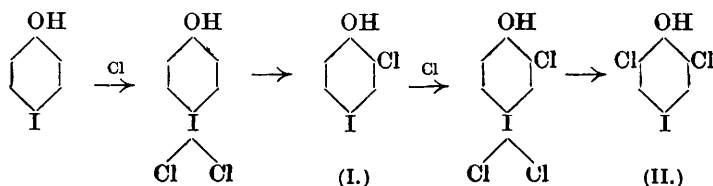
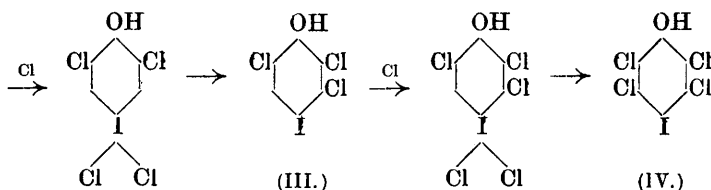


C.—*The Chlorination of Iodophenols. Part I.*  
*The Chlorination of p-Iodophenol.*

By SIDNEY ALBERT BRAZIER, M.Sc. (Priestley Research Scholar of the University of Birmingham), and HAMILTON McCOMBIE.

WHEN an ice-cold solution of *p*-iodophenol in carbon tetrachloride is saturated with chlorine, a yellow, crystalline iodo-dichloride is precipitated. This substance is very unstable, and, in the course of a few minutes, undergoes decomposition, liberating hydrogen chloride and forming 2-chloro-4-iodophenol (I). This substance, in turn, when subjected to the action of chlorine, also yields an unstable iodo-dichloride, which decomposes to form 2:6-dichloro-4-iodophenol (II). On repeating the process with the latter compound, an unstable iodo-dichloride is again obtained, from which, by decomposition, 2:3:6-trichloro-4-iodophenol (III) results. This compound, on further chlorination and decomposition of the iodo-dichloride first formed, gives 2:3:5:6-tetrachloro-4-iodophenol (IV). The chain of reactions can be represented as follows:





Various decompositions of iodo-dichlorides with evolution of chlorine and hydrogen chloride have been described, but in the majority of cases these decompositions have been effected only by the action of heat.

Willgerodt (*J. pr. Chem.*, 1886, [ii], **33**, 154) describes the decomposition of iodobenzene dichloride, stating that it evolves all its chlorine at 115—120°. Later (*Ber.*, 1893, **25**, 3494), the same observer remarks that this iodo-dichloride, when exposed to moist air, decomposes with evolution of hydrogen chloride. Keppler (*Ber.*, 1898, **31**, 1136) has shown that iodobenzene dichloride when kept in sealed tubes, even in the dark, decomposes with the formation of *p*-chloriodobenzene. Somewhat similar results have been obtained by Werner in his work on the effect of heat on various iodo-dichlorides (*Trans.*, 1907, **91**, 529).

Willgerodt (*Ber.*, 1894, **27**, 590) and also Willgerodt and Schlösser (*Ber.*, 1900, **33**, 692) state that the iodonaphthalene dichlorides decompose on keeping, giving chlorine substituted products. Again, Willgerodt and Smith (*Ber.*, 1904, **37**, 1312) state that *p*-iodoazobenzene dichloride evolves chlorine rapidly when exposed to the air. Willgerodt and Roggatz (*J. pr. Chem.*, 1900, [ii], **61**, 424) state that iodomesitylene dichloride decomposes, even in solution, forming chloriodomesitylene, with evolution of chlorine and hydrogen chloride.

*o*-Iodoanisole and *o*-iodophenetole also yield unstable iodo-dichlorides. Jannasch and Hinterkirch (*Ber.*, 1898, **31**, 1710) showed that *o*-iodoanisole dichloride, on keeping, or on adding to potassium iodide, yields 5-chloro-2-iodoanisole; *o*-iodophenetole behaves in the same way.

*p*-Iodoanisole and *p*-iodophenetole, the preparations of which are described by Liebrecht (*D.R.-P.* 161725, *Abstr.*, 1906, i, 257), when chlorinated, are said by Mascarelli and Martinelli (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 183) to yield ring-substituted products quite easily.

Willgerodt and Simonis (*Ber.*, 1906, **39**, 276) describe the chlorination of *p*-iodoaceto-*m*-toluidide, which yields an iodo-dichloride, from which 6-chloro-4-iodoaceto-*m*-toluidide results on decomposition.

The only statement which the authors have been able to discover

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about the chlorination of iodophenols is one by Willgerodt (*Ber.*, 1892, **25**, 3495) to the effect that when *o*-iodophenol or 2:4:6-tri-iodophenol is treated with chlorine in chloroform solutions, compounds result in which the iodine has been displaced by chlorine.

The constitutions of the compounds formed when the iodo-dichlorides undergo decomposition were established by subjecting the first two decomposition products to the action of nitric acid. In both cases the same product resulted, and this was shown to be 6-chloro-2:4-dinitrophenol. This compound has been prepared by various observers, and its constitution is undoubted. It is produced by the action of nitric acid on *o*-chlorophenol (Griess, *Annalen*, 1859, **109**, 286; Faust and Müller, *ibid.*, 1874, **173**, 312), from *o*-nitrophenol by chlorination and subsequent nitration (Faust and Saame, *Annalen, Suppl.*, 1869-70, **7**, 195), and similarly from *p*-nitrophenol (Seifart, *ibid.*, 197).

Whilst the simple phenols yield unstable iodo-dichlorides which readily decompose, giving ring-substitution products, stable iodo-dichlorides are easily obtained from the acetyl and benzoyl derivatives of the phenols. An exception to this generalisation is *p*-iodophenyl acetate, the iodo-dichloride of which is found to decompose after having been kept for ten days. In this connexion the observation of Mascarelli and Martinelli (*loc. cit.*) as to the instability of the iodo-dichlorides derived from *p*-iodo-anisole and -phenetole, is of great interest.

When attempts were made to convert 2:3:5:6-tetrachloro-4-iodophenol into an iodo-dichloride, even if the solution was saturated with chlorine for several hours, only the unchanged compound could be obtained. This inhibitive action of the two ortho-substituents on the production of iodo-dichlorides has been commented on by Willgerodt. This experimenter noticed (*Ber.*, 1910, **43**, 2755) that tetrachloriodobenzene could not be caused to yield an iodo-dichloride when the two positions adjacent to the iodine atom are occupied by chlorine atoms. Willgerodt and Meyer (*Annalen*, 1911, **385**, 351) noticed similar behaviour in the case of 4:6-dichloro-5-iodo- $\psi$ -cumene.

Another curious example of the influence of substituents on the course of a reaction was encountered in the preparation of the benzoyl derivatives of these phenols. Benzoylation in presence of sodium hydroxide yielded quite satisfactory results when one at least of the ortho-positions relative to the hydroxyl groups was occupied by hydrogen. This is shown in the case of the benzoylation of *p*-iodophenol and 2-chloro-4-iodophenol. When, however, both ortho-positions relative to the hydroxyl group are occupied

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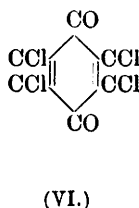
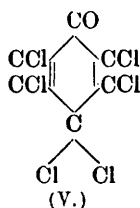
by chlorine atoms, benzoyl chloride in presence of sodium hydroxide yielded practically no benzoyl derivative. If, however, the sodium hydroxide is replaced by pyridine, the reaction proceeds quite smoothly.

A study of the melting points of the different series of compounds described in this paper gives some interesting results.

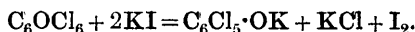
Phenol.	Benzoyl derivative.	Iodo-dichloride.	Acetyl derivative.	Iodo-dichloride.	
91°	125°	132—133°	38°	116°	<i>p</i> -iodophenol
54	72	126—127	49	123	2-chloro-4-iodophenol
91—92	62—63	125	72	126	2:6-dichloro-4-iodophenol
51—52	oil	133—134	82	146	trichloroiodophenol
72	110—111	—	105	—	tetrachloroiodophenol

From the accompanying table it is seen that, in the case of the phenols, the unsymmetrical compounds have lower melting points than the symmetrical ones. This is seen in the case of 2-chloro- and 2:3:6-trichloro-4-iodophenol. The benzoyl derivatives, however, do not follow this rule. In the case of the acetyl derivatives and their iodo-dichlorides, the melting points rise steadily with the introduction of each chlorine atom.

If, instead of employing an ice-cold solution of *p*-iodophenol for these chlorination experiments, chlorine is led into a solution warmed to 50—60°, the solution is found to darken with liberation of iodine, and hydrogen chloride is evolved. If the chlorination is continued until no more hydrogen chloride is given off, four different products can be isolated from the reaction mixture, namely, (1) 2:3:5:6-tetrachloro-4-iodophenol (IV); (2) pentachlorophenol; (3) hexachlorocyclohexadienone (V); and (4) chloro-anil (VI):



The constitutions of all these substances were easily established. Hexachlorocyclohexadienone, on treatment with potassium iodide, yielded pentachlorophenol with liberation of iodine; this reaction was easily followed quantitatively, and was found to be in agreement with the equation:



## EXPERIMENTAL.

The *p*-iodophenol used in these experiments was prepared from *p*-aminophenol by the diazo-reaction in 30 per cent. sulphuric acid (compare Noelting and Stricker, *Ber.*, 1887, **20**, 3018). The crude substance, which melted at 90—91°, was used for the chlorinations without further purification.

*p*-Iodophenyl Acetate,  $C_6H_4I \cdot OAc$ .

Willgerodt (*Ber.*, 1909, **42**, 3767) states that he was unable to obtain this compound in crystalline form. Wohlleben (*Ber.*, 1909, **42**, 4374) also describes it, and gives its melting point at 32—32·5°. We obtained it easily by the following method. Ten grams of *p*-iodophenol, mixed with 3 grams of acetic anhydride, were heated on a water-bath for a few minutes, a few drops of concentrated sulphuric acid were added, and the reaction mixture was poured into water. It crystallised from methyl alcohol in small, white leaflets melting at 38°. (Found,  $I=48\cdot61$ . Calc.,  $I=48\cdot48$  per cent.)

The *Iodo-dichloride*.—Willgerodt (*loc. cit.*) states that on chlorinating a solution of *p*-iodophenyl acetate, yellow crystals separated, but decomposed rapidly in the solution.

We found that on chlorinating *p*-iodophenyl acetate in carbon tetrachloride solution, small, yellow needles separated, which melted and decomposed at 116°. After remaining for several days without apparent change, the crystals decomposed rapidly with evolution of hydrogen chloride:

0·1518 gave 0·2384  $AgCl + AgI$ .

$C_8H_7O_2Cl_2I$  requires  $AgCl + AgI = 0\cdot2380$ .

*Action of Chlorine on p*-Iodophenol. *Preparation of 2-Chloro-4-iodophenol*,  $C_6H_3ClI \cdot OH$ .

Ten grams of powdered *p*-iodophenol were dissolved in 250 c.c. of carbon tetrachloride. The solution, cooled in ice, was saturated with chlorine, and fine crystals soon separated. The chlorination was continued for fifteen to twenty minutes, after which the crystals were collected. If the crystals were allowed to remain in the liquid too long, decomposition of the iodo-dichloride began. The filtered solution was again chlorinated, when a further crop of crystals was obtained. The crystals were transferred quickly to a small beaker, which was then cooled in ice. After a short time decomposition began with a violent evolution of hydrogen chloride. When decomposition was complete, the resulting product,

which was very dark in colour, was exposed to a strong draught for some time, and a much paler product was obtained. A theoretical yield of the iodo-dichloride was obtained, which gave from 10 to 12 grams of the crude decomposition product. This was recrystallised from carbon tetrachloride, when it was deposited in needles melting at  $54^{\circ}$ . The substance was very soluble in methyl and ethyl alcohols, benzene, or light petroleum:

0.1329 gave 0.1962  $\text{AgCl} + \text{AgI}$ .

$\text{C}_6\text{H}_4\text{OClI}$  requires  $\text{AgCl} + \text{AgI} = 0.1976$ .

On treatment with concentrated nitric acid, this compound yields 6-chloro-2:4-dinitrophenol, which melts at  $110\text{--}111^{\circ}$ . This establishes the constitution.

*2-Chloro-4-iodophenyl Acetate*,  $\text{C}_6\text{H}_3\text{ClI}\cdot\text{OAc}$ .

When recrystallised twice from methyl alcohol, this substance melted at  $49^{\circ}$ . It is very soluble in alcohol or benzene, but crystallises from methyl alcohol in long, triangular prisms:

0.1931 gave 0.2451  $\text{AgCl} + \text{AgI}$ .

$\text{C}_8\text{H}_6\text{O}_2\text{ClI}$  requires  $\text{AgCl} + \text{AgI} = 0.2466$ .

The *iodo-dichloride* is a fine, yellow powder melting and decomposing at  $123^{\circ}$ . After being kept for about ten days, it decomposed with evolution of hydrogen chloride:

0.1395 gave 0.2484  $\text{AgCl} + \text{AgI}$ .

$\text{C}_8\text{H}_6\text{O}_2\text{Cl}_3\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2526$ .

*2-Chloro-4-iodophenyl Benzoate*,  $\text{C}_6\text{H}_3\text{ClI}\cdot\text{OBz}$ .

This was prepared by the Schotten-Baumann reaction, a theoretical yield being obtained. The substance, crystallised twice from methyl alcohol, gave crystals melting at  $72^{\circ}$ :

0.1691 gave 0.1772  $\text{AgCl} + \text{AgI}$ .

$\text{C}_{13}\text{H}_8\text{O}_2\text{ClI}$  requires  $\text{AgCl} + \text{AgI} = 0.1784$ .

The *iodo-dichloride* melted and decomposed at  $126\text{--}127^{\circ}$ . This substance, in contradistinction to the iodo-dichloride of the acetyl derivative, was quite stable:

0.1117 gave 0.1718  $\text{AgCl} + \text{AgI}$ .

$\text{C}_{13}\text{H}_8\text{O}_2\text{Cl}_3\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.1730$ .

*2:6-Dichloro-4-iodophenol*,  $\text{C}_6\text{H}_2\text{Cl}_2\text{I}\cdot\text{OH}$ .

Ten grams of the crude 2-chloro-4-iodophenol were dissolved in 150 c.c. of carbon tetrachloride and chlorinated. The dichloride separated quickly in fine, yellow crystals, and, after chlorinating for fifteen to twenty minutes, the crystals were collected. Further

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crops of the dichloride were obtained by successive chlorinations of the filtrate. The dichloride, after filtration, rapidly decomposed, giving a dark-coloured decomposition product, which was recrystallised from a mixture of equal quantities of methylated spirit and water. After two recrystallisations, needles melting at  $91-92^{\circ}$  were obtained.

2:6-Dichloro-4-iodophenol is readily soluble in methyl alcohol, methylated spirit, or light petroleum:

0.1144 gave 0.2053  $\text{AgCl} + \text{AgI}$ .

$\text{C}_6\text{H}_3\text{OCl}_2\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2064$ .

On treatment with concentrated nitric acid this compound yields 6-chloro-2:4-dinitrophenol, which melts at  $110-111^{\circ}$ . This establishes the constitution.

2:6-Dichloro-4-iodophenyl Acetate,  $\text{C}_6\text{H}_2\text{Cl}_2\text{I} \cdot \text{OAc}$ .

This was recrystallised three times from methyl alcohol, and gave long needles melting at  $72^{\circ}$ . It is very soluble in ethyl alcohol, benzene, or light petroleum:

0.1413 gave 0.2215  $\text{AgCl} + \text{AgI}$ .

$\text{C}_8\text{H}_5\text{O}_2\text{Cl}_2\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2238$ .

The *iodo-dichloride* forms light, yellow crystals, melting and decomposing at  $126^{\circ}$ :

0.1201 gave 0.2394  $\text{AgCl} + \text{AgI}$ .

$\text{C}_8\text{H}_5\text{O}_2\text{Cl}_2\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2417$ .

2:6-Dichloro-4-iodophenyl Benzoate,  $\text{C}_6\text{H}_2\text{Cl}_2\text{I} \cdot \text{OBz}$ .

This was prepared by the method described by Einhorn and Hollandt (*Annalen*, 1898, **301**, 95).

2.8 Grams of benzoyl chloride were added gradually to a well-cooled solution of 4 grams of pure dichloriodophenol dissolved in 40 grams of pyridine. The mixture was allowed to remain overnight, and was then poured into dilute sulphuric acid. After two days the mass became solid, and was collected and crystallised from methyl alcohol. The substance is fairly soluble in methyl alcohol, ethyl alcohol, or benzene, and forms crystals melting at  $62-63^{\circ}$ :

0.1869 gave 0.2471  $\text{AgCl} + \text{AgI}$ .

$\text{C}_{13}\text{H}_7\text{O}_2\text{Cl}_2\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2482$ .

The *iodo-dichloride* was obtained in stable, yellow leaflets melting and decomposing at  $125^{\circ}$ :

0.1224 gave 0.2123  $\text{AgCl} + \text{AgI}$ .

$\text{C}_{13}\text{H}_7\text{O}_2\text{Cl}_2\text{I}$  requires  $\text{AgCl} + \text{AgI} = 0.2134$ .

*2:3:6-Trichloro-4-iodophenol*,  $C_6HCl_3I \cdot OH$ .

Five grams of pure dichloriodophenol dissolved in 50 c.c. of carbon tetrachloride were saturated with chloride. The dichloride separated as a fine, almost amorphous powder, which rapidly decomposed after collection. The resulting product was recrystallised several times from a mixture of alcohol and water, or from light petroleum, and separated in small, white needles melting at 51—52°:

0.1158 gave 0.2357  $AgCl + AgI$ .

$C_6H_2OCl_3I$  requires  $AgCl + AgI = 0.2379$ .

*2:3:6-Trichloro-4-iodophenyl Acetate*,  $C_6HCl_3I \cdot OAc$ .

This substance, when recrystallised three times from methyl alcohol, forms white needles melting at 82°:

0.1039 gave 0.1905  $AgCl + AgI$ .

$C_8H_4O_2Cl_3I$  requires  $AgCl + AgI = 0.1891$ .

The *iodo-dichloride* melts and decomposes at 146°:

0.1084 gave 0.2349  $AgCl + AgI$ .

$C_8H_4O_2Cl_5I$  requires  $AgCl + AgI = 0.2365$ .

*2:3:6-Trichloro-4-iodophenyl Benzoate*,  $C_6HCl_3I \cdot OBz$ .

This substance could not be obtained in a crystalline form.

The *iodo-dichloride* melts and decomposes at 133—134°:

0.1105 gave 0.2127  $AgCl + AgI$ .

$C_{13}H_6O_2Cl_5I$  requires  $AgCl + AgI = 0.2111$ .

*2:3:5:6-Tetrachloro-4-iodophenol*,  $C_6Cl_4I \cdot OH$ .

This compound was obtained by the decomposition of the *iodo-dichloride* derived from trichloriodophenol. It was, however, more easily obtained by the steam distillation of the crude product obtained on chlorinating *p*-iodophenol in warm solution. After several recrystallisations from a mixture of alcohol and water, or from light petroleum, it yielded white needles melting at 72°:

0.1064 gave 0.2418  $AgCl + AgI$ .

$C_6HOCl_4I$  requires  $AgCl + AgI = 0.2405$ .

All attempts to convert 2:3:5:6-tetrachloro-4-iodophenol into an *iodo-dichloride* resulted in the recovery of the unchanged substance.



*2:3:5:6-Tetrachloro-4-iodophenyl Acetate*,  $C_6Cl_4I \cdot OAc$ .

This was obtained, when recrystallised from methyl alcohol, in clusters of fine needles melting at  $105^\circ$ . The iodo-dichloride could not be obtained:

0.1158 gave 0.2330  $AgCl + AgI$ .

$C_8H_3O_2Cl_4I$  requires  $AgCl + AgI = 0.2342$ .

*2:3:5:6-Tetrachloro-4-iodophenyl Benzoate*,  $C_6Cl_4I \cdot OBz$ .

On recrystallisation from methyl alcohol, this compound separated in small plates melting at  $110-111^\circ$ . The iodo-dichloride could not be obtained:

0.1319 gave 0.2335  $AgCl + AgI$ .

$C_{13}H_5O_2Cl_4I$  requires  $AgCl + AgI = 0.2310$ .

*Action of Chlorine on a Warm Solution of p-Iodophenol.*

On chlorinating *p*-iodophenol in warm carbon tetrachloride solution, four different products resulted, namely, (1) 2:3:5:6-tetrachloro-4-iodophenol, (2) pentachlorophenol, (3) hexachloro-cyclohexadienone, and (4) chloroanil.

The solution of 20 grams of *p*-iodophenol in 200 c.c. of carbon tetrachloride was warmed to about  $50^\circ$ , and a stream of chlorine was passed into the solution. The iodo-dichloride, at first formed, rapidly decomposed with evolution of hydrogen chloride. The chlorination was continued until all evolution of hydrogen chloride had ceased; a dark-coloured solution was obtained. When the carbon tetrachloride had been distilled off, a dark product remained, which contained free iodine.

By steam distillation of this crude product the more volatile tetrachloro-*p*-iodophenol was easily obtained.

By fractional crystallisation of the crude product from light petroleum, white needles melting at  $186-187^\circ$  were obtained. Analysis showed this to be pentachlorophenol. (Found,  $Cl = 66.47$ . Calc.,  $Cl = 66.60$  per cent.)

Pentachlorophenol is described by Erdmann (*Annalen*, 1841, **37**, 343), Erdmann and Laurent (*Annalen*, 1843, **48**, 309), Schützenberger (*Bull. Soc. chim.*, 1865, [ii], **4**, 103), and by Weber and Wolf (*Ber.*, 1885, **18**, 335). The pentachlorophenol yielded an acetate melting at  $147-148^\circ$ , which is the melting point given by Weber and Wolf (*loc. cit.*).

*Pentachlorophenyl Benzoate, C<sub>6</sub>Cl<sub>5</sub>·OBz.*

This compound was obtained in small, white needles melting at 159° after recrystallisation from absolute alcohol. It was almost insoluble in most solvents in the cold, and only sparingly soluble in hot alcohol:

0·1274 gave 0·2459 AgCl. Cl=47·76.

C<sub>13</sub>H<sub>5</sub>O<sub>2</sub>Cl<sub>5</sub> requires Cl=47·91 per cent.

Hexachlorocyclohexadienone resulted when *p*-iodophenol was chlorinated in warm solution, the solvent being carbon tetrachloride that had been employed for other chlorinations, and in the purification of which no special precautions had been taken. The solution was maintained at 50—60° during the chlorination. The solvent was distilled off, and the resulting product was recrystallised from methyl alcohol, when light, yellow tablets melting at 107° were obtained. The substance did not contain iodine, but on being added to potassium iodide solution immediately liberated iodine.

Analysis showed the compound to be hexachlorocyclohexadienone, which has been described by Langer (*Annalen*, 1882, **215**, 122), Hugounenq (*Ann. Chim. Phys.*, 1890, [vi], **20**, 559), Morel (*ibid.*, 561), and Zincke and Schaum (*Ber.*, 1894, **27**, 546). (Found, Cl=70·71. Calc., Cl=70·76 per cent.)

By the action of potassium iodide on hexachlorocyclohexadienone, pentachlorophenol was obtained, and iodine was liberated. This reaction was followed quantitatively, and it was found that 0·1561 gram gave 0·1314 gram of iodine. The equation C<sub>6</sub>Cl<sub>6</sub>O + 2KI = C<sub>6</sub>Cl<sub>5</sub>OK + KCl + I<sub>2</sub> requires 0·1317 gram of iodine.

Hexachlorocyclohexadienone, by the action of sodium in methyl alcohol, gave the 1:3:3:4-tetramethyl ether of 1:3:3:4-trichloropentahydroxycyclohexadiene, melting at 142—143°, as described by Zincke and Schaum (*loc. cit.*).

Traces of chloroanil (melting at 282°) were also obtained in some cases. It was isolated on extracting with alcohol, in which it is only sparingly soluble.

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