

## Syntheses of Anthranilic Acid and Some Derivatives from *o*-Nitrotoluene

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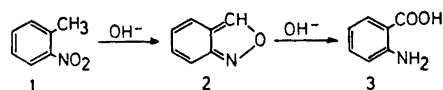
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Ethanol was used as solvent in an attempt to increase the yield in the conversion of *o*-nitrotoluene (1) to anthranilic acid (3) under basic conditions. This resulted in a yield of 13 % of anthranilic acid. 2-Carboxy-2'-methyl-azobenzene (4) was isolated in low yield.

Reaction of *o*-nitrotoluene with ammonia in the vapour phase resulted in the formation of *o*-aminobenzamide (6) in 30 % yield. If silica gel was used as a catalyst, *o*-aminobenzonitrile (8) was the product (30 % yield). The mechanism of formation of *o*-aminobenzamide was discussed and the possible intermediacy of anthranil (2) considered.

The interaction between the nitro group and the *o*-benzyl carbon atom in *o*-nitroaromatic compounds has long been a subject of interest.<sup>1</sup> A prominent reaction of such compounds is an intramolecular reduction-oxidation resulting in a more reduced nitro atom and a more oxidized carbon atom than in the starting compound. The reduction-oxidation takes place under a variety of conditions: by the influence of light,<sup>2</sup> or by basic<sup>3,4</sup> or acidic<sup>5</sup> catalyses.

One well-known reduction-oxidation reaction is the formation of anthranilic acid (3) from *o*-nitrotoluene (1) under basic conditions.<sup>3,4</sup> The reaction is generally assumed to proceed *via* anthranil (2):



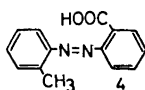
By using  $\text{K}^{18}\text{O}/\text{H}_2^{18}\text{O}$ , Kukhtenko<sup>6</sup> showed one of the carboxylic oxygens in anthranilic acid to come from the nitro group, and the other from  $\text{KOH}/\text{H}_2\text{O}$ . This result was in agreement with the reaction mechanism above, although a bimolecular reaction analogous to the monomolecular one cannot

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be excluded, especially as the formation of, *e.g.*, *o*-toluidine shows intermolecular reduction-oxidations to have taken place. The yield of anthranilic acid (3) from *o*-nitrotoluene under aqueous basic conditions was low (ca 15 %), and the large number of by-products made the isolation difficult. The reaction was run under rather severe conditions (heating to 200° in 70 % aqueous KOH<sup>3,4</sup>) and the yield might improve if less violent circumstances were applied.

In an attempt to mitigate the reaction conditions, *o*-nitrotoluene was refluxed with KOH or NaOH in ethanol. However, the yield of anthranilic acid was as low (13 %) as in the reactions run in water,<sup>4</sup> the new reaction conditions did not give any advantage from a preparative point of view.

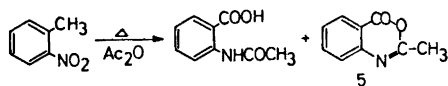
One new product was isolated: 2-carboxy-2'-methyl-azobenzene (4):



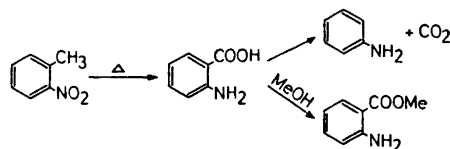
The structure was elucidated from its electronic spectrum ( $\lambda_{\max}$  434 nm and 323 nm) which indicated that the substance contained an azobenzene chromophore and from the IR spectrum which indicated carboxyl groups to be present. The structure was confirmed by comparison with an authentic sample made from *o*-nitrosobenzoic acid and *o*-toluidine. The compound 4 showed an interesting IR spectrum as it had an unusually high carbonyl frequency (1740  $\text{cm}^{-1}$ ), even higher than that of the methyl ester of 2-carboxyazobenzene (1730  $\text{cm}^{-1}$ ). The high carbonyl frequency was probably due to a strong internal hydrogen bond between the carboxyl hydrogen and the azo group, leaving the carbonyl oxygen "free" from the normal intermolecular hydrogen bond in carboxylic acids. 4-Carboxyazobenzene had a "normal" carbonyl frequency at 1690  $\text{cm}^{-1}$ . The intramolecular hydrogen bond of 2-carboxyazobenzene and its influence on the IR spectrum have been discussed by Ross and Warwick.<sup>7</sup>

The formation of anthranilic acid from *o*-nitrotoluene in the condensed phase was obviously hampered both by intermolecular reduction-oxidations and by condensation reactions (giving, *e.g.*, azo compounds and polymers). One possible way to avoid the intermolecular reactions would be to work in very dilute solution. This, however, would make the method less attractive from a preparative point of view. Another possibility would be to run the reaction in the vapour phase and this point was investigated further.

The formation of anthranilic acid from *o*-nitrotoluene in vapour phase was first reported by Löb,<sup>8</sup> who made *o*-nitrotoluene and water vapour react on a red-hot metal wire. Later, Löken<sup>9</sup> obtained *N*-acetylanthranilic acid and acetylanthranil (5) by the thermal reaction of *o*-nitrotoluene vapour with acetic anhydride:



In their studies of the thermal decomposition of nitroaromatics, Fields and Meyerson<sup>10</sup> found that *o*-nitrotoluene did not give the products usually obtained from aromatic nitro compounds *via* free radical pathways. Instead, the main product was aniline, indicating the formation of anthranilic acid followed by decarboxylation. When they run the thermolysis in the presence of methanol vapour, anthranilic acid was indeed isolated as the methyl ester. The yield was as high as 30–40 %.<sup>10</sup>



In our hands, their method gave only modest yields of methyl anthranilate (7 %), aniline (5 %), and *o*-cresol (8 %) together with large amounts of tar. A similar result was found when triethyl phosphate was tried as catalyst. When silica gel was used as catalyst, the yield of methyl anthranilate was even lower (0–3 %), and *o*-toluidine became the major product (13–20 %, Table 3).

The possibility that methanol reacted with anthranilic acid or some precursor like anthranil (2) by a nucleophilic mechanism was then considered. By trying different nucleophiles one could hope to find more efficient reagents to trap anthranilic acid or its precursor. Ammonia was tried, and the main product from the reaction was *o*-aminobenzamide (6) in *ca.* 30 % yield. The yields of this compound and identified by-products in a typical run (Run 3 in Table 4) are given in Table 1. In our hands, ammonia was thus superior to methanol in the reaction with anthranilic acid or its precursors.

The effects of the reaction temperature, the contact time, and the proportion of ammonia to *o*-nitrotoluene on the conversion of *o*-nitrotoluene and the yield of *o*-aminobenzamide were investigated. The results are given in Table 4. The investigations were of exploratory nature and were not intended for kinetic calculations. With a contact time of 10 sec, *o*-nitrotoluene started to react at approximately 400°, and at 600° 100 % had reacted (100 % conver-

Table 1. Thermolysis of *o*-nitrotoluene with ammonia at 550° (6.3 mol NH<sub>3</sub>/mol *o*-nitrotoluene). Contact time 10 sec.

Product	Percentage yields of reacted <i>o</i> -nitrotoluene
<i>o</i> -Aminobenzamide	29
Aniline	23
<i>o</i> -Toluidine	0
<i>o</i> -Cresol	<i>ca.</i> 1
<i>o</i> -Aminobenzonitrile	<i>ca.</i> 1
<i>o</i> -Hydroxybenzonitrile	<i>ca.</i> 1

sion). The yield of *o*-aminobenzamide calculated on the basis of reacted *o*-nitrotoluene was fairly insensitive to variations in reaction conditions. When the reaction temperature was varied between 500 and 550°, the ratio of ammonia to *o*-nitrotoluene between 2:1 and 92:1 and the contact time between 1 and 10 sec, the yield of *o*-aminobenzamide only varied between 24 and 35 % (Table 4). The yield of aniline was even less sensitive to variation in the reaction conditions; the variations described above caused the aniline yield to vary between 19 and 23 %, and without ammonia, a 15 % yield of aniline was obtained (Run, 5, Table 4).

The path of formation of *o*-aminobenzamide from *o*-nitrotoluene and ammonia is not clear, and the reaction might have taken place in the gas phase or in the tar in the reactor. One possible reaction path would be by formation of anthranilic acid which could then react further with ammonia to give the amide. However, when a solution of anthranilic acid in 1,2-dimethoxyethane was vaporized and brought into contact with ammonia at 500°, the ratio of *o*-aminobenzamide to aniline was *ca.* 1:10 as compared to *ca.* 15:10 for the reaction starting with *o*-nitrotoluene. A major part of the *o*-aminobenzamide from the reaction of *o*-nitrotoluene was thus not formed *via* anthranilic acid.

Another possible precursor for the amide would be anthranil (2), postulated as an intermediate in the formation of anthranilic acid from *o*-nitrotoluene in the liquid phase.<sup>6</sup> When anthranil was reacted with ammonia at 500°, *o*-aminobenzamide was indeed obtained as the major product. However, *o*-aminobenzonitrile was isolated together with the amide. The ratio of amide to nitrile was 3:1, well below that found when *o*-nitrotoluene was reacted with ammonia at 500° (amide:nitrile 100:1).

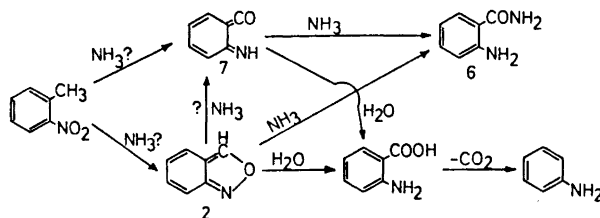
When *o*-aminobenzamide was formed from *o*-nitrotoluene, one mol of water was formed for each mol of amide. The possibility existed that the amide was indeed formed *via* anthranil, but that the water present either prevented the formation of *o*-aminobenzonitrile or hydrolyzed it to *o*-aminobenzamide. The ammonolysis of anthranil was therefore repeated in the presence of water vapour. The result was, however, almost the same as in the absence of water.

A further possibility was that either *o*-nitrotoluene itself or a reaction product of *o*-nitrotoluene with ammonia either prevented the formation of *o*-aminobenzonitrile from anthranil or catalyzed the hydrolysis of the nitrile to *o*-aminobenzamide. To test this point, a mixture of *o*-nitrotoluene and anthranil was reacted with ammonia at 500°.

Analysis of the reaction mixture showed it to contain *o*-aminobenzamide and aniline, but no *o*-aminobenzonitrile. The yields of *o*-aminobenzamide and aniline were of the same magnitude as found when anthranil and *o*-nitrotoluene alone were present. (Table 5).

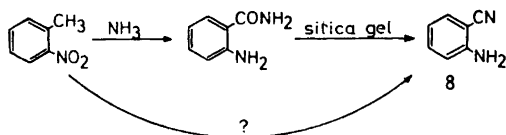
From this result, anthranil (2) could no longer be excluded as an intermediate in the formation of *o*-aminobenzamide from *o*-nitrotoluene. It might also be an intermediate in the formation of aniline *via* anthranilic acid. It was of course possible that anthranil was not an intermediate in the reaction of *o*-nitrotoluene, but that it was transformed to such an intermediate, *e.g.* 7.

This and several other questions are left to be answered: Why was *o*-aminobenzonitrile not found when *o*-nitrotoluene and anthranilic acid were



reacted together? Why was the yield of aniline virtually insensitive to the excess ammonia used in the reaction with *o*-nitrotoluene (Table 4)? If aniline was one of the products from competition between water and ammonia for anthranil as indicated above, one would not have expected such constancy. Further research will be necessary to answer these and other questions.

The dehydration of amides to nitriles in the gas phase has been described by Mitchell and Reid.<sup>11</sup> They used silica gel as a catalyst for the reaction. With silica gel in the reactor instead of Vycor chips, *o*-aminobenzonitrile (8) was the expected product from the reaction of *o*-nitrotoluene with ammonia:



Experiments showed this to be the case and yields of *ca.* 30 % (Table 6) of *o*-aminobenzonitrile were obtained.

However, not only the dehydration was catalyzed by the silica gel, but also the reaction of *o*-nitrotoluene as evident from Table 2. It was thus not possible to exclude a route from *o*-nitrotoluene to *o*-aminobenzonitrile which did not include *o*-aminobenzamide. Alumina and molecular sieves were tried as catalysts. Both gave lower yields of *o*-aminobenzonitrile than did silica gel. (10 % for alumina and 8 % for molecular sieves) (Table 6). However, both catalyzed the reactions of *o*-nitrotoluene (Table 2).

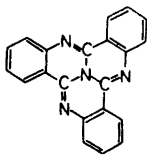
The increased reactivity may, however, not have been caused by catalysis of

Table 2. Reactivity of *o*-nitrotoluene in vapour phase over various reactor fillings.

Reactor filling	Reactor temp., °C	Contact time, sec.	% Reacted <i>o</i> -nitrotoluene
Vycor chips	500	10	30
Silica gel	450	5.5	93
Alumina	400	5.5	97
Molecular sieves	400	5.5	93

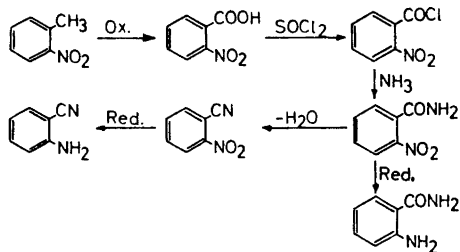
the reactions between the nitro group and the methyl group of *o*-nitrotoluene. Table 6 shows a significant yield of *o*-toluidine to occur in the catalyzed reactions. In the uncatalyzed reactions on the other hand, no *o*-toluidine was detected. The situation was the same when *o*-nitrotoluene was reacted with methanol (Table 3). The increased reactivity of *o*-nitrotoluene over silica gel, alumina, or molecular sieves may therefore have been caused by an increase in the rate of reaction of the nitro group and the "protecting" gas (*i.e.* ammonia or methanol).

From the catalyzed reactions there was also isolated a yellow, crystalline compound in low yield ( $\leq 1\%$ ). This compound had unusual thermal stability and could be sublimed at 400 to 500° without destruction. The mass spectrum indicated a molecular weight of 320. The molecular weight indicated the substance to have originated from three molecules of *o*-aminobenzonitrile. By inspection of molecular models, the most probable structure was that of tricycloquinazoline (9).<sup>12</sup> Comparison of physical data with those reported in the literature<sup>13,14</sup> confirmed the identification of (9).



9

The described methods for the preparation of *o*-aminobenzamide and *o*-aminobenzonitrile indicate the potential of gas phase reactions in preparative organic chemistry. Traditional synthesis in the liquid phase starting from *o*-nitrotoluene would normally include the following steps, using four steps to



make *o*-aminobenzamide and five to make *o*-aminobenzonitrile as compared to the one-step syntheses reported here. Even if the yields of *o*-aminobenzamide and *o*-aminobenzonitrile by the gas phase reactions were only moderate (*ca.* 30%), they compare favorably with the total yields in the liquid phase reactions indicated above.

## EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer Model 257. The electronic spectra were recorded on a Beckman DK-2 spectrophotometer. Gas chromatographic (GLC) analyses were carried out on a Perkin-Elmer F 11 gas chromatograph, with a hydrogen flame ionisation detector and using a 10 % SE 30 column. The internal standard method was used in quantitative analyses.

*Reaction of o-nitrotoluene in basic ethanol.* KOH (20 g) was crushed in *o*-nitrotoluene (115 g) and added to ethanol (95 %, 80 ml). The mixture was heated to 70°. A vigorous reaction started. Heating was stopped and the mixture refluxed for 10 min. After 40 min the mixture was poured into water (500 ml) and extracted four times with ether. The ether phase contained *o*-nitrotoluene (78 g, 63 % of starting material) and *o*-toluidine (2.7 g, 10 % of reacted *o*-nitrotoluene). The amounts of these two components were determined by GLC. The aqueous phase was acidified (pH 3.7) and extracted five times with ether. After drying and evaporation, a black paste (13.3 g) was obtained. Sublimation of a sample of the paste indicated it to contain anthranilic acid (4.5 g, 13 % of reacted *o*-nitrotoluene). Anthranilic acid (3.7 g, m.p. 142–144°) was isolated from the paste by extraction with aqueous HCl, neutralization to pH 3.7 and recrystallization of the precipitated product from ethanol. From the mother liquor, 2-carboxy-2'-methyl-azobenzene (4) was isolated (0.7 g, m.p. 138–140°), IR (CHCl<sub>3</sub>, 5 %): broad band from 3300–2500, maxima at 3000 and 2700 cm<sup>-1</sup>, 1740, 1600, 1450, 1280, 1160 cm<sup>-1</sup>. Electronic spectrum: λ<sub>max</sub> 434 nm (ε = 900 M<sup>-1</sup> cm<sup>-1</sup>), 323 nm (ε = 17 800 M<sup>-1</sup> cm<sup>-1</sup>). Thin layer chromatography (TLC) on silica gel, and elution with CHCl<sub>3</sub>:EtOH:AcOH 80:5:5 showed compound 4 to have R<sub>F</sub> 0.65 as compared to 0.85 for anthranilic acid. Substituting the equivalent amount of NaOH for the KOH previously used in the reaction gave essentially identical results to those described and the same was the case if *o*-nitrotoluene was dropped into a heated solution of KOH in ethanol.

*2-Carboxy-2'-methyl-azobenzene (4).* *o*-Nitrosobenzoic acid (1.0 g) and *o*-toluidine (0.75 g) were heated for 3 h at 50° in acetic acid (100 ml). The mixture was poured into water, extracted with ether and gave *o*-nitrosobenzoic acid (0.2 g) and 2-carboxy-2'-methylazobenzene (4) (0.4 g, m.p. 131–134°). Recrystallization from ethanol gave 0.15 g of 4, m.p. 139–140°, with IR, electronic spectrum and TLC behaviour identical to the compound isolated from the reaction of *o*-nitrotoluene.

*4-Carboxyazobenzene.* This compound was prepared by heating equimolar amounts of nitrosobenzene and *p*-aminobenzoic acid in acetic acid. 4-Carboxyazobenzene crystallized from the solution, m.p. after two recrystallizations from chloroform: 243–245° (lit.<sup>15</sup> 240°). IR (KBr): broad band from 3500–2400 cm<sup>-1</sup>, maxima at 3050, 2660 and 2550 cm<sup>-1</sup>, 1690, 1610, 1430, 1300, 1220, 870, 780, 690 cm<sup>-1</sup>. Electronic spectrum: λ<sub>max</sub> 444 nm (605 M<sup>-1</sup> cm<sup>-1</sup>).

*Methyl 2-carboxyazobenzene* was obtained from nitrosobenzene and methyl anthranilate. It was isolated by chromatography on silica gel and distilled (b.p. 100–110°/0.005 mmHg) IR (5 % CHCl<sub>3</sub>): 3010, 2960, 1730, 1600, 1440, 1300, 1130, 1090 cm<sup>-1</sup>. Electronic spectrum: λ<sub>max</sub> 440 nm (430 M<sup>-1</sup> cm<sup>-1</sup>).

*The gas phase reactions of o-nitrotoluene.* These reactions were run by evaporating *o*-nitrotoluene at 250° in a gas stream and bringing the gas mixture into the reactor. The reactor consisted of a vertical 60 cm long Vycor tube, o.d. 18 mm, equipped with a thermocouple well with o.d. 8 mm. The reactor was heated either by an electric heating coil (Reactor A) or by a furnace in the form of an electrically heated fluidized bed with silicon carbide (Crystolon No. 90) as the heat conductor (Reactor B). This bath was made according to the construction of Erlandson and Lundin.<sup>16</sup> In the reactor heated directly with heating wire, the temperature varied ± 20° and this reactor was used only for the introductory experiments. When the fluidized bed was used the temperature varied by ± 2° in the reactor.

*The gas phase reaction of o-nitrotoluene and methanol.* A mixture of 10 mol MeOH and 1 mol *o*-nitrotoluene was vaporized at 250° and blown into the reactor (Reactor B) by nitrogen. The results are given in Table 3.

*The gas phase reaction of o-nitrotoluene and ammonia.* This reaction was tried under a variety of conditions (Table 4). *o*-Nitrotoluene was vaporized at 250° in a stream of ammonia and blown into the reactor filled with Vycor chips. The products from the reactor were condensed and the gasses from the condensation passed through two washing

Table 3. Pyrolysis of *o*-nitrotoluene in the presence of methanol (10 mol methanol/mol *o*-nitrotoluene).

Reactor temperature °C	Contact time, sec	Reacted <i>o</i> -nitrotoluene, % <sup>a</sup>	Yields, % <sup>b</sup>			
			aniline	<i>o</i> -toluidine	<i>o</i> -cresol	Me anthranilate
603	15	100	6	0	8	7
599–602	11	100	5	0	10	7
499–502 <sup>c</sup>	11	54	14	0	8	7
532–556 <sup>d</sup>	6	98	9	13	5	0
442–456 <sup>d</sup>	6	93	6	20	2	3

<sup>a</sup> Analyzed by GLC.

<sup>b</sup> Analyzed by GLC, yields as percent of reacted *o*-nitrotoluene.

<sup>c</sup> 1 % triethyl phosphate added to the *o*-nitrotoluene-methanol mixture.

<sup>d</sup> Reactor A, silica gel as catalyst.

bottles containing methanol cooled to  $-75^{\circ}$ . The products were analyzed by GLC or liquid chromatography on silica gel and identified by IR spectra, m.p. (if crystalline) and GLC.

*Reaction of anthranilic acid with ammonia. 1. Examination for possible decarboxylation during evaporation.* A solution of anthranilic acid in 1,2-dimethoxyethane (6.0 ml/h, containing 1.5 g anthranilic acid (0.18 mmol/min) and 4.5 g 1,2-dimethoxyethane (0.83 mmol/min)) was pumped into an evaporator consisting of an electrically heated quartz tube filled with quartz chips. The evaporator was heated to  $250^{\circ}$  and ammonia (330 ml/min, 13 mmol/min) passed through during evaporation. The vapours were condensed and contained, in addition to 1,2-dimethoxyethane, only aniline and anthranilic acid in a ratio 1:1 as judged from TLC. No *o*-aminobenzamide was present.

*2. Anthranilic acid and ammonia.* After this test had shown part of the anthranilic acid to be evaporated unchanged, the vapours from the evaporator were passed into

Table 4. Pyrolysis of *o*-nitrotoluene (ONT) in the presence of ammonia.

Run No.	Reactor temp.	Contact time, sec	Mol NH <sub>3</sub> / Mol ONT	Reacted-ONT %	Yields, per cent of reacted ONT.	
					<i>o</i> -Amino-benzamide	Aniline
1	400	10	6.3/1	5	—	—
2	500	10	6.3/1	30	30	20
3	550	10	6.3/1	84	29	23
4	600	10	6.3/1	100	22	23
5	500	5	0	60	0	15
6	550	5	1/1	75	10	21
7	550	5	2/1	66	24	25
8	550	5	5/1	70	30	23
9	550	5	10/1	72	32	20
10	550	5	30/1	71	34	19
11	550	5	92/1	65	35	22
12	550	1	20/1	37	32	21
13	550	5	20/1	87	27	20
14	550	10	20/1	95	29	21



the reactor heated to 500°. During 1.5 h, 9.0 ml solution (containing 2.3 g anthranilic acid) was evaporated. The product from the reactor (1.24 g) contained aniline (1.05 g), and *o*-aminobenzamide (0.06 g). Assuming *ca.* 50 % of the anthranilic acid to have been decarboxylated to aniline during the evaporation (see above), 0.5 g (5 mmol) of the aniline was formed in the reactor at 500° together with 0.06 g (0.4 mmol) of *o*-aminobenzamide. The ratio of aniline to *o*-aminobenzamide from the reaction at 500° was thus 5:0.4, *i.e.* *ca.* 10:1. The amounts of aniline and *o*-aminobenzamide were determined by GLC and column chromatography.

*Reaction of anthranil with ammonia. 1. Examination of the evaporation process.* Anthranil (4.75 g/h) was pumped into the evaporator (heated to 200°) for 1 h. Ammonia (330 ml/min) was passed through the evaporator. The condensate from the evaporator (2.4 g, 50 %) consisted of pure anthranil as judged from IR, TLC, and GLC.

*2. Anthranil and ammonia at 500°.* The vapours from the evaporation were passed into the reactor heated to 500° for 1 h (4.75 g of anthranil, 40 mmol). The product from the reactor consisted of tricycloquinazoline (20 mg) and an oil (2.53 g). The oil contained *o*-aminobenzamide (1.6 g, 12 mmol, 30 %), *o*-aminobenzonitrile (0.5 g, 4 mmol, 10 %), and aniline (0.07 g, 2 %); no unreacted anthranil was detected. Ratio of *o*-aminobenzamide to *o*-aminobenzonitrile: 3:1. The products were determined by GLC and column chromatography.

*3. Anthranil and ammonia in the presence of water at 500°.* Anthranil (4.75 g/h, 0.67 mmol/min, totally 4.75 g) was evaporated in ammonia (330 ml/min, 13 mmol/min) as described above. The vapours were passed into the reactor at 500°, after being mixed with water vapour (0.64 g/h, 0.60 mmol/min, totally 0.64 g) at the top of the reactor. Analysis of the reaction product (GLC and column chromatography) showed it to contain *o*-aminobenzamide (1.22 g, 22 %), *o*-aminobenzonitrile (0.45 g, 9.5 %) and aniline (0.18 g, 5 %) together with small amounts of several unidentified substances.

*4. Anthranil and o-nitrotoluene with ammonia at 500°.* Anthranil (3.31 g) and *o*-nitrotoluene (3.31 g) were evaporated together in ammonia gas as described above. GLC analysis of the reaction mixture showed it to contain *o*-aminobenzamide (2.77 g), aniline (0.51 g), and *o*-nitrotoluene (1.28 g, 39 %). No *o*-aminobenzonitrile was detected. In Table 5, the yields from this reaction are compared to what would have been expected from *o*-nitrotoluene and anthranil alone with ammonia. In the calculations, the mean of the yields from the reactions of anthranil with and without water was used, and it was assumed that all *o*-aminobenzonitrile in these runs would have given *o*-aminobenzamide in the presence of *o*-nitrotoluene.

Table 5. The yields (g) from the reactions of *o*-nitrotoluene or anthranil alone with ammonia compared with the yields from the reaction of these two combined with ammonia. (For further explanations, see text above.)

Substance	Found from the combined reaction	Calculated		
		From <i>o</i> -nitrotoluene	From anthranil	Totally
<i>o</i> -Aminobenzamide	2.77	0.5	1.4	1.9
Aniline	0.51	0.23	0.13	0.36

*Reaction of o-nitrotoluene with ammonia at 500°.* *o*-Nitrotoluene (4.4 g/h, 0.53 mmol/min) was evaporated with ammonia (330 ml/min, 13 mmol/min) for 1 h as described for anthranil, and the vapours passed into the reactor at 500°. The product (3.13 g) was analyzed by GLC and TLC and contained *o*-nitrotoluene (2.05 g, 47 % of starting material), *o*-aminobenzamide (0.61 g, 26 % of reacted *o*-nitrotoluene), aniline (0.28 g, 17 % of reacted *o*-

Table 6. Reaction of *o*-nitrotoluene (ONT) with ammonia and catalyst.

Run	Reactor temp.	Mol NH <sub>3</sub> Mol ONT	Contact time, sec	Reacted ONT %	Yields in percent of reacted ONT			
					<i>o</i> -amino-benzonitrile	<i>o</i> -toluidine	aniline	Catalyst
15	450	28/1	5.5	93	25	5	15	Silica gel
16	400	28/1	5.5	40	34	11	5	
17	550	28/1	5.5	100	8	36	15	
18	400	28/1	5.5	93	0.5	9	4	Molecular sieves
19	400	28/1	5.5	97	10	16	15	
20	350	28/1	5.5	72	13	14	7	Alumina

nitrotoluene) and *o*-aminobenzonitrile (ca. 6 mg, 0.2 % of reacted *o*-nitrotoluene). Ratio of *o*-aminobenzamide to *o*-aminobenzonitrile ca. 100:1.

*Reaction of o-nitrotoluene with ammonia in the presence of catalysts.* These reactions were run analogously to the ones described in Table 4. The results are given in Table 6.

*Tricycloquinazoline.* From the catalytic reactions above, a yellow crystalline compound was isolated. The compound (m.p. 313–315°) sublimed at 400–500° (heating directly with a Bunsen burner). The base peak of the mass spectrum was at  $m^+/e = 320$ . Other prominent peaks:  $m^+/e$  206 (18 %), 160 (60 %) and 102 (24 %). Electronic spectrum (CHCl<sub>3</sub>),  $\lambda_{\max}$ : 450 nm ( $\epsilon = 2560 \text{ M}^{-1} \text{ cm}^{-1}$ ), 425 nm ( $\epsilon = 8000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 398 nm ( $\epsilon = 22\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 378 nm ( $\epsilon = 23\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 309 nm ( $\epsilon = 30\,400 \text{ M}^{-1} \text{ cm}^{-1}$ ), 296 nm ( $\epsilon = 31\,900 \text{ M}^{-1} \text{ cm}^{-1}$ ), 285 ( $\epsilon = 23\,700 \text{ M}^{-1} \text{ cm}^{-1}$ ).

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