LXXXVI.—*The Mercuration of Aromatic Substances. Part II.* o-*Nitrotoluene.*

By SAMUEL COFFEY.

THE position taken up by the acetoxymercuri-group in the mercuration of benzenoid compounds is sometimes anomalous; thus in the mercuration of nitrobenzene 50 and 40% of the *o*- and *m*-compounds respectively are formed, whilst with toluene the proportions of the three isomerides are $o : m : p = 43 : 13 : 44$ (J., 1925, **127**, 1029).

In the mercuration of the three mononitrotoluenes, which has now been studied, the reaction does not follow the expected course. This paper deals with the results obtained on mercurating *o*-nitrotoluene. When a third substituent is introduced into this compound, the 1 : 2 : 6 and 1 : 2 : 4-derivatives are generally the chief products. Of the four possible chloromercuri-*o*-nitrotoluenes, the 1 : 2 : 4-compound was isolated in quantity, the 1 : 2 : 6-compound was proved to be present in relatively large amounts, and the formation of the 1 : 2 : 3- or 1 : 2 : 5-derivative also was demonstrated. Attempts that were being made to discover which of these two was actually present were abandoned when the author was informed that Dr. Kenner, working at Sheffield, had obtained the 1 : 2 : 3-derivative in considerable quantity by mercurating *o*-nitrotoluene.

Although nitrotoluenes react with mercuric oxide and hot caustic soda solution to give compounds containing mercury in the side chain (Reissert, *Ber.*, 1907, **40**, 4209), no mercurinitrotoluenes containing mercury directly attached to the nucleus are known. These are readily obtained when *o*-nitrotoluene is heated with mercuric acetate at 140°.

For comparison and in order to see whether the 1 : 2 : 3- and

1 : 2 : 5-derivatives differed at all in physical properties from the normal substitution products, 4-chloromercuri- and 5-chloromercuri-2-nitrotoluene were made synthetically through the corresponding sulphinic acids (compare Peters, *Ber.*, 1905, **38**, 2567).

EXPERIMENTAL.

Mercuration of o-*Nitrotoluene.*—From the product of reaction in boiling acetic acid, only mercurous acetate and the internal anhydride of monohydroxymercuri-acetic acid were isolated.

The mercuration was best carried out as follows : Mercuric acetate (1 part) and *o*-nitrotoluene (4 parts) were heated gradually with occasional shaking. At 110—120°, the mercuric salt became orange-red and viscous, the solution frothed slightly, and acetic acid distilled off. As the temperature increased, the red mass gradually disappeared and a pale yellow solution formed. A temperature of 140—150° was attained after an hour's heating and was maintained until the product failed to respond to a test for mercuric ions (4 hours). After 12 hours, a brown, amorphous solid, containing a little free mercury but consisting mainly of mercurous acetate, separated.

The clear nitrotoluene solution was then poured into a large volume of ether and left for 24 hours, when an almost colourless, amorphous solid separated. This had a high mercury content and apparently consisted of polymercuri-compounds; it was free from monoacetoxymercuri-derivatives. The ether was distilled off, the clear yellow solution treated with an excess of sodium chloride solution to convert the acetoxymercuri-compounds into the more easily purified chloro-derivatives, and the excess of nitrotoluene removed as quickly as possible in a current of steam. The main product of the reaction remained as a heavy, almost colourless mass. This was broken up and allowed to dry in the air. The yields (in grams) of the various products obtained in different experiments were :

	I.	II.	III.	IV.
Nitrotoluene used	210	310	1000	360
Mercuric acetate	50	75	200	90
Insoluble in nitrotoluene	3	7½	18	5
Insoluble in ether	9	15½	35	15
Main product	40	55	166	69

This crude main product contained a small amount of nitrotoluene which was retained very tenaciously but was finally removed by extraction with ether in a Soxhlet apparatus. The residue melted at 120—155° and consisted only of monochloromercuri-*o*-nitrotoluenes (Found : N, 3·75. $C_7H_6O_2NClHg$ requires N, 3·8%).

Separation and Orientation of 4-*Chloromercuri*-2-*nitrotoluene.*—By crystallising the crude product (160 g.) twice from 500 c.c. of hot acetone the pure compound was obtained in silky needles, m. p. 220·5—221° (corr.), having, when dry, the appearance of asbestos. By working up the mother-liquors a total yield of 32 g. was obtained (Found: N, 3·7; Hg, 53·9. Calc., N, 3·8; Hg, 53·9%).

4-Chloromercuri-2-nitrotoluene is sparingly soluble in all usual solvents except acetone and hot glacial acetic acid. By treatment with the theoretical quantity of bromine in chloroform it was slowly but quantitatively converted into 4-bromo-2-nitrotoluene, which crystallised from methyl alcohol in slender needles, m. p. 44·5—45°; when it was crystallised very slowly it was obtained in large, pale yellow, brittle prisms (compare Hübner and Roos, *Ber.*, 1873, **6**, 799).

Most organic mercury compounds react with iodine very readily, but the reaction of 4-chloromercuri-2-nitrotoluene with an equivalent of iodine in chloroform required 11 or 12 days for completion, theoretical yields being obtained of mercuric chloride, mercuric iodide, and 4-iodo-2-nitrotoluene, which crystallised from methyl alcohol in small, brittle prisms, m. p. 60·5—61°, identical with that obtained by Heynemann (*Annalen*, 1871, **158**, 345) and Reverdin (*Ber.*, 1897, **30**, 3001).

4-*Bromomercuri*-2-*nitrotoluene* was prepared by treating a solution of the chloro-compound in aqueous acetone with potassium bromide; after boiling for a few minutes, it was cooled, filtered, and the solid washed with water, and recrystallised from acetone. It is a heavy, crystalline powder, m. p. 241° (corr.), less soluble than the chloro-compound.

4-*Iodomercuri*-2-*nitrotoluene*, prepared in a similar manner, melts at 286° with slight decomposition. It was recrystallised from acetone, in which it was only sparingly soluble.

4-*Mercuribis*-2-*nitrotoluene*.—No mercuri-bis-nitro-compounds are known with the exception of mercuribistrinitrobenzene, obtained by heating mercuric trinitrobenzoate. The mercuribisnitrotoluene was obtained by carefully reducing the above chloro-compound with the calculated quantity of sodium sulphide. Under these conditions the chloromercuri-group is attacked before the nitro-group, owing no doubt to the fact that *o*-nitrotolyl mercuric sulphide is first formed and this unstable compound on warming undergoes spontaneous decomposition. In this way, the reducing agent is effectually "fixed" and cannot react with the nitro-group.

4-Chloromercuri-2-nitrotoluene (3·7 g.) was shaken in a solution of crystallised sodium sulphide (1·2 g.) for 3 hours, being thereby converted into the colourless sulphide. The mixture was heated on the water-bath for 2 hours, the black product filtered off, washed, dried, boiled with acetone, and the solution filtered hot. The black, inky extract, containing colloidal mercuric sulphide, thus obtained was filtered again when cold, the black, colloidal mercuric sulphide passing through the filter and leaving a white, crystalline solid. This spectacular method of purification was repeated until no more solid was obtained. The product was pure 4-*mercuribis*-2-*nitrotoluene*, which crystallises from acetone in a woolly mass of needles, m. p. 291° (corr.) (Found: Hg, 42·0. $C_{14}H_{12}O_4N_2Hg$ requires Hg, 42·4%). On boiling for 3 hours with one equivalent of mercuric chloride in alcohol, it gave an almost theoretical yield of pure 4-chloromercuri-2-nitrotoluene, its constitution being thus determined.

Existence of 6-*Chloromercuri*-2-*nitrotoluene*.—The remainder of the mixed chloromercurinitrotoluenes (see p. 638) was suspended in chloroform and treated with bromine (1 mol.), and the bromonitrotoluenes, which were purified by distillation in steam, were obtained in quantitative yield as a golden-yellow oil, freezing at low temperatures to a buttery mass. Attempts to separate this oil into its constituents by means of freezing, fractional distillation in steam, or a vacuum, or by crystallisation, failed. The nitro-compounds were therefore reduced to the corresponding bromotoluidines by warming for 2 hours with sodium sulphide in aqueous alcoholic solution on the water-bath. The amines were distilled in steam, an excess of hydrochloric acid was added to the distillate, and the mixed hydrochlorides were fractionally crystallised; but no pure compound could thus be isolated. The mixture of bases was therefore acetylated, and 7·2 g. of the product were fractionally crystallised as follows. The solution in 50 c.c. of hot 50% acetic acid was filtered, and cooled very rapidly, when 2·1 g. (A) separated, m. p. 150—158°. On standing, the mother-liquor deposited 0·7 g. (B) of pale brown needles, m. p. 159—161°. Only solids with low melting points could be obtained from the final mother-liquor.

On recrystallisation from 10 c.c. of 50% acetic acid (A) gave 1·6 g., m. p. 163—164°, and further recrystallisation from benzene furnished colourless needles of constant m. p. 165·5° (corr.). On hydrolysis this acetyl compound gave a base, m. p. 32°, which was converted into a *benzoyl* derivative, m. p. 160° (corr.). The base was compared with 4-bromo-*o*-toluidine; the latter also melted at 32°, and its acetyl derivative at 165·5—166° (compare Janney, *Annalen*, 1913, **398**, 359), as did also a mixture with (A). The benzoyl compounds were also identical. The yield of 4-bromoaceto-*o*-toluidide isolated was 23%, corresponding to 18% of the original mixed mercurated nitrotoluenes. Hence the total amount of 4-chloromercuri-2-nitrotoluene accounted for is 38%.

The product (B) on recrystallisation from benzene gave 0·55 g.

of long needles, m. p. 162—163°; a mixture with (A) melted at 120—130°. Hydrolysis furnished a liquid base, which was proved to be 6-bromo-*o*-toluidine as follows: 2 : 6-dinitrotoluene was reduced, as described by Noelting (*Ber.*, 1904, **37**, 1018), to 6-nitro-*o*-toluidine. This was diazotised and converted into 6-bromo-*o*-nitrotoluene, m. p. 38°. The latter was reduced to a liquid base, which gave a theoretical yield of the acetyl compound (B) on treatment with acetic anhydride; it melted at 164·5° (corr.).

Some of the melting points of this acetyl compound given in the literature are erroneous; Friedländer, Bruckner, and Deutsch (*Annalen*, 1912, **388**, 30) give it as 163°.

Proof of the Presence of 3- *or* 5-*Chloromercuri*-2-*nitrotoluene*.—Many attempts were made to isolate other derivatives of the bromotoluidines, the bromodinitrotoluenes (obtained by nitrating the mixture of bromonitrotoluenes), or the nitrotoluenesulphonic acids (obtained by sulphonating the original mercuri-compounds), but without success. A small quantity of 3 : 5-dibromo-*o*-toluidine was isolated, which indicated the presence of one or both of the compounds in question, but a more direct proof was obtained by eliminating the amino-group from the mixed bromotoluidines and showing the presence of *m*-bromotoluene in the product.

A mixture of the dry amines, absolute alcohol (4 parts), and 20% oleum (2 parts) was warmed with an excess of sodium nitrite, and the product distilled in steam. The bromotoluenes, which passed over together with a brown substance, were purified by steam distillation from an alkaline solution and repeated fractional distillation, a colourless liquid, b. p. 179—190°, being finally obtained which only partly solidified at − 80°. Hence it was not a mixture of the *o*- and *p*-isomerides only. The mixture was oxidised to the corresponding bromobenzoic acids, and the latter were separated as already described in Part I. In this way pure *m*-bromobenzoic acid, m. p. 154°, was isolated, the presence thus being proved of a substance in the original mixture having the chloromercuri-group in the meta-position with respect to a methyl group and in the ortho- or para-position with respect to a nitro-group; which is abnormal for direct substitution.

Synthesis of 5-*Chloromercuri*-2-*nitrotoluene. Preparation of* 2-*Nitrotolyl* 2-*Nitrotoluene*-5-*sulphazide*.—Almost all the nitrotoluenesulphinic acids are unknown. Since the usual methods of preparation failed here, a process devised by Limpricht (*Ber.*, 1887, **20**, 1238) was used.

Sulphur dioxide was passed into a suspension of 6-nitro-*m*-toluidine (10 g.) in 100 c.c. of alcohol at 0° until absorption ceased. The resulting solution was treated at 0° with nitrous fumes or with a saturated solution of 20 g. of potassium nitrite with constant stirring. The mixture was kept in ice over-night and at room temperature for 2 days and then poured into water. The bright orange precipitate (9 g.) thus obtained was extracted with boiling alcohol, in which it was only sparingly soluble, and crystallised from glacial acetic acid, *2-nitrotolyl 2-nitrotoluene-5-sulphazide* separating in deep orange prisms, m. p. 157—158° (violent decomp.) (Found : N, 15·5. $C_{14}H_{14}O_6N_4S$ requires N, 15·3%).

Fission of a sulphazide by boiling sodium hydroxide solution usually proceeds smoothly: $R{\cdot}SO_2{\cdot}NH{\cdot}NHR' + NaOH = R{\cdot}SO_2Na + R'H + N_2 + H_2O$ (compare Escales, *Ber.*, 1885, **18**, 896). From the nitrotoluene compounds, however, much tar was produced and the acids were difficult to obtain pure by the usual methods. In the preparation of 2-nitrotoluene-5-sulphinic acid and other nitrosulphinic acids good use has been made of the fact that they form insoluble ferric salts, which are unchanged by dilute acids (Thomas, J., 1909, **95**, 342).

The preceding sulphazide was boiled with a slight excess of baryta until no more nitrotoluene escaped with the steam. The deep reddish-brown solution was filtered hot through a wet filter to remove tar, acidified, well diluted, filtered from a little more tar, and treated with an excess of ferric chloride solution. The copious precipitate of ferric salt obtained was boiled with ammonia, the solution filtered from ferric oxide and evaporated to a small volume. On acidification a pale yellow oil separated. This was extracted with ether, and on removal of the solvent, *2-nitrotoluene-5-sulphinic acid* separated in small, colourless needles (Found: equiv., 203. $C_7H_7O_4NS$ requires equiv., 201·1. Found for the ferric salt: Fe, 8·3. $C_{21}H_{18}O_{12}N_3S_3Fe$ requires Fe, 8·3%).

The sulphinic acid was boiled with a 50% aqueous alcoholic solution of mercuric chloride for a week, the solid which separated being filtered off periodically. After washing and drying, the crude chloromercuri-compound was extracted with hot acetone; pure *5-chloromercuri-2-nitrotoluene* crystallised from the solution in a felted mass of small, shining needles, m. p. 210°. In solubility and general properties it was very similar to the 4-isomeride.

2-Nitrotoluene-4-sulphinic Acid.—When a dilute solution of diazotised 6-nitro-*p*-toluidine was treated with sulphur dioxide and copper powder, a tarry mass was produced immediately. Better results were obtained by working in strongly acid solution, but even then the sulphazide was produced and not the free acid. The base (10 g.) was dissolved in sulphuric acid (75 c.c.) and water (75 c.c.), cooled to 0°, and diazotised; the latter reaction took place very slowly. The solution was saturated at 0° with sulphur dioxide, and 30 g. of freshly prepared copper powder were added. When the vigorous evolution of gas had ceased, the blue solution was filtered from excess copper and poured into water. The orange precipitate of crude sulphazide (yield 8 g.; no sulphinic acid appeared to be produced) was hydrolysed with hot ammonium hydroxide solution, much tar being produced. The sulphinic acid, which was isolated through the ferric salt as described above, first separated as an oil but was finally obtained as a white, crystalline solid, m. p. 95°. It reacted readily with mercuric chloride in alcoholic solution, giving 4-chloromercuri-2-nitrotoluene identical with that isolated from the mercuration product of *o*-nitrotoluene.

The author wishes to express his thanks to Professor J. N. Collie for the facilities afforded him in his laboratory, and also to the Trustees of the Ramsay Memorial Trust for the grant of a fellowship, during the tenure of which this investigation was carried out.

THE RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.
[*Received, November 27th,* 1925.]