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PHOTOINDUCED REACTIONS—L
PHOTOLYSIS OF HALOGENOPHENOLS IN AQUEOUS ALKALI AND IN AQUEOUS CYANIDE[1,2]

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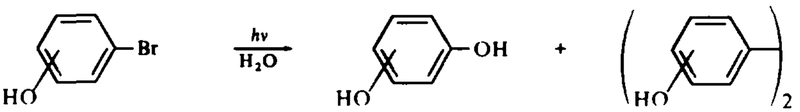
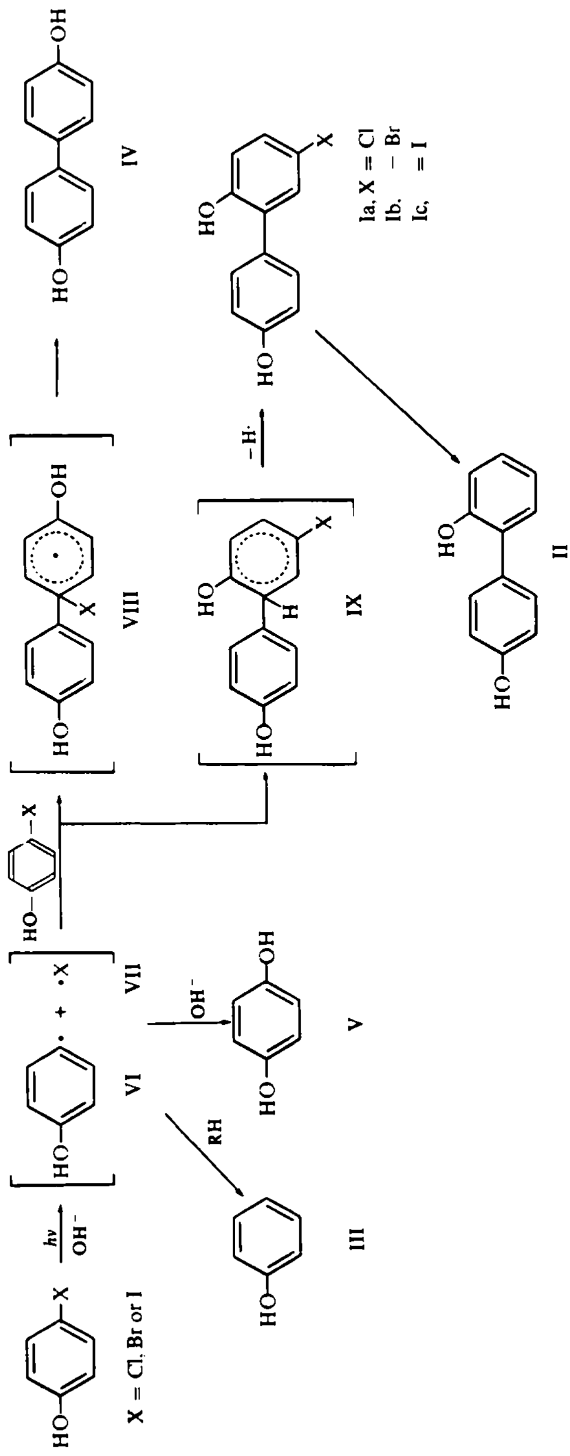
Abstract—On irradiation in aqueous alkali, several monohalogenophenols were found to react in several ways depending on the position of a substituent halogen. *p*-Substituted halogenophenols yielded 2,4'-dihydroxy-4-halogenodiphenyl (I), 2,4'-dihydroxydiphenyl (II), and phenol (III), in addition to the already known products, hydroquinone (V) and 4,4'-dihydroxydiphenyl (IV). The yield of V decreased in the order of Cl > Br > I, while those of III and IV increased in the order of Cl < Br < I. The effects of alkali concentration and of temperature on the reaction were examined with *p*-chlorophenol. Higher concentration of alkali and higher temperature accelerated the reaction and favoured the formation of III and V. *m*-Chlorophenol, on the other hand, gave resorcinol in high yield, which shows the electrophilic nature of the excited *m*-chlorophenol. *o*-Chlorophenol gave only a complex mixture of products including a large amount of a resinous material. Irradiation of *p*-halogenophenols in aqueous cyanide yielded *p*-cyanophenol in good yields, accompanied by a small amount of hydroquinone, while irradiation of *m*-chlorophenol gave resorcinol in high yield, accompanied by a small amount of *m*-cyanophenol. *o*-Chlorophenol again gave only intractable products. Reactions with a light at 2537 Å and with that over 2900 Å were substantially the same, although longer period of irradiation was required in the latter case. Some mechanistic discussions are included.

PHOTOLYSIS of aryl halides is well known to lead to the homolytic fission of a carbon-halogen bond.[3] These include halogenophenols. Thus, irradiation of monohalogenophenols gives phenol in methanol[4] and phenylphenols in benzene.[5] Grabowski[6] has found by polarographic analysis that photolysis (3130 Å) of chloro- and bromo-phenols in aqueous alkali results in the replacement of a halogen with an OH to yield the corresponding dihydroxybenzenes. Joschek and Miller[7] have shown that a diluted aqueous solution of bromophenols yields, on irradiation at 2537 Å, the corresponding symmetrical dihydroxydiphenyls in addition to the corresponding dihydroxybenzenes;



Both groups of workers interpret the primary photo-dissociative processes as the homolytic fission of a carbon-halogen bond. Their studies seemed, however, insufficient in the detailed product-analysis. Therefore, we have examined the preparative-scale photolysis of monohalogenophenols in aqueous alkali and later in aqueous cyanide. The results have been shown not to be always consistent with those by the predecessors.[6,7]


HO
X
hν
OH⁻
X = Cl, Br or I
HO
VI
+
•X
VII
HO
X
HO
X
OH
VIII
HO
OH
IV
RH
HO
III
OH⁻
HO
OH
V
HO
HO
H
X
IX
-H·
HO
HO
X
Ia, X = Cl
Ib, = Br
Ic, = I
HO
HO
II

Photolysis of halogenophenols in aqueous alkali

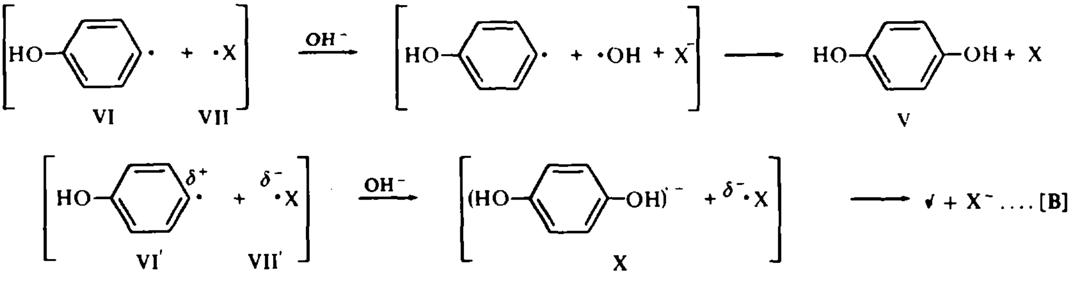
It was found that irradiation of *p*-halogenophenols yields, in addition to the already known products,[6, 7] 2,4'-dihydroxy-4-halogenodiphenyl (I) and/or 2,4'-dihydroxydiphenyl (II), and phenol (III), all of which have never been found in this series of reactions. 4,4'-Dihydroxydiphenyl (IV) obtained by Joschek *et al.*[7] could, however, not be detected or could be obtained only in low yield. In a typical run, a solution of *p*-chlorophenol (2·25 g) and KOH (10 g) in water (200 ml) was irradiated with a *ca* 10 W low-pressure mercury lamp of Vycor housing (2537 Å) under bubbling nitrogen for 5 hr at 40°. The products were found to consist of the starting material (45% recovery), Ia (7%), II (28%), III (4·8%) and hydroquinone (V, 27%). Similar irradiations were carried out with *p*-bromo- and *p*-iodophenols, and the results are summarized in Table 1. In all cases, II was the major product, but I was isolated only in the case of *p*-chlorophenol. The yield of V increased in the order of I < Br < Cl while those of III and IV decreased in the order of I > Br > Cl.

The effects of alkali concentration and temperature on the reaction were examined with *p*-chlorophenol (Table 2 and 3). At higher alkali concentration and at higher temperature, (i) the rate of reaction, (ii) the yields of III and V, (iii) the ratio II/Ia, and (iv) the total yield of Ia $\sim$ V, tend to increase. The nature of the reaction was not essentially altered when a diluted solution of *p*-chlorophenol was irradiated (Exp. 11).

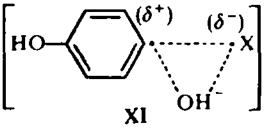
Similar irradiations were carried out with a light at longer wavelengths ($\geqslant$2900 Å). The results (Table 4) show that there is no essential difference between the decomposition with a light at 2537 Å and with those over 2900 Å.

The outline of the reaction scheme may be written as on p. 3102.

Homolytic cleavage of a carbon-halogen bond of *p*-halogenophenols may be operative. Formation of hydroquinone (V) may be rationalized by either Eq. A or Eq. B;



A mechanism as formulated in Eq. A resembles that proposed by Grabowski.[6] The halogen atom of a photochemically produced radical pair (VI and VII) abstracts an electron from a hydroxide ion to yield a halide ion and an OH radical which then couples with the phenyl radical (VI) to form V. Dependence of the yield of V on the nature of halogen may be attributed to the change in the ability of an atomic halogen to abstract an electron from a hydroxide ion. An alternative explanation is formulated in Eq. B. An excited molecule of *p*-halogenophenol dissociates into a pair of radicals with some polar character (VI' and VII'). The positively charged phenyl radical (VI') then reacts with a hydroxide ion to form an intermediate (X) which is eventually converted to V by the abstraction of an electron from X by the halogen atom (VII'). The facility of X formation, and thus the yield of V, would be controlled by the degree of the polar character of the reactive phenyl residue, which depends on the nature of the counterpart halogen. The latter mechanism seems to somewhat resemble that suggested by Joschek and Miller,[7] although the polar nature of the radical pair has not been taken into consideration. The real reaction path, however, might be approached with more accuracy if both the schemes (Eqs A and B) are considered to be operative at the same time, that is, if a concerted reaction involving a transition state like XI is assumed;



XI

The formation of I and IV is explained by the addition of the *p*-hydroxyphenyl radical (VI or VI′) to a molecule of halogenophenol to yield cyclohexadienyl radical intermediates, IX and VIII. Recombination of the radicals (VI) to form IV as suggested by Joschek *et al.*[7] seems less probable, because the probability of the radical (VI) to encounter with another molecule of VI should be much smaller than that with the phenol. The dehalogenated dihydroxydiphenyl (II) must arise through thermal or photochemical reduction of I in aqueous alkali as shown from the fact that the ratio II/Ia increased with higher alkali concentration (Table 2), with higher reaction temperature (Table 3), and with longer irradiation period.

Similar irradiations were carried out with *o*- and *m*-chlorophenols (Table 5). *o*-Chlorophenol did not give the expected products but gave only a complex mixture of products which consisted mainly of a resinous material. This is inconsistent with findings by Grabowski[6] and by Joschek *et al.*[7] who have reported that irradiation of *o*-halogenophenols gives catechol and/or 2,2′-dihydroxydiphenyl. On the other hand, *m*-chlorophenol gave resorcinol in high yield. It is consistent with the recent findings by Pinhey and Rigby[8] that the chlorine in *m*-chlorophenol can be easily replaced by an alkoxyl group on irradiation in an alcohol. The excited state of the *m*-isomer, thus must have a relatively strong electrophilic character as they suggest.

Photolysis of halogenophenols in aqueous cyanide

Irradiation of *o*-, *m*- and *p*-halogenophenols were also carried out in the presence of a cyanide in place of a hydroxide (Table 6). These halogenophenols were again found to behave quite differently from each other as in the alkaline irradiations. All of the *p*-halogenophenols yielded *p*-cyanophenol in good yields*, accompanied by small amounts of hydroquinone and 2,4′-dihydroxydiphenyl (Exp. 21–27). In all cases, even in case of *p*-iodophenol, neither mono-(*ortho*-) nor poly- (2,4-di- or 2,4,6-tri-) halogenated phenol could be detected in the reaction mixture. This suggests that, on reaction with cyanide, the halogen of a *p*-halogenophenol is eliminated rather as a halide ion than as an atomic halogen. Molecular iodine, which should be formed if an atomic iodine is liberated in the system, must iodinate a phenol in this alkaline condition to yield the above mentioned halogeno(iodo-)phenols. The formation of *p*-cyanophenol may thus be accounted for in a similar way as that of hydroquinone on irradiation in aqueous alkali;

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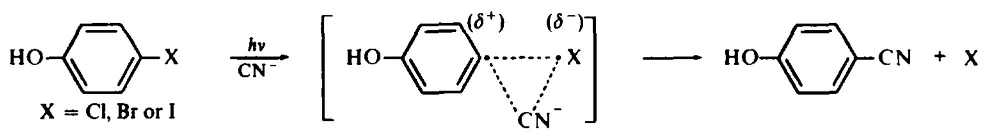
* As an analogy, Rosenmund *et al.*[9] have found in the early days of organic photochemistry that *p*-bromo- and *p*-chlorobenzoic acids yield terephthalic acid in good yields when irradiated in water in the presence of KCN and $Cu(CN)_2$ at refluxing temperature.



The difference in the facility to lose an electron between a cyanide ion (to yield a cyano radical) and a hydroxide ion (to yield a hydroxy radical) would account for the better yields of the cyanophenol on irradiation in aqueous cyanide as compared to those of hydroquinone in aqueous hydroxide. No rational account can, however, be made at present for the fact that the yield of hydroquinone increases while that of *p*-cyanophenol decreases at higher temperature (Exp. 22).

During the above experiments, it was found that a prolonged irradiation of *p*-iodophenol gave *p*-hydroxybenzaldehyde in considerable yield in addition to *p*-cyanophenol (Exp. 26). It was demonstrated that it is derived photochemically from the cyanophenol in this condition, as described elsewhere.[10]

On the other hand, *m*-chlorophenol yielded resorcinol in high yield, accompanied by a small amount of *m*-cyanophenol (Exp. 30, 31). An apparently striking difference between the reactivities of the excited *m*- and *p*-chlorophenols may be explained by assuming either that the electrophilic character of the excited state molecule of *m*-chlorophenol or of the reactive species therefrom is so strong that it can react not only with a hydroxide ion but also with a water molecule to yield resorcinol, or that it can react much faster with a hydroxide ion than with a cyanide ion. *o*-Chlorophenol gave only a complex mixture of products containing a large quantity of a resinous material (Exp. 28, 29), as in the irradiation in aqueous alkali. It is obvious from Table 6 that the reaction with light at 2537 Å and those over 2900 Å are substantially the same.

As a summary, *o*-, *m*-, and *p*-halogenophenols in aqueous alkali or cyanide behave quite differently from each other on irradiation. Homolytic fission of a carbon-halogen bond from the excited state of *p*-halogenophenol seems to be operative. Distribution of the products is determined depending on the nature of the halogen. The excited *m*-chlorophenol has an electrophilic nature. No consideration can be made on *o*-chlorophenol, since it gave no identifiable product on irradiation. However, it seems to remain unresolved whether the differences in the nature of the excited states (or the reactive species therefrom) of these halogenophenols are so substantial or not, since they were found to react photochemically with a phenol in water in an apparently analogous fashion with each other. This will be published elsewhere.

TABLE 1. PHOTOLYSIS (2537 Å) OF *p*-HALOGENOPHENOLS IN AQUEOUS ALKALI.[a]

Exp. No.	p-X-C_6H_4OH	Recov. (%)	Products (%)[b]				
			I	II	III	IV	V
1	X=Cl	45	7	28	4·8	0	27
2	Br	15	∼0	23	11·5	1·5	9·0
3	I	38	∼0	34	13	3·2	0

[a] A solution of a *p*-halogenophenol (17·3 ∼ 17·5 mmole) and KOH (*ca* 0·18 mole) in water (200 ml) was irradiated for 5 hr at *ca* 40°.

[b] The yields are based on the reacted starting phenol.

Table 2. Effect of concentration of alkali on the photolysis (2537 Å) of *p*-chlorophenol in water[a]

Exp. No.	Alkali (equiv.)	Irrad. Time (hr)	Recov (%)	Products (%)[b]					Total yield of Ia ~ V (%)
				Ia	II	III	IV	V	
4	0	20[c]	72	31	~0	1·4	0	0	32
5	1	5	53	23 ~ 27		2·7	0	17	43~47
6[d]	10	5	45	7	28	4·8	0	27	67
7	50	5	39	30 ~ 35		3·1	0	33	66~71

[a] A solution of *p*-chlorophenol (17·5 mmole) and KOH in water (200 ml) was irradiated at *ca* 40°.

[b] The yields are based on the reacted starting phenol.

[c] In the course of the reaction, an opaque material was deposited on the surface of the lamp tube, which retarded the reaction.

[d] Identical with Exp. 1.

Table 3. Effect of temperature on the photolysis (2537 Å) of *p*-chlorophenol in aqueous alkali[a]

Exp. No.	Temp. (°C)	Irrad. Time (hr)	Recov. (%)	Products (%)[b]					Total yield of Ia ~ V (%)
				Ia	II	III	IV	V	
8	12–16	5	71	33 ~ 38		1·7	0	8·7	43~48
9[c]	40	5	45	7	28	4·8	0	27	67
10	60–70	4	48	1·7	21	10·7	0	50	84
11	15[d]	1	58	33	13	*e*	0	5·8	

[a] A solution of *p*-chlorophenol (17·5 mmole) and KOH (0·18 mole) in water (200 ml) was irradiated.

[b] The yields are based on the reacted starting phenol.

[c] Identical with Exp. 1.

[d] A solution of *p*-chlorophenol (1·8 mmole) and KOH (18 mmole) in water (200 ml) was irradiated.

[e] The yield could not be estimated.

Table 4. Photolysis (≳ 2900 Å) of *p*-halogenophenols in aqueous alkali[a]

Exp. No.	p-X-C_6H_4OH	KOH (equiv.)	Recov. (%)	Products (%)[b]				
				I	II	III	IV	V
12	X═Cl	0	94	~0	0	0	0	0
13	Cl	1	57	~0	34	tr.	0	1·8
14	Cl	10	57	~0	44	~1	0	1·8
15	Cl[c]	10	60	~0	38	5	0	11
16	Cl	10[d]	56	~0	44	tr.	0	tr.
17	Br	10	43	0	30	~3	tr.	0
18	I	10	31	0	16	5·7	tr.	0

[a] A solution of a *p*-halogenophenol (8·8 mmole) and KOH in water (100 ml) was irradiated for 20 hr at 10–15°.

[b] The yields are based on the reacted starting phenol.

[c] Irradiated for 13·5 hr at 35–38°.

[d] K_2CO_3 was used in place of KOH.

TABLE 5. PHOTOLYSIS (2537 Å) OF *o*- AND *m*-CHLOROPHENOLS IN AQUEOUS ALKALI[a]

Exp. No.	X-C_6H_4OH	Recov. (%)	Products (%)[b]		
			PhOH	HO-C_6H_4-OH	Dihydroxydiphenyls
19	X=*o*--Cl	17·5	tr.	0	Negl.[c]
20	*m*-Cl	30	tr.	74	≲4

[a] A solution of a chlorophenol (17·5 mmole) and KOH (*ca* 0·18 mole) in water (200 ml) was irradiated for 5 hr at 40°.
[b] The yields are based on the reacted starting phenol.
[c] 2.2′- or 2.4′-Dihydroxydiphenyl could not be detected.

TABLE 6. PHOTOLYSIS (AT 2537 Å OR OVER 2900 Å) OF HALOGENOPHENOLS IN AQUEOUS CYANIDE[a]

Exp. No.	X-C_6H_4-OH	Light Source[a]	KCN (equiv.)	Irrad. Time (hr)	Recov. (%)	Products (%)[b]			
						PhOH	HO-C_6H_4-CN	HO-C_6H_4-OH	Dihydroxy-diphenyls
21	X=*p*--Cl	L	10	5	64	tr.	71	2·3	7·4[c]
22	*p*--Cl[d]	L	17	6	19	tr.	34	15	*e*
23	*p*--Cl	H	10	20	37	tr.	75	1	11[c]
24	*p*--Br	L	10	5	74	tr.	68	4.9	2[c]
25	*p*--Br	H	20	5	84	tr.	76	*e*	*e*
26	*p*--I[f]	L	20	106	2	0	54	0	1[c]
27	*p*--I	H	20	95	26	0	65	0	tr.[c]
28	*o*--Cl	L	20	28	tr.	0	0	0	*g*
29	*o*--Cl	H	20	140	29	0	0	0	*g*
30	*m*--Cl	L	20	72	1·6	0	7·5	72	*g*
31	*m*-Cl	H	20	94	33	tr	8·2	65	*g*

[a] A solution of a halogenophenol (L, 17·5 mmole; H, 8·6 mmole), KOH (L, *ca* 17·5 mmole; H, *ca* 8·6 mmole) and KCN in water (L, 200 ml; H, 100 ml) was irradiated at 10–20° with a light at 2537 Å (L) or with that over 2900 Å (H).
[b] The yields are based on the reacted starting phenol.
[c] 2.4′-Dihydroxydiphenyl.
[d] Irradiated at 40°.
[e] Not examined.
[f] *p*-Hydroxybenzaldehyde was obtained as a minor product in 18% yield.
[g] Formed in very low yield if at all.

EXPERIMENTAL

M.ps are uncorrected. The starting materials were commercially available and used without further purification. Their purities were checked by VPC and TLC. The products were identified or detected by comparison with authentic samples by IR spectra. VPC (stationary phase, silicone DC on celite; carrier gas, H_2; temp, 190–240°) and TLC (silica gel; solvent, benzene-AcOEt-AcOH, 19:2:1). The color reagents, iodine vapor and 3-methyl-2-benzothiazolone hydrazone,[11] were used for detection of phenolic compounds (TLC).

General procedure

A Table 1. A soln of a *p*-halogenophenol (17·3–17·5 mmole) and KOH (*ca* 0·18 mole) in distilled water (200 ml) was irradiated for 5 hr at *ca* 40° with a *ca* 10 W low-pressure mercury lamp with Vycor housing (2537 Å) under bubbling N_2. After irradiation, the soln was acidified with HCl aq under the atmosphere of N_2, and extracted with ether. The ethereal layer was separated, dried over Na_2SO_4, and evaporated to dryness. The residue was analyzed by VPC and column chromatography on silica gel (*ca* 60 g).

B Table 2, 3 *and* 5. Irradiation and working up of the mixture were carried out in a similar manner as described in A.

C Table 4. A soln of a *p*-halogenophenol (8·8 mmole) and KOH in water (100 ml) was irradiated for 20 hr at 10–15° with a 100 W high-pressure mercury lamp of Pyrex housing (> 2900 Å) under bubbling N_2. The reaction mixture was worked up as described in A.

D Table 6. Irradiation and working up of the reaction mixture were carried out in a similar way to that described in A or C.

Isolation of the products

With p-*chlorophenol in aqueous alkali* (*Exp.* 1). Chromatography of the products on silica gel (benzene) gave a mixture of products containing the starting phenol and III. Elution with benzene-ether (19:1) gave 0·32 g of colorless crystals which consisted of a mixture of the dihydroxydiphenyls. Further elution with the same solvent mixture (9:1) yielded 0·30 g crude V. recrystallization of which from water gave V as colorless prisms, m.p. 169–172°. identical with an authetic sample, m.p. 171–173° (TLC and IR). Careful rechromatography of the mixture of the dihydroxydiphenyls eluted with benzene-ether (200:1) yielded 73 mg of crystals of Ia, recrystallization of which from benzene afforded colorless plates, m.p. 118–119°. (Found; C, 65·60; H, 4·15; Cl, 16·37. $C_{12}H_9O_2Cl$ requires: C, 65·32; H, 4·11; Cl, 16·07); ν^{Nujol} ~ 3250 and 827 cm^{-1}; $\lambda_{\text{max}}^{\text{EtOH}}$ 257 (log ε, 4·13) and 298 mμ (log ε, 3·88); τ CCl_4 (as its dimethyl ether) 2·50 ~ 3·45 (7H, m), 6·30 (3H, s) and 6·36 (3H, s). Reduction with Pd/C yielded II (see below). Further elution with the same solvent mixture gave 0·25 g of colorless crystals, recrystallization of which from $CHCl_3$ yielded II as colorless plates. m.p. 164–165·5°, identical with an authetic sample,[12] m.p. 165–166·5° (TLC, IR and VPC); $\lambda_{\text{max}}^{\text{EtOH}}$, 251 (log ε, 4·26) and 287 mμ (log ε, 3·99).

With p-*iodophenol in aqueous cyanide* (*Exp.* 26). An aliquot (21/25) of the mixture was chromatographed. Elution with benzene yielded 0·11 g crystals which contained 71 mg *p*-iodophenol (VPC and TLC). Further elution gave 0·94 g colorless crystals of *p*-cyanophenol. contaminated by 15 mg 2,4′-dihydroxydiphenyl (VPC and TLC). Recrystallization from benzene (active charcoal) yielded *p*-cyanophenol as colorless plates, m.p. 111–112·5°, identical with an authentic sample,[13] m.p. 112–114° (IR, TLC and VPC). Final eluate gave 0·58 g of a crystalline mixture of products. which was rechromatographed to yield 0·31 g colorless crystals, recrystallization of which from benzene gave *p*-hydroxybenzaldehyde as colorless plates. m.p. 119–121°, identical with an authentic sample, m.p. 117–118 (IR and TLC).

With m-*chlorophenol in aqueous cyanide* (Exp. 30). Chromatography of the mixture eluted with benzene yielded 0·13 g colorless oil containing 37 mg *m*-chlorophenol (VPC). Elution with benzene-ether (19:1) gave 0·15 g colored crystals, recrystallization of which from benzene gave *m*-cyanophenol as colorless plates, m.p. 82–84°, lit.[14] m.p. 80–85°. The IR spectrum was identical with an authentic sample ($\nu_{\text{max}}^{\text{Nujol}}$ 2250 cm^{-1}). Elution with benzene-ether (9:1) gave 1·35 g resorcinol as colorless crystals, identical with an authentic sample (IR, TLC and VPC).

With o-*chlorophenol in aqueous cyanide* (*Exp.* 28). Chromatography of the products eluted with benzene-ether gave only a complex mixture of products from which no identified product could be detected. Elution with ether and acetone yielded 1·33 g of resinous material.

REFERENCES

[1] Part XLIX. T. Matsuura, A. Horinaka, H. Yoshida and Y. Butsugan, *Tetrahedron* **27**, 3095 (1971) dedicated to Emeritus Professor Munio Kotake for commemoration of his seventy-seventh birthday.

[2] A preliminary communication appeared in, K. Omura and T. Matsuura, *Chem. Comm.* 1394 (1969)

[3] [a] R. K. Sharma and N. Kharasch, *Angew. Chem.* **80**, 691 (1968);
[b] Refs cited in Ref 5-*b*

[4] N. Kharasch and P. Friedman, *Abstract of Papers* p. 27S. Organic Chemistry Division, 148*th National Meeting of the American Chemical Society*, III, Sept. (1964)

[5] [a] W. Wolf and N. Kharasch, *J. Org. Chem.* **30**, 2493 (1965);
[b] T. Matsuura and K. Omura, *Bull. Chem. Soc., Japan* **39**, 944 (1966);
[c] G. E. Robinson and J. M. Vermon, *Chem. Comm.* 977 (1969)

[6] Z. R. Grabowski, *Z. Physik. Chem.* **27** 239 (1961)

[7] H. I. Joschek and I. Miller, *J. Am. Chem. Soc.* **88**, 3269 (1966)

[8] J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Letters* 1267 (1969)
[9] K. W. Rosenmund, K. Luxat and W. Tiedemann, *Ber. Dtsch. Chem. Ges.* **56B**, 1951 (1923)
[10] K. Omura and T. Matsuura, *Chem. Comm.* 1516 (1969)
[11] E. Kamata, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan. Pure Chem. Sect.*) **87**, 380 (1966)
[12] E. Licke, *J. Prakt. Chem.* (2), **8**, 43 (1873)
[13] F. Ahrens, *Ber. Dtsch. Chem. Ges.* **20**, 2952 (1887)
[14] A. A. Goldberg and A. H. Wragg, *J. Chem. Soc.* 4227 (1958)