separated had m. p. 216—217° (efferv.), and on basification yielded almost pure 3-phenyl-4-*p*-anisylcinnoline (17 g.; m. p. 167—169°), moderately soluble in hot alcohol, from which it separated in yellow jagged needles, m. p. 169—170.5° (Found: C, 81.1; H, 5.3; N, 9.1.  $C_{21}H_{21}ON_2$  requires C, 80.75; H, 5.1; N, 9.0%).

**4-*p*-Anisyl-3-methylcinnoline.**—The carbinol, prepared as above from 2-amino-4'-methoxybenzophenone (25 g.), magnesium (16.1 g.), ethyl iodide (110 g.), and ether (575 c.c.), was dehydrated, and the product diazotised, in the manner described above. The cinnoline (crude, 26 g.) crystallised from aqueous alcohol in yellow leaflets, m. p. 131—133° (Found: C, 77.15; H, 5.45; N, 11.95.  $C_{16}H_{14}ON_2$  requires C, 76.8; H, 5.6; N, 11.2%).

**2-(2'-Nitrostyryl)pyridine.**—Since this work was completed, conditions for the large-scale preparation of this nitrostilbazole have been described by Ruggli and Cuenin (*Helv. Chim. Acta*, 1944, 27, 649); the material used in the present work was prepared by a modification of the procedure of Shaw and Wagstaff (*J.*, 1933, 77), 5 g. of *o*-nitrobenzaldehyde yielding 4.4 g. of almost pure nitrostilbazole. A bath temperature of 165—170° was necessary; at 135—140° the reaction was incomplete and unreacted aldehyde (1.5 g.) was recovered.

**2-(2'-Aminostyryl)pyridine.**—A solution of the nitro-compound (5 g.) in glacial acetic acid (40 c.c.) was kept at 90—95° and treated with iron filings (5 g.), added in portions during 1 hour with frequent shaking; three 10 c.c. portions of water were added at the start of the reaction and at half-hourly intervals thereafter. After a total of 80 minutes, the mixture was diluted with water and the amine extracted with ether, the extract being washed with water, aqueous sodium carbonate, and again with water, dried, and evaporated. A solution of the residue in ether-ligroin (b. p. 40—60°) deposited the pure base (3.1 g.) in bright yellow, long, soft needles, m. p. 85—86°, with high power of crystallisation (Räth and Lehmann, *loc. cit.*, give m. p. 98—99°). The substance showed pronounced basic properties, and the yield could probably have been increased by neutralising the acetic acid before extracting the amine. A dilute solution of the base in ether showed a splendid blue fluorescence. The diacetyl derivative was obtained by refluxing a solution of the base in 5 parts of acetic anhydride for  $\frac{1}{2}$  hour followed by addition of water and evaporation in an exhausted desiccator; it crystallised from ether-ligroin (b. p. 40—60°) in thin colourless rhombs, m. p. 111—112° (Found: C, 72.75; H, 5.55; N, 10.4.  $C_{17}H_{16}O_2N_2$  requires C, 72.8; H, 5.75; N, 10.0%).

**Reactions of Diazotised 2-(2'-Aminostyryl)pyridine.**—No crystalline product could be obtained when a solution of the amine in 2*N*-hydrochloric acid was diazotised and made alkaline with ammonia. A solution of the amine (800 mg.) in glacial acetic acid (5 c.c.) was treated with concentrated hydrochloric acid (5 c.c.), and the resultant suspension of the hydrochloride was cooled in ice and diazotised with excess (10 c.c.) of 2½% aqueous sodium nitrite; portions of the clear yellow solution thus formed were treated as follows. (i) The solution (8 c.c.) was kept at 5—10° for 40 hours. It still gave a strong coupling reaction with alkaline  $\beta$ -naphthol, and was then heated on the steam-bath; when the brisk evolution of nitrogen ceased the solution was made alkaline with aqueous sodium carbonate, which precipitated a pale sticky resin. A solution of this product in aqueous alcohol deposited crude 2-(2'-hydroxystyryl)pyridine; this was dissolved in warm aqueous sodium hydroxide, and the solution, after filtration from a little insoluble material, was acidified with hydrochloric acid and the excess of acid neutralised by sodium bicarbonate solution. The precipitated hydroxystilbazole, which possessed well-marked amphoteric properties, crystallised from aqueous alcohol in colourless hexagonal plates, m. p. 143—144° (Found: C, 79.15; H, 5.7; N, 7.2. Calc. for  $C_{13}H_{11}ON$ : C, 79.1; H, 5.6; N, 7.1%). Chiang and Hartung (*J. Org. Chem.*, 1945, 10, 21) give m. p. 125° and 130—132° for unanalysed samples; Butter (*Ber.*, 1890, 23, 2697) gives m. p. 132°; both sets of workers prepared this substance from  $\alpha$ -picoline and salicylaldehyde.

(ii) A portion of the diazotised solution (6 c.c.) was diluted with water (18 c.c.), kept at 5—10° for 40 hours, treated with sodium acetate until neutral to Congo-red, and then left at room temperature. Gassing occurred for some days, and a high-melting, amorphous solid was precipitated, from which no crystalline product could be obtained by means of organic solvents, hydrochloric acid, or sodium hydroxide.

(iii) The remainder (6 c.c.) of the solution was added during 2—3 minutes to a solution of cuprous chloride (2 g.) in concentrated hydrochloric acid (8 c.c.) and water (6 c.c.); immediate effervescence and separation of solid occurred, and after the addition of more water (4 c.c.) the mixture was kept at 70—80° for 10 minutes and filtered cold. The solid (A) was a copper-containing complex. In a second experiment, crude (A) was recrystallised from hot 2*N*-hydrochloric acid, yielding pale yellow needles (1.5 g. from 1 g. of amine), m. p. 120—123° after being dried in an evacuated desiccator: the substance turned green on exposure to air. When boiled with water, (A) was converted into a new substance (B), m. p. 184—186°, apparently insoluble in water, alcohol, acetone, and acetic acid; (B), like (A), contained copper. A solution of (B) in warm pyridine gave a precipitate of 2-(2'-chlorostyryl)pyridine on addition of water; the filtrate contained chloride ions, but only a trace of chloride ion could be detected in the filtrate from a suspension of (B) in boiling water. Decomposition of (B) to the chlorostyrylpyridine could also be effected with aqueous ammonia, and (incompletely) by means of aqueous dioxan. A solution of (B) in 2*N*-hydrochloric acid did not regenerate (A), but deposited what appeared to be the hydrochloride of the chlorostyrylpyridine in fine, almost colourless needles, m. p. 184—186° after prolonged drying [strongly depressed by admixture with (B)] (Found: C, 54.45; H, 4.75; Cl, 24.7.  $C_{13}H_{11}NCl_2 \cdot 2H_2O$  requires C, 54.15; H, 5.2; Cl, 24.65%). The free chlorostyrylpyridine was most simply prepared by treating a hot solution of (A) (0.8 g.) in very dilute nitric acid with excess of ammonia; the resultant solid was filtered off, washed and crystallised from aqueous ammoniacal alcohol, from which the base (0.45 g.) formed colourless, lustrous, prismatic needles, m. p. 77—78° (Found: C, 72.35; H, 4.7; Cl, 16.45.  $C_{13}H_{10}NCl$  requires C, 72.4; H, 4.7; Cl, 16.5%). A specimen of hydrochloride, prepared from this base by solution in moderately concentrated hydrochloric acid and evaporation in an exhausted desiccator, had almost the same m. p. (182—183°) as that previously described, but a mixture of the two samples melted at 165—170°. This result may possibly be due to hydration of one or the other sample.

2-(2'-Aminostyryl)quinoline.—This was prepared from the nitro-compound, but much unchanged material was recovered when the conditions of Maurer and Stark (*Ber.*, 1937, **70**, 2054) were followed. This was due to the insolubility of the nitro-compound in the acid mixture recommended by these authors, and reduction proceeded smoothly when the nitro-compound was dissolved in a hot mixture of acetic acid, 2*N*-hydrochloric acid, and concentrated hydrochloric acid (2 : 2 : 1 by volume). This solution was then treated according to the procedure of Maurer and Stark; 8.2 g. of nitro-compound yielded 6 g. of amine, m. p. 157—158°.

Reactions of Diazotised 2-(2'-Aminostyryl)quinoline.—(a) The deep red solution formed by warming the amine (1.5 g.) with glacial acetic acid (7.5 c.c.) was cooled and treated with concentrated hydrochloric acid (5 c.c.), and the resultant suspension was diazotised with aqueous sodium nitrite (4.8 c.c. of 10%). Part (5.5 c.c.) of the clear yellow solution thus formed was added to a solution of cuprous chloride [prepared from 4.4 g. of copper sulphate crystals (*Org. Synth.*, Coll. Vol. I., p. 170)] in concentrated hydrochloric acid (10 c.c.); rapid reaction occurred with separation of a solid, and the temperature rose to 30—35°. After  $\frac{1}{2}$  hour at 75—80°, the mixture was left at room temperature for 48 hours, and finally boiled for 5 minutes and filtered. The solid was apparently a covalent copper compound (cf. the pyridine derivative already described), as it was impossible to free it from copper by washing with hydrochloric acid and water. Decomposition with aqueous ammonia and crystallisation from ammoniacal alcohol yielded solvated crystals of 2-(2'-chlorostyryl)quinoline, which after being dried and crystallised from ethyl acetate-ligroin (b. p. 40—60°) formed almost colourless hard nodules of prismatic needles, m. p. 78—79° (Found: C, 77.0; H, 4.65; Cl, 13.1.  $C_{17}H_{12}NCl$  requires C, 76.8; H, 4.6; Cl, 13.4%).

(b) When the diazotised solution was heated, mixtures of the foregoing chloro-compound and the corresponding phenol were produced. Dilution of the solution with varying amounts of water, followed either by immediate heating or by heating after keeping the solution for a week at 5°, had no effect, qualitatively, on the result: the effect of these variations on the proportion of chloro-compound to phenol was not studied, but the phenol predominated. A typical experiment was the following. The diazotised solution (from 1.5 g. of amine) was heated for  $\frac{3}{4}$  hour at 80—85° without dilution with water. The solution was then evaporated to dryness in an exhausted desiccator, after which the residue was partitioned between 5% aqueous sodium hydroxide and ether; the latter yielded 1.07 g. of resinous material (A). Acidification of the alkaline extract with dilute hydrochloric acid gave 0.3 g. of crude phenol, which was freed from hydrochloride by solution in aqueous sodium hydroxide, addition of acetic acid, and precipitation with aqueous ammonia. Crystallisation from ammoniacal alcohol and finally from alcohol or ethyl acetate yielded 2-(2'-hydroxystyryl)quinoline in soft yellow needles (alcohol) or small, brittle prisms (ethyl acetate), m. p. 212—213° (Found: C, 82.3, 82.65; H, 5.6, 5.4; N, 5.85, 6.1. Calc. for  $C_{17}H_{13}ON$ : C, 82.5; H, 5.3; N, 5.7%); Wallach and Wüsten (*Ber.*, 1883, **16**, 2009), and Dzierzowski (*ibid.*, 1894, **27**, 1980), who prepared this substance from quinaldine and salicylaldehyde, give m. p. 209—210° and 209° respectively. The substance is insoluble in ammonia and moderately soluble in aqueous sodium hydroxide; it showed marked basic properties, yielding a soluble acetate and a sparingly soluble deep yellow hydrochloride (with cold dilute hydrochloric acid). The acetoxy-compound (acetic anhydride; reflux) was isolated from weakly ammoniacal solution. After crystallisation from aqueous alcohol, and finally from ligroin (b. p. 60—80°), it formed faintly yellow clusters of stout prismatic needles, m. p. 89—90° (Found: C, 78.7; H, 5.15.  $C_{19}H_{15}O_2N$  requires C, 78.8; H, 5.2; N, 4.8%). The same substance was produced when the phenol hydrochloride was refluxed with acetic anhydride for 1—1½ hours, but the yield was smaller, and the product (m. p. 92—94°) could not be obtained pure (Found: C, 79.45; H, 5.55; N, 5.45%).

Owing to the somewhat sparing solubility of the foregoing phenol in aqueous sodium hydroxide, the "neutral" fraction (A) contained much of this substance. Crystallisation of 1.27 g. of this mixture from a little ethyl acetate gave 0.4 g. of nearly pure phenol. The mother liquor was evaporated to dryness, and the residue treated with a hot alcoholic solution of picric acid (1 g.); 1.25 g. of the crude picrate, m. p. 212—218°, of 2-(2'-chlorostyryl)quinoline separated, m. p. 236—237° after crystallisation from methyl ethyl ketone, in which it is sparingly soluble, separating in small, soft, bright yellow, lustrous needles (Found: C, 55.85; H, 3.55; N, 11.35.  $C_{17}H_{12}NCl \cdot C_6H_3O_7N_3$  requires C, 55.8; H, 3.05; N, 11.3%). Decomposition of this picrate with either ammonia or sodium hydroxide, followed by ether-extraction, etc., gave the crude chloro-base as a resin. A portion of this material was treated with dilute hydrochloric acid; the precipitated hydrochloride, very sparingly soluble in dilute hydrochloric acid, crystallised from acetic acid-ether in long, ochre-coloured needles, m. p. 248—251° (Found: N, 4.85; Cl, 22.8.  $C_{17}H_{13}NCl_2$  requires N, 4.6; Cl, 23.5%). The remainder of the resin was treated with hot ligroin (b. p. 60—80°); the solution was decanted from a little insoluble matter, clarified with charcoal, and concentrated, yielding 2-(2'-chlorostyryl)quinoline, m. p. 77—78° alone and mixed with the sample described in (a), and giving a positive Beilstein reaction (Found: C, 76.85; H, 4.7; N, 5.4.  $C_{17}H_{12}NCl$  requires C, 76.8; H, 4.6; N, 5.3%).

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