

## Decarboxylation of 2-Nitrobenzoic Acids

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Decarboxylation of 2-nitrobenzoic acid (0.4 M) in quinoline in the presence of metallic copper or copper(I) oxide or as the copper(I) or copper(II) salts generally gives around 60 % yield of nitrobenzene and around 20 % of 2,2'-dinitrobiphenyl. Heating of silver 2-nitrobenzoate gives nitrobenzene and *ca.* 10 % dinitrobiphenyl whereas decarboxylation with metallic silver gives nitrobenzene but no detectable amounts of dinitrobiphenyl.

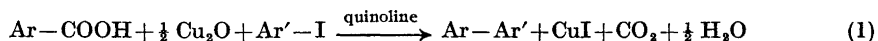
Analogous results were obtained with 2,4-dinitrobenzoic acid whereas no symmetric hexanitrobiphenyl was observed after decarboxylation of 2,4,6-trinitrobenzoic acid. A little 2,2',6,6'-tetranitrobiphenyl was observed in the copper-promoted decarboxylation of 2,6-dinitrobenzoic acid.

Some theoretical and practical implications are discussed.

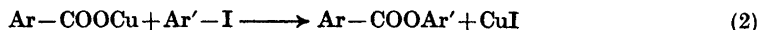
Copper chromium oxide catalysts and metallic copper have been used extensively for decarboxylation of aromatic and unsaturated carboxylic acids.<sup>1</sup> In addition oxidative decarboxylations of benzoic acids to phenols in the presence of copper(II) have been described.<sup>2</sup> Decarboxylations of silver salts of aromatic carboxylic acids have been reported in some special cases (*e.g.* Ref. 3).

Some years ago we screened the rates of decarboxylation of some aromatic carboxylic acids in quinoline in the presence of copper(I) oxide and found, not unexpectedly, that 2-nitrobenzoic acid decarboxylated more rapidly than most other acids.<sup>4</sup>

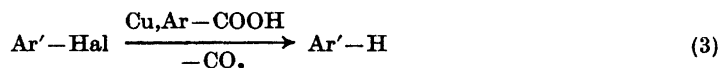
On that basis we investigated the decarboxylation of 2-nitrobenzoic, 2-thenoic and 2-furoic acids in the presence of copper(I) oxide and iodobenzenes in quinoline and found that 2-nitrobiphenyls, 2-phenylthiophenes, and 2-phenylfurans, respectively, were formed.<sup>4-6</sup> This reaction (1), which may be called "decarboxylative coupling", is clearly reminiscent of the Ullmann biaryl synthesis. So far, however, it seems to be restricted to rapidly decarboxylating acids.



With less readily decarboxylating acids, like benzoic acid, formation of esters (2) is often marked, especially when anhydrous copper(I) salts of the acids are used.<sup>7</sup>



Otherwise a "reductive" dehalogenation (3) may also take place and has occasionally been recommended for preparative use,<sup>8</sup> although the fate of the Ar part is not clear.



During further work we observed that significant amounts of 2,2'-dinitrobiphenyl were formed during the copper(I) oxide-promoted decarboxylation of 2-nitrobenzoic acid.

The present work concerns mainly the decarboxylation of 2-nitrobenzoic, 2,4-dinitrobenzoic, 2,6-dinitrobenzoic, and 2,4,6-trinitrobenzoic acids with copper reagents and is centered on the formation of symmetric biphenyls and "normal" decarboxylation products. Also some silver-promoted decarboxylations have been studied, and some exploratory experiments done with other metals and with some other acids.

## RESULTS

In one series of experiments 2-nitrobenzoic acid was heated in quinoline (initially 0.4 M solution) with metallic copper, copper(I) oxide, or copper chromium oxide catalyst, or as the copper(I) or copper(II) salts, at *ca.* 240°. In all cases the carbon dioxide evolution was rapid and practically complete within 15 min.

At first, interest was focused on the formation of 2,2'-dinitrobiphenyl from various reagents, and somewhat to our surprise it was of the same order of magnitude (*ca.* 13–24 %) with zero-, mono-, and divalent copper. The main results are summarised in Table 1.

Table 1. Main products of decarboxylation of 2-nitrobenzoic acid in quinoline at *ca.* 240°. Initial concentrations 1–0.4 M. Average of three experiments.

	Nitrobenzene %	2,2'-Dinitrobiphenyl %
Metallic copper	70	15
Copper(I) oxide	59	24
Copper(I) oxide + 4-Iodomethoxybenzene <sup>a</sup>	27	23
Copper(II) salt	50	22
Copper-chromium oxide	67	4
Copper(I) salt	60	16
Metallic silver	83	—
Silver salt	79	9

<sup>a</sup> 30 % yield of 4-methoxy-2'-nitrobiphenyl.

The amounts of nitrobenzene were not impressive (60–70 %). 2,2'-Dinitrobiphenyl was formed also in the presence of 4-iodomethoxybenzene and copper(I) oxide. The observation that the yield of 2,2'-dinitrobiphenyl here is the same as that in the reaction with copper(I) oxide without iodoarene may be significant. The unsymmetric 4-methoxy-2'-nitrobiphenyl seems to be formed at the expense of the nitrobenzene. This may indicate different intermediates for formation of nitrobenzene and unsymmetric biphenyl on one hand, and 2,2'-dinitrobiphenyl on the other.

The formation of biaryls and normal decarboxylation products from various nitrobenzoic acids in the presence of copper(I) oxide is summarised

Table 2. Main products of decarboxylation of various nitrobenzoic acids (Ar—COOH) in the presence of copper(I) oxide in quinoline at 240°. Initial concentrations 0.4–2.5 M.

Acid	Ar—H %	Ar—Ar %
2-Nitrobenzoic	59	24
2,4-Dinitrobenzoic	61	26
2,6-Dinitrobenzoic	82	4
2,4,6-Trinitrobenzoic	65	—

in Table 2. 2,4-Dinitrobenzoic acid reacts rather like 2-nitrobenzoic acid whereas little symmetric biaryl is formed from 2,6-dinitrobenzoic acid, and none from 2,4,6-trinitrobenzoic acid.

Decarboxylation of silver salts of several benzoic acids was found to be rapid and in several cases gave biaryls (Table 1 and Experimental). Metallic silver proved to be a convenient catalyst for decarboxylation of the nitro-

Table 3. Decarboxylation of various nitrobenzoic acids in the presence of silver powder in quinoline at 240°.

Acid	Ar—H %
2-Nitrobenzoic	83
2,4-Dinitrobenzoic	86
2,6-Dinitrobenzoic	90
2,4,6-Trinitrobenzoic	80

benzoic acids to give the nitroarenes in high yields but no nitrobiaryls (Table 3). The metallic silver was less efficient with 2-fluorobenzoic acid, and no carbon dioxide evolution was detected for benzoic acid itself.

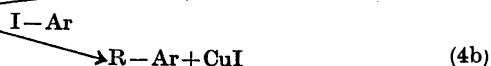
In some exploratory experiments with nickel and palladium we found a slow evolution of carbon dioxide; the rates fall in the series Pd<sup>2+</sup>, Pd<sup>0</sup>, Ni<sup>2+</sup>, Ni<sup>0</sup>.

## DISCUSSION

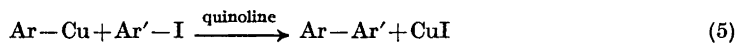
Many carboxylic acids are thought to be thermally decarboxylated as the anions to form carbon dioxide and a carbanion, which may then combine with a proton.<sup>9</sup>

There is strong evidence that 2,4,6-trinitrobenzoic acid is decarboxylated in aqueous solution in that way.<sup>10</sup>

If copper-catalysed decarboxylation proceeds *via* the copper(I) salts of the acids, organocopper(I) compounds would be plausible intermediates (eqn. 4).

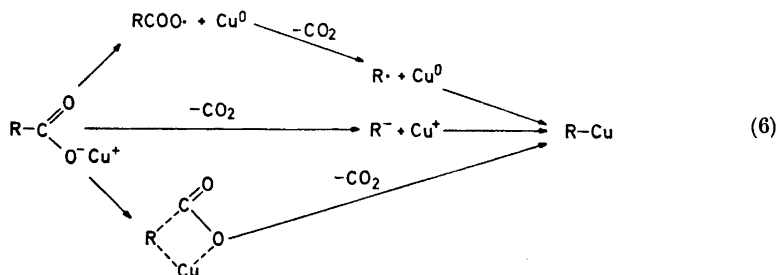


This hypothesis is supported by the decarboxylative coupling since the coupling is analogous to reactions of arylcopper compounds with iodoarenes, which are particularly selective for 2-thienylcopper (eqn. 5).<sup>5</sup> However, so far we have not been able to prepare and investigate 2-nitrophenylcopper.



An analogy to the formation of the postulated arylcopper intermediates is provided by the formation of organomercurials from mercury(II) salts of carboxylic acids.<sup>11</sup>

The formation of an organocopper compound from a copper(I)-carboxylate could apparently proceed by different routes — homolytic, heterolytic, or perhaps even electrocyclic (eqn. 6).



Several organocopper compounds, including arylcoppers, are known to “dimerise” with elimination of elemental copper (eqn. 7). The mechanism for this reaction is not yet fully known. A similar dimerisation to biaryls can be brought about by oxidation — by air or sometimes even by nitro compounds (*cf.* Ref. 12).



One may assume that dimerisation would be favoured if the concentration of the intermediate (organocopper) compound were high.

Such a high concentration would be expected for rapidly decarboxylating acids like 2-nitrobenzoic and 2,4-dinitrobenzoic acids which form appreciable amounts of the symmetrical biaryls and would provisionally support the aryl-copper hypothesis. On the other hand there are several rapidly decarboxylating acids which give little or no symmetric biaryl (2,6-dinitrobenzoic, 2,4,6-trinitrobenzoic, and 2-thenoic acids).

The situation is further complicated by the facts that the decarboxylation is rapid not only for the copper(I) 2-nitrobenzoate but also for the copper(II) salt and even for the acid itself in the presence of metallic copper, and that comparable amounts (13–24 %) of 2,2'-dinitrobiphenyl are formed in all cases (when the initial concentration is 0.4 M).

If 2-nitrophenylcopper were an intermediate, one would also expect it to react with added ketones or aldehydes, in analogy with the reactions described by Gilman and Straley between phenylcopper and, *e.g.*, benzophenone.<sup>13</sup> We have tried the decarboxylations also in the presence of some oxo compounds (see Experimental) but so far no evidence for reaction between the decarboxylating acid and these compounds has been obtained. However, the conditions differ widely and the further interpretation of this negative result should await further investigations. The formation of 2-nitrodiphenylamine (*ca.* 10 %) in some cases, however, could be due to reaction between a 2-nitrophenylcopper intermediate and nitrobenzene.

Another factor which should be considered is the origin and path of the protons replacing the carboxyl group. In decarboxylation of the acids, water formed in a preliminary salt formation would appear to be a natural source. However, even when the salts are decarboxylated under anhydrous conditions, large amounts of the normal decarboxylation product are formed, indicating that the hydrogen may be taken from the solvent or from other reactants. This phenomenon seems to be related also to the "reductive dehalogenation" encountered in the Ullmann biaryl synthesis.<sup>8</sup>

Clearly further work is needed to establish the nature of the reactions involved in the copper-catalysed decarboxylation of nitrobenzoic acids. Also the connection between the decarboxylation and the reactions of nitroarenes with organocopper compounds<sup>14</sup> are of interest.

Decarboxylative dimerisation of 2-nitrobenzoic acid and some other acids in the presence of various copper reagents has been observed independently by Cairncross *et al.*<sup>15</sup> and by Cohen and Schambach.<sup>16</sup>

Cairncross *et al.* have also shown that pentafluorophenylcopper is formed on decarboxylation of copper(I) pentafluorobenzoate, thus providing the first direct demonstration of an organocopper intermediate in the decarboxylation.<sup>15</sup>

## EXPERIMENTAL

Melting points were determined on a micro hot stage. Infrared spectra were recorded on Perkin Elmer No. 421 instrument, and gas chromatograms on an Aerograph 204-1B with 5 or 10 % SE 30 on Chromosorb W. The products were also analysed by thin-layer chromatography on fluorescent silica gel generally using toluene as developer.

Synthetic quinoline ("Min. 99 % puriss") was purified by extracting a solution in hydrochloric acid several times with ether. The solution was alkalinised and the quinoline recovered, dried and distilled.

*General procedure.* A reaction flask (100 ml) equipped with a reflux condenser was charged and heated in a metal bath, usually at 240°, for 1 h.

During some decarboxylations the carbon dioxide evolution was measured. The reaction flask (100 ml) was then fitted with a nitrogen inlet tube, reaching to the bottom, and a reflux condenser. The condenser was connected to an absorption train with a U-tube containing activated charcoal and anhydrous magnesium perchlorate that was connected *via* a three-way valve to tubes for carbon dioxide absorption (Ascarite and magnesium perchlorate). The Ascarite tubes were weighed at short intervals. In all experiments quinoline was used as a solvent. The reaction was interrupted after 60 min and the mixture, when cool, was diluted with *ca.* 200 ml ether. The solids were filtered off and washed with ether. The filtrate was extracted with hydrochloric acid (2 M) in order to remove the remaining quinoline. The ether phase was washed with water, dried with sodium sulphate and evaporated. The residue was investigated by GLC or TLC and separated by distillation or chromatography on silica gel.

*2-Nitrobenzoic acid and copper(I) oxide.* 2-Nitrobenzoic acid (0.01 mole), copper(I) oxide (0.005 mole) and quinoline (25 ml) were kept at 240° for 1 h. Distillation gave nitrobenzene (0.72 g, 59 %, b.p. 60–65°/0.5 mm). The residue was recrystallised from methanol to give 2,2'-dinitrobiphenyl, m.p. 127–128° (0.35 g, 24 %). (Lit.<sup>17</sup> m.p. 127–128°.)

*2-Nitrobenzoic acid and copper.* 2-Nitrobenzoic acid (0.01 mole), copper powder (electrolytic grade, 0.007 mole) and quinoline (25 ml) were kept at 240° for 1 h. Separation of the evaporation residue on silica gel with toluene gave nitrobenzene (0.86 g, 70 %) and 2,2'-dinitrobiphenyl, m.p. 127–128° (0.17 g, 15 %). The reaction was repeated and the crude reaction product was analysed by GLC with naphthalene and 4-methoxybiphenyl as internal standards. The triple analysis gave the following average results: nitrobenzene (70 %) and 2,2'-dinitrobiphenyl (13 %).

*2-Nitrobenzoic acid and copper-chromium oxide catalyst.* 2-Nitrobenzoic acid (0.01 mole), copper chromium oxide<sup>18</sup> (4.3 g; the amount corresponds to 0.014 mole of copper) and quinoline (25 ml) were kept at 240° for 1 h. Yield of CO<sub>2</sub> 86 %. Separation of the evaporation residue on silica gel with toluene-light petroleum (b.p. 40–60°) gave: nitrobenzene (0.82 g, 67 %), 2,2'-dinitrobiphenyl (0.05 g, 4 %), and 0.05 g of a yellow-coloured liquid product. According to TLC this product is more strongly absorbed on silica gel than is 2,2'-dinitrobiphenyl. The infrared spectrum showed a band at 1730 cm<sup>-1</sup>. The product, which is soluble in sodium hydroxide, was not further investigated.

*Copper(I) 2-nitrobenzoate.* 2-Nitrobenzoic acid (0.2 mole) and copper(I) oxide (0.1 mole) were boiled in toluene (*ca.* 300 ml) for 16 h under nitrogen. The water (1.5 ml) was continuously removed by azeotropic distillation. The yellow copper(I) 2-nitrobenzoate was filtered off and washed several times with hot toluene to remove the traces of unreacted acid and copper(II) bis(2-nitrobenzoate)·H<sub>2</sub>O. The copper(I) salt was vacuum dried to constant weight. Yield 96 %. The product was analysed by titration of copper with 0.01 M EDTA solution at pH 7–8 using murexide as indicator, after treatment with nitric acid. (Found: C 36.3; H 2.1; O 27.8; N 6.0; Cu 27.4. Calc. for C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>Cu: C 36.6; H 1.75; O 28.0; N 6.1; Cu 27.7.)

Dry copper(I) 2-nitrobenzoate (0.01 mole) was reacted in quinoline (25 ml) at 240° for 1 h. CO<sub>2</sub> yield 98 %. Separation on silica gel with toluene-light petroleum (b.p. 40–60°) gave: nitrobenzene (0.74 g, 60 %), 2-nitrodiphenylamine (0.05 g, 5 %; m.p. 75–76°, lit.<sup>19</sup> m.p. 75°, UV spectrum in accord with literature values<sup>20</sup>), and 16 % of 2,2'-dinitrobiphenyl.

*Copper(II) bis(2-nitrobenzoate).* Dry copper(II) bis(2-nitrobenzoate) (0.025 mole) was heated in quinoline (25 ml) at 240° for 1 h. CO<sub>2</sub> yield 90 %. Separation on silica gel with 20 % toluene in light petroleum (b.p. 40–60°) gave: nitrobenzene (3.07 g, 50 %); 2,2'-dinitrobiphenyl (1.34 g, 22 %); 1.1 g of yellow oil (mainly 2-nitrodiphenylamine according to GLC and TLC); 1 g of an orange-coloured crystalline substance, m.p. 111–113°, after sublimation.

The reaction was repeated and the reaction product analysed by GLC with naphthalene and 4-methoxybiphenyl as internal standards. Triple analysis gave the following average results: nitrobenzene 50 % and 2,2'-dinitrobiphenyl 21 %.

*2-Nitrobenzoic acid, copper(I) oxide and 4-iodomethoxybenzene.* 2-Nitrobenzoic acid (0.06 mole), 4-iodomethoxybenzene (0.05 mole), copper(I) oxide (0.04 mole) and quinoline (25 ml) were kept at 240° for 1 h. Distillation of the evaporation residue gave a low-

boiling material shown to be nitrobenzene (2 g, 27 %, b.p. 60–65°/0.5 mm). GLC analysis of the residue showed peaks corresponding to 2,2'-dinitrobiphenyl and 2-nitro-4'-methoxybiphenyl. Separation on silica gel with 20 % toluene in light petroleum gave 2-nitro-4'-methoxybiphenyl, m.p. 60–63° (5.3 g, 30 %), and 2,2'-dinitrobiphenyl, m.p. 125–127° (1.7 g, 23 %).

*2-Nitrobenzoic acid and silver.* 2-Nitrobenzoic acid (0.01 mole), silver powder (0.007 mole) and quinoline (25 ml) were kept for 0.5 h at 235–240°. CO<sub>2</sub> yield, 97 %. GLC analysis of the evaporation residue (1.1 g) showed just one peak in the range where nitrobenzene could be expected. Thin layer separation on silica gel with toluene showed only one spot, for nitrobenzene. Triple analysis by GLC with naphthalene as internal standard showed an average yield of 83 % nitrobenzene.

*Silver 2-nitrobenzoate.* Dry silver 2-nitrobenzoate (0.005 mole) was heated in quinoline (25 ml) at 235–240° for 1 h. CO<sub>2</sub> yield, 98 %. GLC analysis of the evaporation residue showed peaks corresponding to nitrobenzene and 2,2'-dinitrobiphenyl. Triple analysis with internal standards gave the following average results: nitrobenzene 79 %, and 2,2'-dinitrobiphenyl 9 %.

*2,4-Dinitrobenzoic acid and copper(I) oxide.* 2,4-Dinitrobenzoic acid (0.1 mole), copper(I) oxide (0.05 mole), and quinoline (40 ml) were heated at 240° for 1 h. The crystalline reaction product (1,3-dinitrobenzene and 2,2',4,4'-tetranitrobiphenyl) was separated on silica gel using toluene, to give 61 % of 1,3-dinitrobenzene (m.p. 88–90°) and 26 % of 2,2',4,4'-tetranitrobiphenyl (m.p. 164°–165°), lit.<sup>21</sup> m.p. 165°. The latter was identified by comparison with the product formed by Ullmann reaction of 2,4-dinitrochlorobenzene.<sup>21</sup>

*2,6-Dinitrobenzoic acid and copper(I) oxide.* 2,6-Dinitrobenzoic acid (0.05 mole), copper(I) oxide (0.025 mole) and quinoline (25 ml) were heated at 240° for 1 h. Separation on silica gel with toluene gave 1,3-dinitrobenzene (8.5 g, 82 %, m.p. 90–92°) and 2,2',6,6'-tetranitrobiphenyl (0.35 g, 4.2 %, m.p. 219–221°), lit.<sup>22</sup> m.p. 218–219°. The latter was identified by comparison with an authentic product.

*2,4,6-Trinitrobenzoic acid and copper(I) oxide.* 2,4,6-Trinitrobenzoic acid (0.01 mole), copper(I) oxide (0.005 mole) and quinoline (40 ml) were heated at 240° for 1 h. Separation on silica gel with toluene gave 65 % of 1,3,5-trinitrobenzene, m.p. 121–122°, and 0.42 g of a product, m.p. 240–242° (after sublimation), molecular weight 349 according to mass spectroscopy. No evidence for the presence of 2,2',4,4',6,6'-hexanitrobiphenyl was obtained.

*2,4-Dinitrobenzoic acid and silver.* 2,4-Dinitrobenzoic acid (0.01 mole), silver powder (0.007 mole), and quinoline (25 ml) were heated at 240° for 1 h. Yield of CO<sub>2</sub> 100 %. TLC and GLC of the crude product showed only one component. Purification on silica gel with toluene gave 86 % of 1,3-dinitrobenzene, m.p. 88–90°.

*2,6-Dinitrobenzoic acid and silver.* 2,6-Dinitrobenzoic acid (0.01 mole), silver powder (0.007 mole) and quinoline (25 ml) were heated at 240° for 1 h. CO<sub>2</sub> yield 100 %, 1.65 g of the crude crystalline reaction product, m.p. 85–94°, was recrystallised from methanol. Both TLC and GLC analysis showed that the product was practically homogeneous. Yield 90 % of 1,3-dinitrobenzene, m.p. 88–91°.

*2,4,6-Trinitrobenzoic acid and silver.* 2,4,6-Trinitrobenzoic acid (0.01 mole), silver powder (0.007 mole) and quinoline (30 ml) were heated at 240° for 1 h. CO<sub>2</sub> yield 100 %. GLC analysis of the evaporation residue showed one peak in the range where 1,3,5-trinitrobenzene could be expected. The crystalline reaction product (2.1 g), recrystallised from methanol, gave 80 % of 1,3,5-trinitrobenzene, m.p. 121–122°.

*Silver 2,4-dinitrobenzoate.* Dry silver 2,4-dinitrobenzoate (0.01 mole) and quinoline (25 ml) were kept at 235–240° for 1 h. CO<sub>2</sub> yield 100 %. The crystalline reaction product, m.p. 80–91°, was analysed by GLC and TLC. Both analyses showed only one component. Recrystallisation gave 1.45 g of 1,3-dinitrobenzene, m.p. 88–90°.

*2-Fluorobenzoic acid and silver.* 2-Fluorobenzoic acid (0.01 mole), silver powder (0.02 mole) and quinoline (25 ml) were kept at 240° for 2 h. CO<sub>2</sub> yield 25 %.

*Silver 2-fluorobenzoate.* Dry silver 2-fluorobenzoate (0.01 mole) and quinoline (25 ml) were kept at 240° for 1 h, CO<sub>2</sub> yield 100 %. GLC of the evaporation residue showed ca. 5 % of 2,2'-difluorobiphenyl. Fluorobenzene, 78 %, was collected in a cold trap.

*2-Thenoic acid and silver.* 240°. Reaction time 1 h. 2-Thenoic acid (0.01 mole), silver powder (0.02 mole) and quinoline (25 ml) were heated at 240° for 1 h. CO<sub>2</sub> yield 98 %. No bithienyl was noticed.

*Benzoic acid and silver.* Benzoic acid (0.01 mole), silver powder (0.02 mole) and quinoline (25 ml) were heated at 240° for 3 h. No CO<sub>2</sub> evolved.

*Silver benzoate.* Dry silver benzoate (0.001 mole) and quinoline (25 ml) were heated at 240° for 2 h. CO<sub>2</sub> yield 100 %. GLC analysis of the evaporation residue showed less than 1 % of biphenyl.

*2-Nitrobenzoic acid and palladium.* 2-Nitrobenzoic acid (0.01 mole), palladium powder (0.007 mole) and quinoline (25 ml) were heated at 240° for 2.5 h. CO<sub>2</sub> yield 36 %. GLC showed that 80 % of the neutral reaction product is nitrobenzene. Quantity of 2,2'-dinitrobiphenyl less than 2 %.

*Palladium 2-nitrobenzoate.* Dry palladium 2-nitrobenzoate (0.005 mole) and quinoline (25 ml) were heated at 240° for 2.5 h. CO<sub>2</sub> yield 57 %. Nitrobenzene was formed but little if any dinitrobiphenyl.

*2-Nitrobenzoic acid and nickel.* 2-Nitrobenzoic acid (0.01 mole), nickel powder (0.007 mole) and quinoline (25 ml) were heated at 240° for 3 h. CO<sub>2</sub> yield 6 %. GLC showed only a peak for nitrobenzene.

*Nickel(II) bis(2-nitrobenzoate).* Dry nickel(II) bis(2-nitrobenzoate) (0.005 mole) and quinoline (25 ml) were heated at 240° for 4 h. CO<sub>2</sub> yield 15 %. GLC showed peaks corresponding to nitrobenzene and 2,2'-dinitrobiphenyl, and one peak analogous to that of the unidentified liquid formed during copper(II) bis(2-nitrobenzoate) decarboxylation.

*2-Nitrobenzoic acid and benzophenone.* 2-Nitrobenzoic acid (0.06 mole), benzophenone (0.05 mole), copper(I) oxide (0.04 mole), and quinoline (25 ml) were heated at 240° for 1 h. Distillation gave 54 % nitrobenzene. Separation of the residue on silica gel gave, with toluene, 20 % 2,2'-dinitrobiphenyl, and subsequently with toluene and chloroform, 70 % of the original benzophenone.

Analogous experiments were done with 2-nitrobenzoic acid and benzaldehyde, 2-nitrobenzoic acid and acetophenone, and 2-nitrobenzoic acid and 4-methoxybenzaldehyde. In all cases the quantities of nitrobenzene and 2,2'-dinitrobiphenyl were similar, and no evidence was obtained for reactions between the nitrobenzoic acid or nitrophenyl groups with the oxo-compounds.

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## REFERENCES

1. Schenkel, H. and Schenkel-Rudin, M. *Helv. Chim. Acta* **31** (1948) 514.
2. Kaeding, W. W. and Collins, G. R. *J. Org. Chem.* **30** (1965) 3750.
3. Sartori, P. and Gollock, A. *Chem. Ber.* **102** (1969) 1765.
4. Nilsson, M. *Acta Chem. Scand.* **20** (1966) 423.
5. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **22** (1968) 1998.
6. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968) 2585.
7. Lewin, A. H. and Cohen, T. *J. Am. Chem. Soc.* **5** (1966) 4521.
8. Bacon, R. G. R. and Hill, H. A. O. *Quart. Rev.* **19** (1965) 95.
9. Brown, M. A. *Quart. Rev.* **5** (1951) 131.
10. Johnson, P. and Moelwyn-Hughes, E. A. *Proc. Roy. Soc. (London)* **1940** 175.
11. Maleanova, L. G. and Nesmeyanow, A. N. *Methods of Elementoorganic Chemistry*, Amsterdam 1967, Vol. 4, p. 259.
12. Whitesides, G. M., Fischer, Jr., W. F., San Filippo, Jr., J. Bashe, R. W. and House, H. O. *J. Am. Chem. Soc.* **91** (1969) 4871.
13. Gilman, H. and Straley, J. M. *Rec. Trav. Chim.* **55** (1936) 821.
14. Björklund, C., Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) *In press*.
15. Cairncross, A., Roland, J. R., Henderson, R. M. and Sheppard, W. A. *Personal communication; J. Am. Chem. Soc.* **92** (1970) 3187.
16. Cohen, Th. and Schambach, R. *Personal communication; J. Am. Chem. Soc.* **92** (1970) 3189.



17. von Niementowski, S. *Ber.* **34** (1901) 3326.
18. Vogel, A. J. *A Text-book of Practical Organic Chemistry*, London 1956, p. 321.
19. Schöpf, A. *Ber.* **23** (1890) 1840.
20. Schroeder, W. A., Wilcox, P. E., Trueblood, K. N. and Dekker, A. O. *Anal. Chem.* **23** (1951) 1740.
21. Ullmann, F. and Bielecki, J. *Ber.* **34** (1901) 2177.
22. Borsche, A. and Rantscheef, Z. *Ann.* **379** (1900) 176.

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