LXXXV.—*Reduction of Emulsified Nitro-compounds.*
Part II. Some Extensions of the Method.

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AN emulsification process such as that described in Part I (this vol., p. 765) is applicable without considerable modification only to such nitro-compounds as are fluid at the ordinary or slightly elevated temperatures. Such nitro-compounds are exceptional in the aromatic series, and only nitrobenzene and *o*-nitrotoluene have been examined. The authors were persuaded by Dr. Herbert Levinstein to ascertain whether the method might not be extended to solid nitro-compounds by introducing into the system a fluid, such as benzene, insoluble in water but capable of wholly or partly dissolving the nitro-compound present. It was found that satisfactory results could be obtained in many instances, as many nitro-compounds are sufficiently soluble in benzene for the purpose, and, further, that, providing the nitro-compound is finely divided, it is not always necessary that it should initially be entirely dissolved in the quantity of benzene used, since, as reduction proceeds, undissolved nitro-compound passes quickly enough into solution. This modification of the original method is especially attractive in such cases where substituted hydroxylamines are the main products, for these substances are usually sparingly soluble in benzene and may often be separated with but slight loss owing to solubility, by mere filtration after addition of ammonium chloride at the critical stage in the reduction.

The reduction by sulphides and hydrosulphides of some of the

nitro-compounds investigated has already been studied by previous workers. This is true, for example, of phenyl-, *p*-tolyl-, and α -naphthylhydroxylamines, all of which were made by Willstätter (*Ber.*, 1908, **41**, 1936) by use of ammonium sulphide in alcoholic solution. The mode of applying sulphides as reducing agents described in the present communications does not appear to have been used before.

EXPERIMENTAL.

Except where, in the text, a statement to the contrary is made, the procedure adopted in each case was as follows :—

The nitro-compound, finely divided if necessary, was dissolved or suspended in from one and a quarter to twice its bulk of benzene, and placed in a stoppered bottle with the requisite quantity of the cold solution of sodium hydrosulphide. The calcium chloride, dissolved in the minimum necessary amount of water, was then added, and the whole shaken to form an emulsion, the shaking being occasionally repeated, if, for example, external cooling was necessary or the emulsion showed signs of deterioration. A lens was used to observe the appearance or disappearance of crystals in the mass.

The hydrosulphide solution was always prepared as described in Part I (*loc. cit.*) and with the same proportion of reagents; namely, hydrated sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), 275 grams; water, 200 c.c., and hydrochloric acid ($D=1\cdot16$), 97 c.c. This solution contains 10·9 per cent. of NaSH , and in the description of each experiment is given the weight of this solution taken.

Analysis of Substituted Hydroxylamines.

In a few cases where new substances have been isolated elementary analyses were carried out. In almost every other case the composition of the hydroxylamine was simply checked by an estimation of the quantity of stannous chloride oxidised in accordance with the equation

the operations being carried out much as in the usual method for estimation of nitro-groups, the excess of stannous chloride being measured after addition of Rochelle salt and bicarbonate by titration with a standard solution of iodine. The process was tested and found accurate with phenylhydroxylamine, and apparently gave satisfactory results in all the other cases tried. For brevity in citing the results of analyses, the quantity of stannous chloride oxidised by the hydroxylamine is expressed in volumes of $N/10\text{-SnCl}_2$.

p-Chlorophenylhydroxylamine from *p*-Chloronitrobenzene.

A solution of 11 grams of *p*-chloronitrobenzene (m. p. 83°) in 15 c.c. of benzene was mixed with 115 grams of the hydrosulphide solution and the whole emulsified by shaking with 10 grams of calcium chloride in water. The temperature was kept below 30° with the aid of external cooling. Crystals soon began to separate from the orange fluid. After one and a quarter hours, 10 grams of solid ammonium chloride were added and the whole was well shaken and filtered, when about 6.6 grams of nearly pure *p*-chlorophenylhydroxylamine remained on the filter; this quantity represents about 67–68 per cent. of that theoretically possible and only 0.22 gram of the product was subsequently found in the aqueous mother-liquor, whilst evaporation of the benzene layer yielded little but unchanged nitro-compound.

In a repetition of the process lasting an hour and a half, with the same quantities of materials, the weight of crystalline solid filtered off was 7.1 grams.

For identification, the substance was crystallised from hot benzene and then melted at 86.5° (compare Bamberger, *Ber.*, 1895, **28**, 245) (0.5008 gram required 3.44 c.c. of $N/10\text{-SnCl}_2$, whence $\text{NH}\cdot\text{OH}=22.2$. $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{OH}$ requires $\text{NH}\cdot\text{OH}=22.3$ per cent.).

On oxidation with acid dichromate and subsequent distillation in a current of steam, it gave *p*-chloronitrosobenzene melting at 86° (Bamberger, *loc. cit.*, p. 249).

p-Bromophenylhydroxylamine from *p*-Bromonitrobenzene.

For this reduction were taken:—*p*-bromonitrobenzene (m. p. 146°), 5 grams; benzene, 7 c.c.; the hydrosulphide solution, 52 grams; calcium chloride, 5 grams, in water. The process took place much as in the preceding case, and after one and a half hours, 5 grams of solid ammonium chloride were added and the solution was filtered. The solid *p*-bromophenylhydroxylamine, thus separated, weighed 3.2 grams, or about 65 per cent. of the maximum possible; about 0.12 gram was found in the aqueous part of the filtrate. After recrystallisation from hot benzene the substance melted at 90° (Bamberger, *loc. cit.*, p. 1221). On oxidation with ice-cold, acid dichromate, 2 grams yielded 1.32 grams of *p*-bromonitrosobenzene melting at 91.5° (*loc. cit.*).

p-Iodophenylhydroxylamine from *p*-Iodonitrobenzene.

Five grams of *p*-iodonitrobenzene (m. p. 166°) were reduced under conditions similar to those employed in the two preceding cases

and for about the same length of time. Approximately 3.0 grams of *p*-iodophenylhydroxylamine, or 64 per cent. of the amount theoretically possible, was at once obtained in solid form. The product, after crystallisation from hot benzene, melted at 103° and was converted by dichromate mixture into *p*-iodonitrosobenzene melting at 101.5° (compare Bamberger, *loc. cit.*, p. 249).

p-Tolylhydroxylamine from *p*-Nitrotoluene.

p-Nitrotoluene was the first solid nitro-compound which the authors studied, and it gave considerable trouble, as reduction by the emulsification process herein described takes place somewhat slowly, and if unduly prolonged leads to loss owing to formation of *p*-toluidine. The best results were obtained with the following conditions :—

p-Nitrotoluene (10 grams) in benzene (20 c.c.) is emulsified by shaking with 147 grams of the hydrosulphide solution and 10 grams of calcium chloride in water. After twenty-four hours at the laboratory temperature the solution is usually yellowish-green, and crystals are present, which may be secured by adding ammonium chloride (15 grams), shaking thoroughly, and filtering. About 4.8 grams of fairly pure *p*-tolylhydroxylamine remain on the filter, and after a recrystallisation from hot benzene the substance melts sharply at 98° (Bamberger, *loc. cit.*, p. 245); about 0.47 gram may be obtained by extraction of the aqueous part of the filtrate (0.9652 gram required 7.88 c.c. of *N*/10-SnCl₂, whence NH·OH=25.7. C₇H₇·NH·OH requires NH·OH=26.0 per cent.).

On oxidation, 2 grams gave 1.21 grams of *p*-nitrosotoluene, volatile in steam and melting at 47° (Bamberger, *loc. cit.*, p. 247).

Reduction of o-Nitrotoluene.

This compound, which, owing to its low melting point, does not require the addition of benzene, has not given satisfactory results. The maximum production of *o*-tolylhydroxylamine observed has been after seventy-two hours, and was about 15 per cent. of that theoretically possible. As crystals do not separate, this estimate has been based on the analysis of the total, washed, ethereal extract, after addition of ammonium chloride to dissolve calcium compounds; the method of analysis was that used by Goldschmidt in his well-known researches on the reduction of nitro-compounds (*Zeitsch. physikal. Chem.*, 1904, **48**, 424, 435; 1905, **56**, 1385; 1910, **71**, 437). No difficulty was experienced in obtaining more direct qualitative proof of the presence of *o*-tolylhydroxylamine in the ethereal extract specified, for on oxidising with acidified dichromate solution and

distilling with a current of steam *o*-nitrosotoluene passed over with the first few c.c. of distillate, set to a pale yellow solid, and separated from alcohol in white needles melting at 71° (*Ber.*, 1895, 28, 245).

As no amines, or only traces, were formed in the foregoing experiments, it may be concluded that the reduction of *o*-nitrotoluene is exceptionally slow, and it seems not improbable that failure to increase the yield by prolonged action of the agent is due to deterioration of the emulsifying precipitate of calcium compounds. This effect, in conjunction with the pressure of the hydrogen sulphide developed at temperatures much above the ordinary, renders it impracticable to heat in an open vessel when reducing with hydrosulphide and calcium chloride emulsions.

Experiments were tried in which *o*-nitrotoluene was emulsified with hot sodium hydrosulphide solution, using kieselguhr as emulsifying agent, but only *o*-toluidine was obtained; with calcium chloride present also, the hydrogen sulphide pressure was inconvenient and very little reduction was effected.

It may be added that Bamberger experienced unusual difficulty in obtaining *o*-tolylhydroxylamine in solid form, and in its slight tendency to separate from benzene it is evident that this compound and *o*-chlorophenylhydroxylamine differ markedly from the corresponding *p*-compounds.

Reduction of o-Chloronitrobenzene.

When this compound is reduced in benzene solution emulsified with the sodium hydrosulphide solution and calcium chloride at the ordinary temperature for two hours, no separation of the hydroxylamine occurs; but if ammonium chloride be then added, the aqueous layer extracted with ether, and the residues obtained by evaporation of the benzene and the ethereal extract combined, an oily product is left which, when tested by Goldschmidt's standard iodine method, gives results indicating a total production of *o*-chlorophenylhydroxylamine amounting to 62 per cent. of that theoretically possible. The substance itself has not been isolated, but the following experiment indicates that the oil in question may be utilised for preparing its derivatives.

The oil (2.0 grams) was oxidised with 4 grams of potassium dichromate in 270 c.c. of water containing 10 c.c. of concentrated sulphuric acid. On finally passing in a current of steam there passed over with the first 20 c.c. of distillate a pale yellow oil which solidified on cooling, yielding 1.30 grams of *o*-chloronitrosobenzene (Found: C=50.8; H=3.1; Cl=24.9. C_6H_4ONCl requires C=50.9; H=2.9; Cl=25.1 per cent.). The new substance dissolves readily in ether, alcohol, chloroform, benzene, and hot light petrol-

eum. It separates from alcohol in colourless needles melting at 56—57°.

m-Bromophenylhydroxylamine from *m*-Bromonitrobenzene.

The quantities used were :—*m*-bromonitrobenzene (m. p. 56°), 5 grams; benzene, 7 c.c.; sodium hydrosulphide solution, 74 grams; calcium chloride, 4 grams, and water. Three hours after emulsification ammonium chloride (5 grams) was added and the whole filtered. There remained on the filter, 2.53 grams of solid *m*-bromophenylhydroxylamine, or about 55 per cent. of the amount theoretically possible, an additional 0.2 gram remaining in the aqueous layer of the filtrate. The recrystallised product melted at 66° (compare *Ber.*, 1896, **29**, 864) and was converted by acidified dichromate solution into *m*-bromonitrosobenzene melting at 78° (compare *Ber.*, 1898, **31**, 1517, *anm.*). The nitroso-compound was analysed (Found: C=38.7; H=2.2; Br=42.8. Calc., C=38.8; H=2.2; Br=43.0 per cent.).

m-Chlorophenylhydroxylamine, $C_6H_4Cl \cdot NH \cdot OH$, from *m*-Chloronitrobenzene.

For this reduction 11 grams of *m*-chloronitrobenzene (m. p. 44.5°) were taken, with benzene (15 c.c.), sodium hydrosulphide solution (147 grams), calcium chloride (10 grams), and the necessary water. The colour of the liquid passed through green to pale orange, and after two and a half hours crystals separated. Ammonium chloride (10 grams) was added, the whole shaken and filtered, when 5.8 grams of nearly pure *m*-chlorophenylhydroxylamine were obtained in solid form. The filtrate yielded only 0.2 gram more.

m-Chlorophenylhydroxylamine crystallises from benzene in colourless plates melting at 49°, and dissolves more readily in benzene, light petroleum, and water than do its isomerides (Found: C=50.1; H=4.2; Cl=24.6. C_6H_5ONCl requires C=50.2; H=4.1; Cl=24.7 per cent.). An alcoholic solution of the compound after exposure to air deposited pale yellow needles melting at 96°, and these were identified as 3:3'-dichloroazoxybenzene, convertible into 3:3'-dichloroazobenzene melting at 100.5° by distillation with iron filings.

m-Chloronitrosobenzene, $C_6H_4Cl \cdot NO$.

This substance was made by oxidising the preceding one with ice-cold dichromate solution in presence of excess of sulphuric acid and finally expelling the product with a current of steam, when it passed over as a green fluid. It dissolves readily, forming green solutions in benzene, alcohol, ether, chloroform, or acetone,

and crystallises from benzene in colourless needles melting at 72° (Found : C=50.8; H=3.0; Cl=24.9. C_6H_4ONCl requires C=50.9; H=2.9; Cl=25.1 per cent.).

α -Naphthylhydroxylamine and α -Naphthylamine from α -Nitronaphthalene.

A solution of 10 grams of α -nitronaphthalene in benzene (15 c.c.) was emulsified with the hydrosulphide solution (115 grams) and calcium chloride (10 grams) in water; the temperature rose rapidly, but was kept below 30° by external cooling. The colour changed slowly to chocolate, and crystals began to separate after four hours; half an hour later ammonium chloride (11 grams) was added, when, on filtration, about 7.75 grams of grey crystals were obtained, which were fairly pure α -naphthylhydroxylamine. No α -naphthylamine was detected either in the crystals or in the filtrate.

Recrystallisation of the solid from benzene gave pale yellow crystals which fused at $78-78.5^{\circ}$, but after exposure in a desiccator for some days melted at $82-83^{\circ}$. These properties and the following analysis of the more fusible solid are in agreement with the observations of Scheiber, who found that this form is a monohydrate (*Ber.*, 1904, **37**, 3055) (0.8992 required 5.28 c.c. of $N/10\text{-SnCl}_2$, whence $NH\cdot OH=18.5$. $C_{10}H_7\cdot NH\cdot OH, H_2O$ requires $NH\cdot OH=18.1$ per cent.).

Even when the proportions of hydrosulphide solution and calcium chloride taken were double those given above and the time of reduction was increased to twelve hours, the main product was still the hydroxylamine, very little naphthylamine being formed. It was not found effective to heat the system, owing, doubtless, to deterioration of the emulsion. As some interest appeared to attach to the possibility of reducing α -nitronaphthalene to α -naphthylamine by an emulsification process, a reversion to the original plan of using kieselguhr as an emulsifying agent was tried. Using α -nitronaphthalene, benzene, and sodium hydrosulphide, but adding kieselguhr instead of calcium chloride and then heating on the water-bath for eight hours, yields of α -naphthylamine up to about 73 per cent. of the theoretical quantity were obtained, but it was soon evident that much time might be spent in attempts to improve the rough process, and the experiments were not further proceeded with.

α -Hydroxylaminoanthraquinone and α -Aminoanthraquinone from α -Nitroanthraquinone.

α -Nitroanthraquinone may be reduced to the hydroxylamine or amino-compound respectively by making suitable variations in the

concentration of hydrosulphide solution. The great difficulty in preparing this nitro-compound in a pure state, however, detracts considerably from the interest of this application of the process.

On emulsifying 5 grams of α -nitroanthraquinone (m. p. 219°) in 150 c.c. of benzene with 56 grams of the hydrosulphide solution and 5 grams of calcium chloride in water, a green coloration, due to formation of soluble salts of the hydroxylamine, is observed (compare *Ber.*, 1882, **15**, 1790; 1883, **16**, 367; 1896, **29**, 2934). The temperature rises, and efficient cooling is necessary to keep the temperature below 30° . After five minutes a brown powder begins to separate, and soon the whole sets to a thick paste which gradually becomes red in colour. If the whole be allowed to remain overnight, subsequent addition of ammonium chloride (5 grams) and filtration yields 4 grams of brick-red, powdery α -aminoanthraquinone, which, however, requires purification from a trace of unchanged nitro-compound, and then melts at 242° .

Using less benzene than in the preceding description and allowing the whole to remain for twenty-four hours, a similar result is obtained, but the quantity of unchanged nitro-compound is larger.

It has not been found possible wholly to arrest the reduction of α -nitroanthraquinone at the intermediate hydroxylamine stage, but by using more dilute hydrosulphide solution than that adopted as suitable in other cases, and by operating for a much shorter time, fair yields of the hydroxylamine in a somewhat impure form may be obtained. The best result was obtained as follows:—

The nitroanthraquinone (5 grams) was suspended in benzene (20 c.c.) and, with the aid of calcium chloride (3 grams), emulsified with 21 grams of the standard hydrosulphide solution which had previously been diluted to 75 c.c. with water; after forty-five minutes ammonium chloride (3 grams) was added and the solid filtered off. By extracting the solid with dilute sodium hydroxide solution and subsequently acidifying, 3.6 grams of α -hydroxyaminoanthraquinone, or 73 per cent. of the theoretical amount, were obtained; after recrystallisation from hot acetone it formed reddish-brown needles melting at 137 — 139° (0.7412 required 3.16 c.c. of $N/10$ - SnCl_2 , whence $\text{NH}\cdot\text{OH}=13.4$. $\text{C}_{14}\text{H}_9\text{O}_3\text{N}$ requires $\text{NH}\cdot\text{OH}=13.4$ per cent.).

Reduction of m-Dinitrobenzene and 2:4-Dinitrotoluene by the Emulsification Process.

A considerable amount of work on the reduction of dinitro-compounds has been carried out by previous workers. The nitrohydroxylamine has been obtained from *m*-dinitrobenzene by Wohl

(D.R.-P. 84138, 1895) and Brand (*Ber.*, 1905, **38**, 4006), using the zinc-dust and electrolytic reduction method respectively. Brand (*J. pr. Chem.*, 1906, [ii], **74**, 449) found that partial reduction of dinitro- and polynitro-derivatives of benzene by sulphides and polysulphides of sodium and ammonium leads mainly to formation of azoxy-compounds or amines, according as there is excess or deficit of hydroxyl ions. Flürsheim and Simon (T., 1908, **93**, 1463), Cohen and Dakin (*ibid.*, 1902, **81**, 26), and Cohen and McCandlish (*ibid.*, 1905, **87**, 1257) may also be consulted.

Application of the emulsification method to *m*-dinitrobenzene, dissolved or suspended in benzene, showed that considerable dilution of the standard hydrosulphide solution is necessary in order to restrain the unusually rapid rise in temperature. The solid product obtained on addition of ammonium chloride was brown to orange, and only 3 : 3'-dinitroazoxybenzene was isolated from it. Reduction of 2 : 4-dinitrotoluene gave similar results, but 3 : 3'-dinitro-4 : 4'-dimethylazoxybenzene was isolated from the product and identified by conversion into 2-nitro-*p*-toluidine by reduction with alcoholic sodium hydrosulphide.

Reduction of Nitroanilines and of p-Nitrophenol.

The difficulty in arresting the reduction of nitroaniline at the hydroxylamine stage has already been realised by previous workers (Goldschmidt, *Zeitsch. physikal. Chem.*, 1905, **56**, 1385; Flürsheim and Simon, T., 1908, **93**, 1463; Elbs, *Zeitsch. Elektrochem.*, 1901, **1**, 134).

When the emulsification method is applied to *m*- or *p*-nitroaniline dissolved or suspended in benzene, slow reduction occurs, but no solid is obtained on addition of ammonium chloride, as the products are too freely soluble in benzene; no evidence of the formation of any substituted hydroxylamine was obtained. The authors have not thought it worth while to work out the optimum conditions for preparing the diamines, which are the main products of the reaction, as the method does not promise to be advantageous in such instances.

The only nitrophenol investigated was *p*-nitrophenol. The emulsification process is difficult to apply in these cases owing to the sparing solubility of the sodium derivatives of the nitrophenols and to the exceptionally slow progress of the reaction. The results obtained on attempting to isolate any reduction products were entirely negative, and no attempt was made to extend the observations in this unpromising field.

Summary.

The emulsification process described in Part I has been extended to the reduction of *o*-nitrotoluene and to a number of nitro-compounds of the aromatic series which are solid at the ordinary temperature.

o-Nitrotoluene and *o*-chloronitrobenzene, the former as such and the latter when dissolved in benzene, do not at once yield solid hydroxylamines, but give oils containing about 15 and 62 per cent. respectively of the corresponding hydroxylamines.

The process gives satisfactory results with *p*-nitrotoluene, *p*-chloronitrobenzene, *p*-iodonitrobenzene, *m*-chloronitrobenzene, *m*-bromonitrobenzene, α -nitronaphthalene, using solutions or suspensions of these compounds in benzene, the β -substituted hydroxylamines being secured at once in solid form and in yields usually exceeding, sometimes considerably, 50 per cent. of the amount theoretically possible, a few units per cent. only remaining in the filtrate.

α -Nitroanthraquinone dissolved or suspended in benzene yields either the corresponding solid hydroxylamine or solid amino-compound, according to the conditions. *m*-Dinitrobenzene and 2:4-dinitrotoluene give mainly the solid dinitroazoxy-compounds.

m-Nitroaniline and *p*-nitroaniline are reduced to the corresponding diamines, but these remain dissolved. The process is not applicable to *p*-nitrophenol.

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[Received, May 3rd, 1921.]