THE VON RICHTER REACTION[1]

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Victor von Richter in 1871–1875 reported (1, 2, 3) the reaction of *p*-nitrobromobenzene with alcoholic potassium cyanide to give *m*-bromobenzoic acid, together with some equally odd reactions of other nitrohalobenzenes with the same reagent. This paper presents experimental confirmation of some of these reports, improvements in the experimental procedure, and investigations of the behavior of additional aromatic nitro compounds with alcoholic potassium cyanide. We believe that we are dealing with a general reaction of aromatic nitro compounds, and present our ideas on its mechanism.

It is remarkable that in the three-quarters of a century elapsed since von Richter's[4] papers, only Holleman (4) has done further work on the same sort of reaction. In Table I Holleman's results are displayed along with von Richter's.
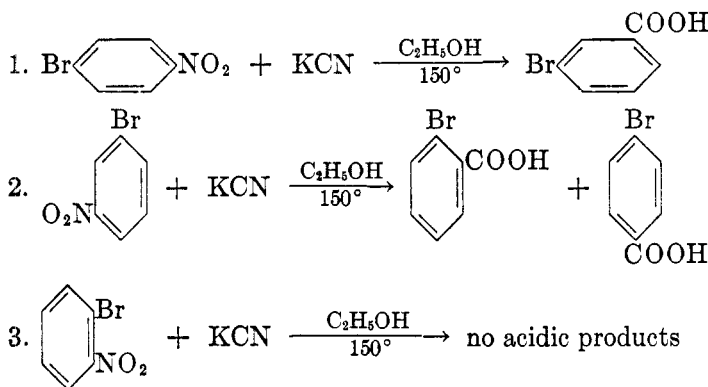
We repeated von Richter's experiments on the three nitrobromobenzenes, and our findings are in substantial agreement with his reports. We found *para*-nitrobromobenzene to give *meta*-bromobenzoic acid, *meta*-nitrobromobenzene to give a mixture of *ortho*- and *para*-bromobenzoic acids (he reported only the *ortho* isomer; a trace of *p*-bromobenzoic acid he ascribed to a minor "Umsetzung"), and *ortho*-nitrobromobenzene to give no acidic products. Our yields were about 20%.

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[4] von Richter encountered this reaction in the course of work on the problem of orientation in disubstituted benzenes, and made arguments about orientation relationships on the basis of it! In his 1875 paper, he recognized the contributions of Körner and others to this problem and provided an interpretation of his reactions that is satisfactory today.

We also discovered that certain other aromatic nitro compounds react in the same way with alcoholic potassium cyanide. Nitrobenzene produced benzoic acid (21%). The nitroanisoles behaved much like the nitrobromobenzenes except that yields were much lower; from *p*-nitroanisole there resulted 3% of *m*-anisic acid, while *p*-anisic acid (1%) was the product from *m*-nitroanisole. *o*-Nitroanisole yielded no acidic products. Incomplete experiments appear to indicate the same sort of behavior in the nitrobiphenyl series.

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TABLE I

PREVIOUS WORK ON THE VON RICHTER REACTION

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STARTING MATERIAL	TEMP., °C.	PRODUCTS	REFERENCE
p-Nitrobromobenzene	180	*m*-Bromobenzoic acid	(1)
m-Nitrobromobenzene	200	*o*-Bromobenzoic acid (40%) + *p*-bromobenzoic acid (trace)	(1, 5)
o-Nitrobromobenzene	200	No acidic products	(1)
p-Nitrochlorobenzene	200	*m*-Chlorobenzoic acid	(1)
m-Nitrochlorobenzene	250–270[a]	*o*-Chlorobenzoic acid	(1)
o-Nitrochlorobenzene		No acidic products	(3)
m-Nitroiodobenzene	200	*p*-Iodobenzoic acid + *o*-iodobenzoic acid	(1)
2-Nitro-4-bromotoluene		*m*-Toluic acid	(3)
3-Nitro-4-bromotoluene		No reaction	(3)
2,5-Dibromonitrobenzene	120–140	2,5-Dibromobenzoic acid (20%)	(2, 3)
2,4-Dibromonitrobenzene	250	3,5-Dibromobenzoic acid	(3)
2,4,6-Tribromonitrobenzene	250	No acidic products	(3)
2,3,4,6-Tetrabromonitrobenzene		No acidic products	(3)
"*o*-Nitrobenzoic acid" (probably *m*-nitrobenzoic acid)		Terephthalic acid	(6)
o-Dinitrobenzene	170	No reaction (in alcohol)	(7)
m-Nitrobenzenesulfonic acid	190–200	*o*-Sulfobenzoic acid (15%) + *p*-sulfobenzoic acid (15%) + 2-amino-4-sulfobenzoic acid + other aminosulfobenzoic acids (see text)	(4)

[a] No reaction at 200°.

It thus appears that a wide variety of aromatic nitro compounds give, with alcoholic potassium cyanide, carboxylic acids in which the carboxyl group, however, occupies a position *ortho* to that previously occupied by the nitro group. We call this general behavior the von Richter Reaction in honor of its discoverer.
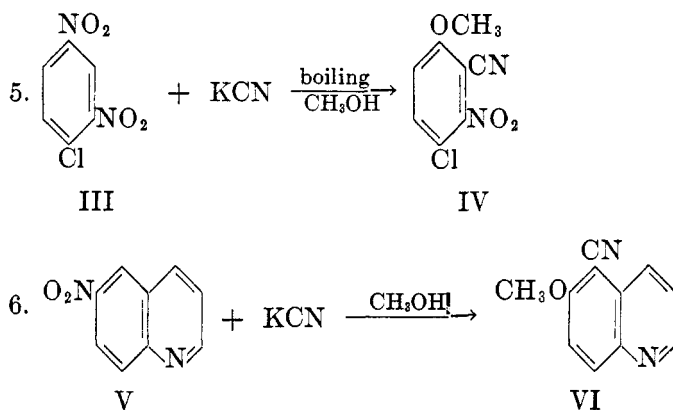
5.

+ KCN $\xrightarrow[\text{CH}_3\text{OH}]{\text{boiling}}$

III   IV

6.
 + KCN $\xrightarrow{\text{CH}_3\text{OH!}}$

V   VI
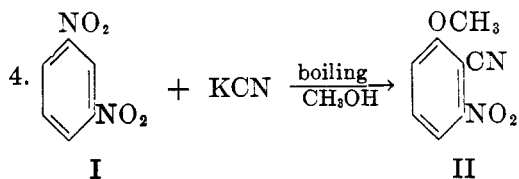
TABLE II

THE VON RICHTER REACTION WITH p-NITROBROMOBENZENE

SOLVENT AND TECHNIQUE	TEMP., °C.	SOLVENT, ML.	YIELD OF m-C$_6$H$_4$-BrCOOH, %	M.P., °C. CRUDE	RECOVERED NEUTRAL MATERIAL	
					YIELD, %	M.P., °C.
Abs. alc., sealed tube	175	25	7	142–145	87	95–110[a]
Abs. alc., sealed tube	195[b]	25	8	114–140	6	58[c]
Alc., 95%, sealed tube	140–150	25	16	152–153[d]	35	greasy
Alc., 48%, sealed tube	145–155	25	22	154.5–155.4[d]	35	118–122[e]
Glycol, 98%, 3 hrs. reflux		75	3	151–154	4	120–125
Glycol, 90%, 3 hrs. reflux		75	10	151–154[d]	21	125–127
Glycol, 75%, sealed tube	170[f]	50	1.7	150–153[d]	90	123–127
Glycol, 50%, 3 hrs. reflux		75	5	153–154	84	123–125
Cyclohexanol, 98%, 3 hrs. reflux		75	1.5	153–154	49	121–125
Glycol, 90%, 3 hrs. reflux[g]		150	16	150–153		

[a] When recrystallized, m.p. 122–124°; did not depress m.p. of p-nitrobromobenzene. [b] Eight hours. [c] Did not depress m.p. of p-nitrophenetole. [d] Did not depress m.p. of m-bromobenzoic acid. [e] Did not depress m.p. of p-nitrobromobenzene. [f] Three hours. [g] Used 8 g. of p-nitrobromobenzene and 30 g. of potassium cyanide.

It should be understood, however, that some aromatic nitro compounds react with alcoholic cyanide in another fashion. m-Dinitrobenzene (I) with potassium cyanide in boiling methanol gives 2-methoxy-6-nitrobenzonitrile (II) (7, 8); 2,4-dinitrochlorobenzene (III) yields 2-nitro-3-chloro-6-methoxybenzonitrile (IV) (9), and similarly 5-cyano-6-methoxyquinoline (VI) is produced from 6-nitroquinoline (V) (10). In these cases, the point of entrance of the cyano group is doubly activated: there are either two nitro groups or a nitro group and a hetero nitrogen atom located so as to activate it. We shall presently devote more attention to these doubly activated compounds.

Experimental considerations. von Richter's reports were lean on experimental detail. Moreover, his identification of products was not wholly satisfying, and

his method for isolating and purifying products was most laborious. Our desire to gain better information on yields and to check the identity of the reported products motivated our repetition of his work on the nitrobromobenzenes; incidentally, we have employed a more simple technique (steam-distillation) for isolating products in pure form.

The structures assigned to von Richter's products were based mainly on their analyses and melting points although in a few cases these halobenzoic acids were converted to hydroxybenzoic acid derivatives by alkali fusion, a reaction which itself might take an abnormal course. In the present work all products were identified by mixed melting points with authentic samples.

von Richter's reactions were run in "alcohol" solution in sealed tubes at 180–200° or higher, although Holleman used water as a solvent for the reaction of potassium m-nitrobenzenesulfonate. To check the effect on yield of variation in conditions such as time, temperature, and solvent composition, we ran a series of reactions mainly on p-nitrobromobenzene. In most of these the molar ratio of cyanide to nitro compound was 2:1. This study showed that although the reaction could be run in 100% or 95% ethanol, a better product was obtained in 50% ethanol-water. It also showed that yield (in lime-dried ethanol) was roughly independent of temperature in the range 155° to 195°, and was not improved by heating for longer than one hour. The latter observation and the recovery of much unreacted starting material suggest that hydrolysis (or alcoholysis) competes with the nitro compound for cyanide ion to the extent that hydrolytic destruction of cyanide is the yield-limiting factor; it is known that cyanide ion is rapidly hydrolyzed in water solution at elevated temperatures (11a).

We were early aware of limitations inherent in the use of ethanol solvent with its requirement of sealed tubes, and sought to find a high-boiling solvent in which the reaction could be run at reflux. Ethylene glycol suggested itself, but yields in 90% and 95% ethylene glycol (b.p. 142° and 152°, respectively) were only 10% as compared to yields of about 20% previously obtained in 50% ethanol. However, when a 12:1 ratio of cyanide to p-nitrobromobenzene was used, the yield in 90% glycol rose to 16%. Although this technique still is not very good so far as yields are concerned, it does represent a tolerable reflux procedure which allows the reaction to be run on a large scale. No unreacted starting material was recovered from runs according to this technique, suggesting that reduction of the nitro group by the alkaline alcoholic solvent or by the large excess of cyanide (12) was now limiting the yield. It is clear that a more satisfactory high-boiling solvent would be desirable.

Reaction mechanism. An acceptable mechanism for this reaction must be consistent with the following facts:

(a) "Normal" replacement of halogen from nitrohalobenzenes by sodium or potassium cyanide in aqueous or alcoholic solution has not been observed. [However, cuprous cyanide gives "normal" replacement of halo by cyano (13)].

(b) Recovered starting materials have been found free from contamination by isomers.

(c) Product structure has a specific relationship to starting material orientation. *para*-Substituted nitrobenzenes give *meta*-substituted benzoic acids free from isomeric contamination, and *meta*-substituted nitrobenzenes give *ortho*- and *para*-substituted benzoic acids with no traces of the *meta* isomer.

(d) There is no evidence that the entering carboxyl has ever taken the same ring position that the nitro group vacated.[5]

(e) Nitro compounds with an *ortho* substituent react less readily than those without substituents *ortho* to nitro. In most cases, *ortho*-substituted nitro compounds have failed to react under conditions which are sufficient for reaction by their *meta*- and *para*-isomers. (See Table I).

(f) Nitrite ion is eliminated in the reaction (3).

We assume that in this reaction a cyano group is introduced into the ring and later hydrolyzed to carboxyl. This assumption is in accord with general chemical experience, and is supported in particular by some observations of Rosenmund and Struck (13).

The above facts rule out three mechanistic possibilities which one is compelled to consider:

There cannot have been rearrangement of the starting material followed by "normal" replacement of nitro by cyano because of (b), (c), and (d). Furthermore, the formation of *ortho* substituted benzoic acids from *meta* substituted nitrobenzenes cannot have gone through *ortho* substituted nitrobenzenes, because the latter are unreactive (e).

There cannot have been "normal" replacement of nitro by cyano followed by rearrangement of the resulting nitrile or one of its hydrolysis products because of (c) and (d).

There cannot have been dissociation of the nitro compound to form a substituted phenyl radical or ion which, after rearrangement or because of its resonance state, later united with a cyano group to form the predecessors of the observed products because of (c). Such a process would lead to formation of the same sort of products from both *meta*- and *para*-substituted nitrobenzenes.

We believe the following is a reasonable mechanism for the von Richter reaction (illustrated for a *p*-substituted nitrobenzene): (A) There is attack by cyanide at an unoccupied position *ortho* to the nitro group; this produces the intermediate ion VII. (B) Ion VII releases in some way a hydride ion which displaces the nitro group; for the transition state in the displacement, VIII is an important resonance structure; resulting from the displacement are nitrite ion and nitrile IX. (C) Hydrolysis of the nitrile yields a *meta*-substituted benzoic acid.

[5] However, it has been reported by Blanksma (*Beilstein*, Erstes Ergänzungswerk, **X**, p. 53) and by Lobry de Bruyn (12) that the nitro group in position 6 of 2-methoxy-5,6-dinitrobenzonitrile is directly replaced by cyano in reaction with alcoholic potassium cyanide.
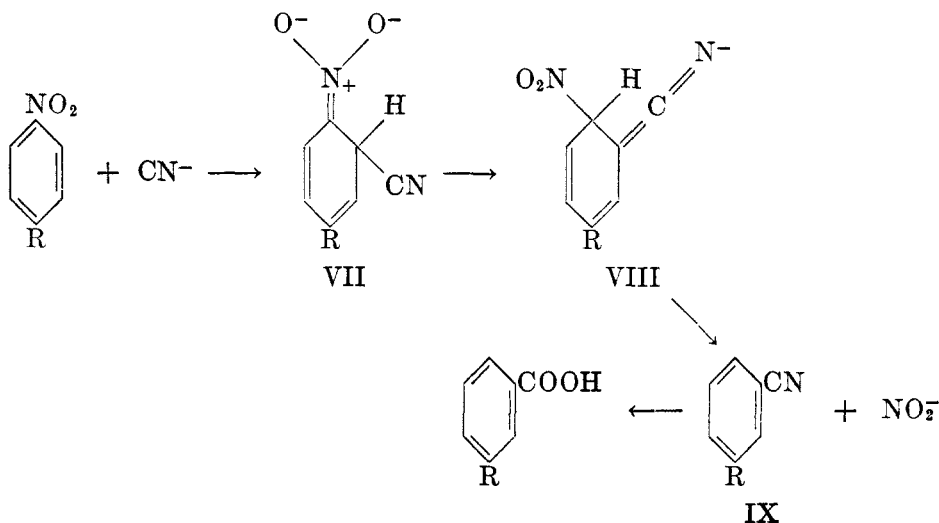
Crucial to this mechanism is our postulate that only attack of cyanide *ortho* to a nitro group can result in the von Richter reaction.[6] The evidence for this is good but not conclusive. That the structures of all observed products are consistent with this postulate is necessary and permissive evidence. One should observe, though, that a few products (such as *ortho*-bromobenzoic acid from *meta*-nitrobromobenzene) could also be regarded as the result of attack *para* to nitro. Exclusive *ortho* attack is strongly supported by the reactions of *m*-dinitrobenzene and 2,4-dinitrochlorobenzene with cyanide ion (equations 4 and 5), in which attack occurs exclusively *between* two nitro groups (*ortho* to both) in spite of the availability of, respectively, two or one positions which are *ortho* to one nitro and *para* to another. In addition, as we shall presently show, the postulate of exclusive *ortho* attack makes comprehensible the failure, in general, of *ortho*-substituted nitro compounds to react.
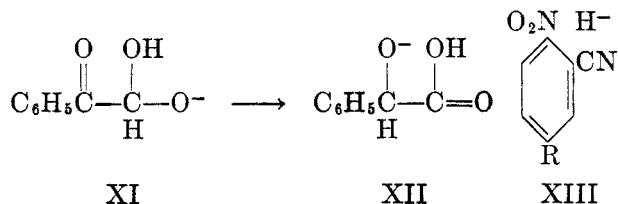
The structure of intermediate VII is analagous to that (X) assigned by Meisenheimer (14) to the stable *sym*-trinitrobenzene—potassium cyanide adduct (15). Regarding VIII, the transition state in the nitro group displacement, it should be noticed that its negative charge resides in the cyano group; in other words, the cyano group, following entry in the first stage of this process, activates replacement of nitro in the second stage.

X
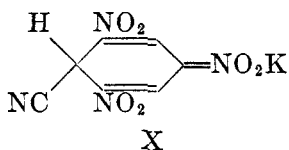
Energy considerations make it improbable that hydride ion is actually set free in the transformation of VII into VIII; more likely there is intramolecular mi-

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[6] Lobry de Bruyn (12) also believed that the point of entry of the cyano group was *ortho* to nitro; his mechanism for the von Richter reaction is in other respects quite different from ours.

gration with the hydrogen atom always more or less bonded to one carbon atom or the other. A similar case occurs in the rearrangement of phenylglyoxal to mandelic acid, for which tracer studies (16, 17) indicate hydride ion migration from XI to XII to be the essential step. For this transformation, Doering, Taylor and Schoenewaldt (16) have sketched a mechanism which avoids the liberation of free hydride ion. In the same vein, one may visualize the transition state in the VII to VIII transformation to be a resonance hybrid of these two structures, with in addition some contribution from structure XIII in which hydride is free.

$$
\underset{\text{XI}}{\overset{\overset{\displaystyle O}{\|} \quad \overset{\displaystyle OH}{|}}{C_6H_5\overset{}{C}-\underset{\underset{\displaystyle H}{|}}{C}-O^-}} \longrightarrow \underset{\text{XII}}{\overset{\overset{\displaystyle O^-}{|} \quad \overset{\displaystyle OH}{|}}{C_6H_5\overset{}{C}-\underset{\underset{\displaystyle H}{|}}{C}=O}} \qquad \underset{\text{XIII}}{\overset{O_2N \quad H^-}{\underset{R}{\bigcirc}CN}}
$$

We may now point out that intramolecular hydride ion transfer along the lines we have postulated would not be possible if cyanide had attacked *para* to nitro. Intermolecular transfer of hydride is conceivable, but it would surely require greater energy of activation and have as well a lower probability factor.

Reactions 4, 5, and 6 occur at lower temperatures than the von Richter reaction. Doubly-activated compounds like *m*-dinitrobenzene would be expected to form complexes with cyanide of type VII or X, with intermediate stability. At the temperatures employed for reactions 4, 5, and 6 there was likely not sufficient activation for hydride migration of the VII to VIII type. Instead, there was evidently oxidation of the complex (probably by nitro groups of other molecules) to a substituted *o*-nitrobenzonitrile which then suffered replacement of nitro by alkoxyl (from the alkaline alcoholic medium) to give the observed products.

The reactions of *m*-nitrobenzenesulfonic acid, in which there is weak activation by the ionized sulfo group, represent borderline behavior. The von Richter reaction (forming *o*- and *p*-sulfobenzoic acids) predominates, but aminosulfobenzoic acids are formed as by-products. Holleman (4) claimed to have isolated 2-amino-6-sulfobenzoic acid, 2-amino-4-sulfobenzoic acid, and 4-amino-2-sulfobenzoic acid in unspecified yields. Identification of aminosulfobenzoic acids is difficult because they decompose without melting when heated; in place of melting points, solubility and conductance values have been used by some workers as characteristics of identity. However, Holleman applied no such criteria; he heeded only analyses and the presence or absence of a blue fluorescence in assigning structures. Comparison with the careful identification of several aminosulfobenzoic acids by van Dorssen (18) has persuaded us that Holleman had evidence only for 2-amino-4-sulfobenzoic acid and probably one other isomer.

This point is of great interest to us, for if the other isomer were 4-amino-2-sulfobenzoic acid, attack of cyanide ion *para* to a nitro group would be shown to be possible, and this would necessitate fundamental alterations in the mechanism we postulate in this paper. It is clear that a re-examination of the action of

aqueous cyanide on *m*-nitrobenzenesulfonic acid with a careful search for 4-amino-2-sulfobenzoic acid as a possible product would be instructive.

The failure of most *ortho*-substituted nitro compounds to react with potassium cyanide probably can be ascribed to steric interference with resonance in the transition state. In the case of *o*-nitrobromobenzene, a large contribution by structure XIV would be essential to make the energy level of the transition state accessible under the reaction conditions used, but structure XIV is of high energy because of the strain on a coplanar nitro group between the two other groups *ortho*-situated (19).

XIV
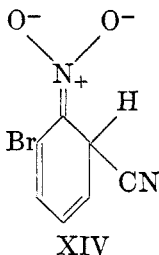
One of the strangest features of the von Richter reaction is the failure of *o*- and *p*-nitrohalobenzenes to give simple replacement of halo by cyano, as one would expect by analogy with other reactions of these compounds. Examination of two recent reviews on the preparation of nitriles (11, 20) reveals, however, that there are only a few isolated examples (and these involve compounds of very unusual structure) in which an aromatic substituent has been replaced by a cyano group in reaction with an alkali cyanide at moderate temperatures; in general, such replacements are obtained only under fusion conditions or by the use of copper compounds. This indisposition of cyanide to replace aromatic substituents is in contrast to its propensity to enter an unsubstituted position on an aromatic nucleus; examples of the latter are the facile cyanation of quinoline compounds by aqueous cyanide (11b) and the action of aqueous-alcoholic potassium cyanide on 1-nitroso-2-naphthol to form 1-amino-4-cyano-2-naphthol (21).

The failure of other common nucleophilic reagents to react with nitro compounds as cyanide does is probably due in part to the circumstance that they would become, after entry *ortho* to nitro, groups such as amino, alkoxyl or mercapto which would not activate the replacement of nitro by hydride. One might expect, from these considerations, sulfinate ions to react with nitro compounds in the von Richter manner, for they would become, after entry, sulfonyl groups which have considerable activating power (22). A number of reactions of sulfinates with nitro compounds have been studied; they appear, however, to go in a "normal" fashion.

EXPERIMENTAL

Melting points are uncorrected.

Materials. Eastman Kodak Co. preparations of the three nitrobromobenzenes and of *m*-nitroanisole were employed. Messrs. Henry Richanbach, David Williams, and Franklin Draper, Jr. graciously prepared for us *p*-nitroanisole, *o*-nitroanisole, and *m*-anisic acid, respectively. Fresh Mallinckrodt Purified granular potassium cyanide was used.

Standard procedure. Nitro compound, potassium cyanide, and solvent were sealed in a stout Pyrex tube which was heated in a furnace. In other cases, the mixture was refluxed in an open apparatus. When cool, the sealed tubes were opened; there was usually a mild pop signifying the release of gas pressure. The reaction mixture was washed into a flask with water and the mixture made strongly basic with sodium or potassium hydroxide. In early runs, the mixture was then refluxed for two hours (to hydrolyze nitriles); this treatment was later discontinued because it did not improve the yield of acids and caused deterioration of unreacted starting material. Steam-distillation of this basic mixture served to remove the organic solvent (ethanol or ethylene glycol) and unreacted starting material; when glycol was the solvent, two liters of distillate were collected *per* 75 ml. of solvent. Starting material was collected by filtration of this distillate.

The residue from the first steam-distillation was acidified and steam was run through again until 500 ml. of distillate had been collected for each gram of starting material used. This distillate, in which one could occasionally see a few crystals of the acid product, was made slightly alkaline with sodium carbonate, boiled down to about 200 ml., and acidified. The precipitated acid product was collected.

Runs with p-nitrobromobenzene. On this compound we tested various modifications of the experimental procedure. Representative runs are summarized in Table II. Except where otherwise noted, 4.0 g. of *p*-nitrobromobenzene and 2.6 g. of potassium cyanide were used with one hour of heating. Absolute ethanol was prepared by the lime method.

Behavior of m-nitrobromobenzene. A mixture of 4 g. of *m*-nitrobromobenzene, 2.6 g. of potassium cyanide, and 25 ml. of 95% ethanol was heated in a sealed tube one hour at 155°. No starting material was recovered when the reaction mixture was treated in the standard way, although 0.92 g. (23%) of crude acid product, m.p. 139–170°, appeared. (There was also 1.09 g. of tar.) The losses in fractional crystallization of this crude acid from water were large, but we estimate that roughly equivalent amounts of *ortho*- and *para*-bromobenzoic acid were present. At any rate, 0.30 g. of the more soluble *ortho* isomer, m.p. 141–142° (mixed m.p. with authentic *o*-bromobenzoic acid, 145–149°) and 0.10 g. of the *para* isomer, m.p. 249° (mixed m.p. with authentic *p*-bromobenzoic acid, 248–252°) were eventually isolated (*ortho*, *meta*, and *para*-Bromobenzoic acids melt at 150°, 155°, and 253° respectively, and melting points of isomer mixtures are strongly depressed).

Behavior of o-nitrobromobenzene. Tubes containing 4 g. of *o*-nitrobromobenzene, 2.6 g. of potassium cyanide, and 25 ml. of lime-dried ethanol were heated at 175° for one hour and for seven hours. Neither yielded, when treated in the standard way, either acidic product or unreacted starting material.

Behavior of nitrobenzene. Nitrobenzene (2.5 g.) and 15 g. of potassium cyanide were allowed to react in refluxing 90% ethylene glycol for three hours. By the standard method of purification, 0.54 g. (21%) of acid of m.p. 111–114° was obtained (no recovery of starting material). Recrystallized, this melted at 120–121° and did not depress the m.p. of authentic benzoic acid.

Behavior of p-nitroanisole. A mixture of 4 g. of *p*-nitroanisole, 3.4 g. of potassium cyanide, and 24 ml. of 48% ethanol in a sealed tube was heated an hour at 170–180°. By treatment of the reaction mixture in the standard way, 0.34 g. (8.5%) of starting material, m.p. 40–47° (recrystallized, it melted at 48–51° and did not depress the m.p. of authentic *p*-nitroanisole), and 0.12 g. (3%) of acid product, m.p. 95–102°, were isolated. Recrystallized, the acid melted at 101.5–102.5°. With authentic *m*-anisic acid of m.p. 104–105°, it gave mixed m.p. 104–105°.

Behavior of m-nitroanisole. A sealed tube containing 4 g. of *m*-nitroanisole, 3.4 g. of potassium cyanide, and 25 ml. of 95% ethanol was heated 85 minutes at 175–190°. By the standard purification procedure, 0.05 g. (1%) of acid, m.p. about 170° were obtained. After recrystallization from dilute ethanol, its m.p. was 180–182°. With authentic *p*-anisic acid of the same m.p., the mixed m.p. was not depressed. Recovered starting material, m.p 30–35°, weighed 0.81 g. (20%).

Behavior of o-nitroanisole. A sealed tube containing 4 g. of *o*-nitroanisole, 3.4 g. of potassium cyanide, and 25 ml. of 48% ethanol was heated an hour at 175–185°. The standard

isolation procedure yielded 1.0 g. of a neutral oil, presumably unreacted *o*-nitroanisole, but no acid product.

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