On the Mechanism of Oxidation by Cuprous Chloride, Pyridine and Air. III. On the Mechanism of Oxidative Cleavage of Benzil, α-Methyl Benzoin and Hydrobenzoin[*]

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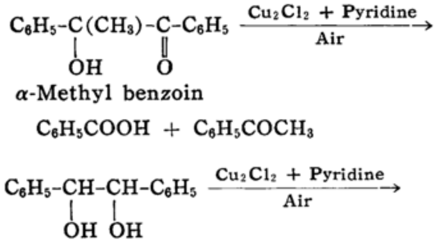
An earlier work reported that by aerial oxidation catalyzed by cuprous chloride in a pyridine solution, benzoin, benzil, α-methyl benzoin and hydrobenzoin were oxidized to break down as follows[1].



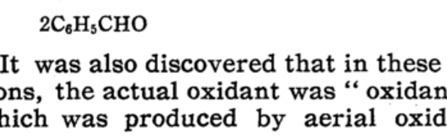
$$\underset{\text{OH}}{\underset{|}{C_6H_5\text{-}CH}}\text{-}\underset{\text{O}}{\underset{\|}{C}}\text{-}C_6H_5 \xrightarrow[\text{Air}]{Cu_2Cl_2\ +\ \text{Pyridine}}$$

Benzoin

$$C_6H_5\text{-}CO\text{-}CO\text{-}C_6H_5$$

Benzil

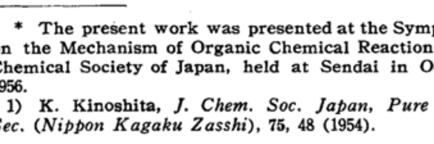
$$\xrightarrow[\text{Air}]{Cu_2Cl_2\ +\ \text{Pyridine}} 2C_6H_5COOH \qquad (1)$$



$$C_6H_5\text{-}\underset{\text{OH}}{\underset{|}{C(CH_3)}}\text{-}\underset{\text{O}}{\underset{\|}{C}}\text{-}C_6H_5 \xrightarrow[\text{Air}]{Cu_2Cl_2\ +\ \text{Pyridine}}$$

α-Methyl benzoin

$$C_6H_5COOH + C_6H_5COCH_3 \qquad (2)$$



$$C_6H_5\text{-}\underset{\text{OH}}{\underset{|}{CH}}\text{-}\underset{\text{OH}}{\underset{|}{CH}}\text{-}C_6H_5 \xrightarrow[\text{Air}]{Cu_2Cl_2\ +\ \text{Pyridine}}$$

Hydrobenzoin

$$2C_6H_5CHO \qquad (3)$$

It was also discovered that in these reactions, the actual oxidant was "oxidant A" which was produced by aerial oxidation of cuprous chloride pyridine complex[2]. In this paper, the mechanism of oxidative cleavage of the above compounds is discussed.

Experimental

Materials.—Benzil was prepared by oxidation of benzoin with nitric acid, and recrystallized from alcohol, m.p. 94~95°C[4]. α-Methyl benzoin was prepared by reaction of benzil with methyl magnesium iodide, and recrystallized from ligroin (b.p. 80~100°C), m.p. 90~91°C[5]. Hydrobenzoin was prepared by reduction of benzoin with aluminum *iso*-propylate, and recrystallized from aqueous alcohol, m.p. 135~136°C[6].

(1) Preparation of Catalysts.—(a) "Oxidant A": Cuprous chloride (4.0 g., 2/100 mol.) in pyridine (50 cc.) was oxidized with air for 2 hr. at room temperature.

(b) "Oxidant B": Potassium hydroxide (2.2 g., 4/100 mol.) in methyl alcohol (50 cc.) was added with stirring to cupric chloride pyridine complex (prepared from $CuCl_2 \cdot 2H_2O$ (6.8 g., 4/100 mol.) and pyridine (50 cc.)).

(c) "Oxidant C": Cuprous acetate pyridine complex[3] (prepared from $Cu(OAc)_2 \cdot H_2O$ (3.8 g., 2/100 mol.) and pyridine (50 cc.)), was oxidized with air for 2 hr. at room temperature.

(d) "Oxidant D": Potassium hydroxide

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[*] The present work was presented at the Symposium on the Mechanism of Organic Chemical Reaction of the Chemical Society of Japan, held at Sendai in October, 1956.

[1] K. Kinoshita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 48 (1954).

[2] K. Kinoshita. ibid., **75**, 175 (1954).

[3] K. Kinoshita, Part II of this series in This Bulletin, **32**, 780 (1952).

[4] R. Adams, "Organic Synthesis", Vol. I, John Wiley & Sons, Inc., New York (1921), p. 25.

[5] R. Nodzu et al., *J. Chem. Soc. Japan* (*Nippon Kagaku Kaishi*), **59**, 1237 (1938).

[6] H. Lunde, *Ber.*, **70**, 1520 (1937).

(2.2 g., 4/100 mol.) in methyl alcohol (50 cc.) was added with stirring to cupric acetate pyridine complex (prepared from $Cu(OAc)_2 \cdot H_2O$, (7.6 g., 4/100 mol.) and pyridine (50 cc.)).

(2) **Oxidation of Benzil.**—(a) When methyl alcohol (50 cc.) was added to "oxidant A", the color of the solution turned to green. A mixture of benzil (2.0 g., 1/100 mol.) and the greenish solution was stirred at 30°C for 2 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water and extracted with aqueous sodium carbonate solution. After removal of the ether, a trace of the substance remained. The sodium carbonate solution was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). After removal of the ether, the residue was sublimed to give benzoic acid (2.1 g., 86%); it melted at 121~122°C alone or with an authentic sample of benzoic acid.

The same results were obtained with "oxidant C" or "oxidant D" in place of "oxidant A".

(b) When trimethylamine hydrochloride (7.8 g., 6/100 mol.) was added to "oxidant C or D", trimethylamine was separated, and dark blue needles appeared. The mixture of benzil (2.0 g., 1/100 mol.) and the resulting complex was treated as above. No benzoic acid was obtained. Benzil 1.8 g., 90%) was recovered; it melted at 94~95°C alone or with an authentic sample of benzil.

(3) **Oxidation of Hydrobenzoin.**—(a) A mixture of hydrobenzoin (2.0 g., 1/100 mol.), methyl alcohol (10 cc.) and "oxidant A" (prepared from Cu_2Cl_2 (2.0 g., 1/100 mol.)) was stirred at 30°C for 4 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water, and extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was treated with aqueous sodium hydrogen sulfite solution. The mixture was filtered. The precipitate was washed with water and dried. Hydrobenzoin (1.3 g., 65%) was recovered; m.p. 135~136°C, its melting point was not depressed on admixing with an authentic sample. From the sodium hydrogen sulfite solution, benzaldehyde phenyl hydrazone (0.8 g., 20%) was obtained; m.p. 155~156°C (Lit. 156°C). It was identified with benzaldehyde phenyl hydrazone by a mixed melting point determination and an analysis.

Anal. Found: C, 79.36; H, 6.38; N, 14.32. Calcd. for $C_{13}H_{12}N_2$: C, 79.59; H, 6.12; N, 14.28%.

From the sodium carbonate solution, a trace of benzoic acid was obtained. It was identified by converting it into salicylic acid[7].

(b) A mixture of hydrobenzoin (2.0 g., 1/100 mol.) and "oxidant C or D" was stirred for 4 hr. in a stream of air. Although the oxidation was attempted at 30, 60 and 80°C, no oxidation products were obtained, and hydrobenzoin (1.8 g., 90%) was recovered; it melted at 135~136°C alone or with an authentic sample of hydrobenzoin.

(4) **Reaction of Cupric Chloride with Hydrobenzoin in the Presence of Potassium Hydroxide.** — When cupric chloride (1.7 g., 1/100 mol.) in methyl alcohol (20 cc.) was added to a mixture of hydrobenzoin (4.0 g., 2/100 mol.), potassium hydroxide (2.8 g., 5/100 mol.), pyridine (20 cc.) and methyl alcohol (20 cc.), a deep blue solution was formed. When ethylene glycol was used in place of hydrobenzoin, a similar result was obtained. But in the absence of such glycols, brown precipitate appeared. Even after this deep blue solution was kept for 24 hr. room temperature, cuprous oxide did not appear.

(5) **Oxidation of α-Methyl Benzoin.**—(a) A mixture of α-methyl benzoin (2.0 g., 0.8/100 mol.), "oxidant A" and methyl alcohol (50 cc.) was stirred at 30°C for 4 hr. in a stream of air. The resulting mixture was acidified with 6N-H_2SO_4, and extracted with ether (500 cc.). The ethereal layer was washed with water, and extracted with aqueous sodium carbonate solution. After removal of the ether, the residue was treated with aqueous semicarbazide hydrochloride and sodium acetate solution. The resulting mixture was filtered and washed with benzene. The residue was pure acetophenone semicarbazone (0.6 g., 40%); m. p. 197~198°C (Lit. 198°C). It was indentified with acetophenone semicarbazone by a mixed melting point determination and an analysis.

Anal. Found: C, 61.15; H, 6.52; N, 23.72. Calcd. for $C_9H_{11}ON_3$: C, 61.00; H, 6.25; N, 23.72%.

After removal of the benzene, the residue was recrystallized from ligroin (b. p. 80~100°C). α-Methyl benzoin (0.7 g., 35%) was recovered; m.p. 90~91°C, its melting point was not depressed on admixing with an authentic sample. From the sodium carbonate solution, benzoic acid (0.5 g., 50%) was obtained; it melted at 121~122°C alone or with an authentic sample of benzoic acid.

(b) A mixture of α-methyl benzoin (2.0 g., 0.8/100 mol.) and "oxidant C or D", was stirred for 4 hr. in a stream of air. Although the oxidation was attempted at 30, 60 and 80°C, no oxidation products were obtained, and α-methyl benzoin (1.7 g., 85%) was recovered, m.p. 90~91°C; its melting point was not depressed on admixing with an anthentic sample.

Results and Discussion

Cuprous acetate pyridine complex has a similar catalytic activity as cuprous chloride pyridine complex for aerial oxidation of benzil. Hydroxy cupric acetate pyridine complex (Experiment 1d) has a similar activity as cuprous acetate pyridine complex for these reactions (Experiment 2a). Furthermore, the oxidation of benzil is hardly retarded at all by an excess of methyl alcohol (Table I).

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[7] H. Meyer, "Nachweis und Bestimmung Organischer Verbindungen", Julius Springer, Wien (1933), p. 314.

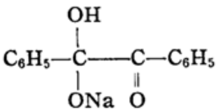
TABLE I. EFFECT OF METHYL ALCOHOL ON THE OXIDATION OF BENZIL

Catalyst	Copper salt in the catalyst g.	Methyl alcohol cc.	Benzoic acid g. (%)
Oxidant A*	Cu_2Cl_2, 4.0	50	2.1 (86)
Oxidant A*	Cu_2Cl_2, 4.0	100	2.1 (86)
Oxidant B*	$CuCl_2\cdot 2H_2O$, 6.8	50	2.0 (82)
Oxidant B*	$CuCl_2\cdot 2H_2O$, 6.8	100	2.0 (82)

Benzil (2.0 g.) was treated.
* Cf. Experiment 1.

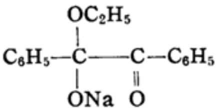
It was reported that strong bases were capable of combining to the keto group of benzil in alcohol[5,8]. (Reactions 4 and 5).

$C_6H_5{-}CO{-}CO{-}C_6H_5 + NaOH \rightleftarrows$



$$C_6H_5{-}\overset{OH}{\underset{ONa}{C}}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \qquad (4)$$

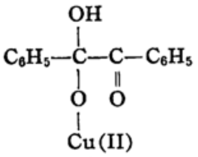
$C_6H_5{-}CO{-}CO{-}C_6H_5 + NaOC_2H_5 \rightleftarrows$



$$C_6H_5{-}\overset{OC_2H_5}{\underset{ONa}{C}}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \qquad (5)$$

"Oxidant A, B, C** and D**" are belived to be strong bases[9]. Since "oxidant B" I is considered to have hydroxy group[9], it can also combine with benzil at its keto group to form II —— this addition reaction seems not to be easily retarded with an excess of methyl alcohol. Since "oxidant A" and "oxidant B" bear a remarkable resemblance, a similar intermediate may be produced by reaction of benzil with "oxidant A".

$C_6H_5{-}CO{-}CO{-}C_6H_5 + \underset{I}{Cu(II){-}OH} \rightleftarrows$



$$C_6H_5{-}\overset{OH}{\underset{\underset{Cu(II)}{|}}{\underset{O}{C}}}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \qquad (6)$$

II

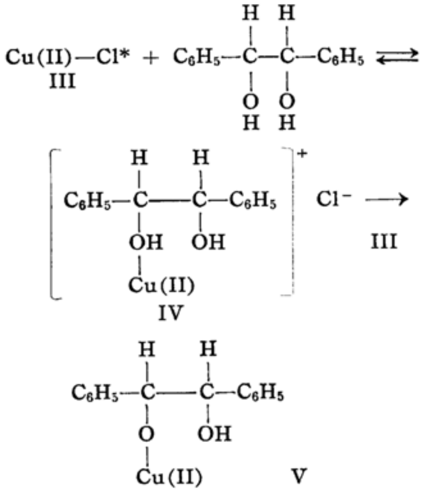
An attempt to oxidize hydrobenzoin by aerial oxidation catalyzed by "oxidant C" or "oxidant D" is unsuccessful even at 80°C. (Experiment 3b), although it is oxidized to benzaldehyde by aerial oxidation catalyzed by "oxidant A" or "oxidant B". Furthermore, an excess of methyl alcohol retards the oxidation (Table II).

TABLE II. EFFECT OF METHYL ALCOHOL ON THE OXIDATION OF HYDROBENZOIN

Catalyst	Methyl alcohol cc.	Benzaldehyde g. (%)	Benzoic acid g. (%)	Sample (Recovered) g. (%)
Oxidant A*	0	1.0 (50)	0.1 (4)	0.6 (30)
Oxidant A*	10	0.4 (20)	trace	1.3 (65)
Oxidant A*	50	0.2 (10)	trace	1.5 (75)
Oxidant B**	10	0.5 (25)	trace	1.1 (55)
Oxidant B**	50	trace	trace	1.7 (85)

Hydrobenzoin (2.0 g.) was treated.
* Cu_2Cl_2, 2.0 g. ** $CuCl_2\cdot 2H_2O$, 1.7 g.

These results are similar to those obtained in the aerial oxidation of aniline[3]. Thus a similar intermediate to that postulated in the oxidation of aniline, may be produced (Reaction 7) (Ref. 3).

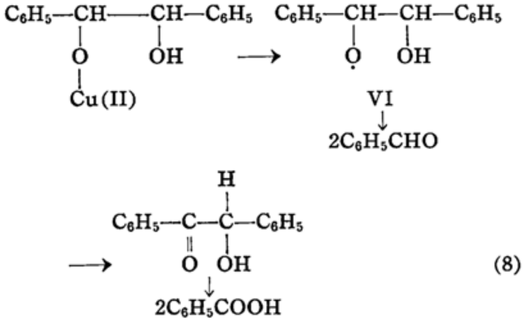


$$\underset{III}{Cu(II){-}Cl^*} + C_6H_5{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}C_6H_5 \rightleftarrows \underset{IV}{\left[C_6H_5{-}\overset{H}{\underset{\underset{Cu(II)}{OH}}{C}}{-}\overset{H}{\underset{OH}{C}}{-}C_6H_5\right]^+} Cl^- \longrightarrow III$$

$$C_6H_5{-}\overset{H}{\underset{\underset{Cu(II)}{O}}{C}}{-}\overset{H}{\underset{OH}{C}}{-}C_6H_5 \quad V \qquad (7)$$

* Cu(II)-Cl stands for "oxidant A".

If V is converted directly into benzaldehyde, a free racidal such as VI would appear in this reaction.



$$C_6H_5{-}\underset{\underset{Cu(II)}{O}}{CH}{-}\underset{OH}{CH}{-}C_6H_5 \longrightarrow C_6H_5{-}\underset{\dot{O}}{CH}{-}\underset{OH}{CH}{-}C_6H_5 \;\; VI \downarrow 2C_6H_5CHO$$

$$\longrightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{\underset{OH}{C}}{-}C_6H_5 \downarrow 2C_6H_5COOH \qquad (8)$$

On the one hand, VI seems to be converted into benzaldehyde. On the other hand, VI seems to be converted into benzoin, which is further oxidized to benzoic acid. Thus, if VI appears in this reaction, a good amount of benzoic acid may be

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8) A. Lachmann, *J. Am. Chem. Soc.*, **45**, 1509 (1923).
** Cf. Experiment 1.
9) K. Kinoshita, Part I of this series in This Bulletin, **32**, 777 (1959).

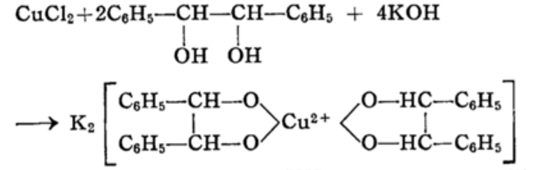
obtained. Since this assumption is not supported by the experimental results[1], it is postulated that such a free radical as VI hardly ever appears in this reaction. Moreover, if VI were intermediate, the stability of benzyl alcohol to "oxidant A" (Ref. 2) would be inexplicable.

Deep blue color is developed upon the addition of cupric chloride—methyl alcohol solution—to a mixture of hydrobenzoin and potassium hydroxide—pyridine-methyl alcohol solution (Experiment 4). For the following reason (1—3), this complex seems to be a chelate compound such as VII.

(1) In the absence of hydrobenzoin, this complex is never formed.

(2) In the presence of ethylene glycol in place of hydrobenzoin, a similar complex is formed.

(3) It was reported that *bis*-glycolatocopper(II) complex was produced upon the addition of cupric nitrate to aqueous erythritol anhydride solution in the presence of sodium hydroxide[10].



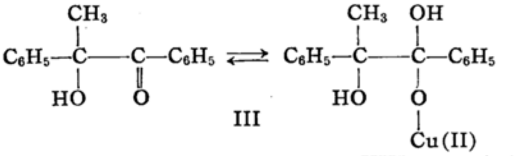
$$CuCl_2+2C_6H_5-\underset{OH}{CH}-\underset{OH}{CH}-C_6H_5+4KOH$$

$$\longrightarrow K_2\left[\begin{matrix}C_6H_5-CH-O\\ |\\ C_6H_5-CH-O\end{matrix}\!>\!Cu^{2+}\!<\!\begin{matrix}O-HC-C_6H_5\\ |\\ O-HC-C_6H_5\end{matrix}\right]$$

VII (9)

Cuprous oxide does not appear even after 24 hr. from this deep blue solution and the formation of chelate compounds such as VII seems to have no effect upon the oxidation of hydrobenzoin.

Because strong bases can combine with the keto group of α-methyl benzoin in alcohol[5,11], an intermediate VIII may be produced by the reaction of α-methyl benzoin with "oxidant A" (Reaction 10).



$$C_6H_5-\overset{CH_3}{\underset{HO}{C}}-\underset{O}{\overset{\|}{C}}-C_6H_5 \rightleftarrows C_6H_5-\overset{CH_3}{\underset{HO}{C}}-\overset{OH}{\underset{\underset{Cu(II)}{|}}{\underset{O}{C}}}-C_6H_5$$

III VIII (10)

However, α-methyl benzoin is not oxidized in aerial oxidation catalyzed by "oxidant C" or "oxidant D" (Experiment 5b). Furthermore, the oxidation of α-methyl benzoin is retarded by an excess of methyl alcohol (Table III).

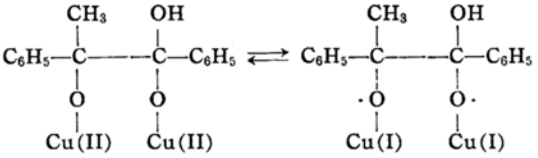
TABLE III. EFFECT OF METHYL ALCOHOL ON OXIDATION OF α-METHYL BENZOIN

Catalyst	Methyl alcohol	Benzoic acid	Acetophenone	Sample (Recovered)
	cc.	g. (%)	g. (%)	g. (%)
Oxidant A*	0	0.8 (80)	0.8 (80)	0.1 (5)
Oxidant A*	50	0.5 (50)	0.4 (40)	0.7 (35)
Oxidant A*	100	0.2 (20)	0.2 (20)	1.3 (65)
Oxidant B**	50	0.5 (50)	0.5 (50)	0.6 (30)
Oxidant B**	100	trace	trace	1.7 (85)

α-Methyl benzoin (2.0 g.) was treated.
* Cu_2Cl_2, 4.0 g. ** $CuCl_2\cdot 2H_2O$, 6.8 g.

These results suggest that the hydroxy group of α-methyl benzoin in VIII must be combined with "oxidant A" to form IX.

The oxidative cleavage of IX probably takes place through activated complex X (Ref. 3). As two unpaired electrons are located on both oxygen atoms of α-methyl benzoin respectively in X, it causes a cleavage of α-methyl benzoin (Reaction 11)***.



$$C_6H_5-\overset{CH_3}{\underset{\underset{Cu(II)}{|}}{\underset{O}{C}}}-\overset{OH}{\underset{\underset{Cu(II)}{|}}{\underset{O}{C}}}-C_6H_5 \rightleftarrows C_6H_5-\overset{CH_3}{\underset{\underset{Cu(I)}{|}}{\underset{\cdot O}{C}}}-\overset{OH}{\underset{\underset{Cu(I)}{|}}{\underset{O\cdot}{C}}}-C_6H_5$$

IX X

$$\longrightarrow C_6H_5COCH_3+C_6H_5COOH+2Cu(I) \quad (11)$$

Benzil or hydrobenzoin may be oxidized under the same mechanism as described above.

In Part II, the mechanism of the formation of azobenzene in aerial oxidation of aniline catalyzed by cuprous chloride, was discussed[3]. It is believed that the copper-nitrogen linkage in oxidative dimerisation of aniline, is similarly situated to the copper-oxygen linkage in oxidative cleavage of α-methyl benzoin. Thus, the oxidative dimerisation of aniline and oxidative cleavage of α-methyl benzoin, are carried out through similar mechanism.

Summary

(1) Benzil is oxidized by aerial oxidation catalyzed by "oxidants A, B, C and D".

(2) α-Methyl benzoin or hydrobenzoin is oxidized by aerial oxidation catalyzed by "oxidants A and B" only. This reac-

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[10] H. B. Jonassen et al., *J. Am. Chem. Soc.*, **77**, 2667 (1955). Ref. L. Segal et al., ibid., **78**, 273 (1955): N. V. Sidgwick, "The Chemical Elements and their Compounds", Vol. I, Oxford University Press, London (1950), p. 171; W. Traube et al., *Ber.*, **69**, 2655 (1936).

[11] D. B. Sharp et al., *J. Am. Chem. Soc.*, **74**, 5643 (1952).

*** Bawn et al. reported that the biradical with the structure $\cdot CH-CH_2-CH_2-CH\cdot$ has a strong tendency to break up the linkage between C(2) and C(3); E. H. Bawn et al., *Trans. Faraday Soc.*, **35**, 889 (1939).

tion is retarded by methyl alcohol.

(3) The mechanism of oxidative cleavage of benzil, α-methyl benzoin and hydrobenzoin, is described. It is also considered that the oxidative cleavage of benzil, α-methyl benzoin and hydrobenzoin, and the oxidative dimerisation of aniline[3] are carried out through similar mechanism.

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