

205. *The Mercuration of Nitrotoluidines.*

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ALTHOUGH the mercuration of nitroaniline has been carried out (Kharasch, Lommen, and Jacobson, *J. Amer. Chem. Soc.*, 1922, **44**, 793), no work has been done on substituted nitroanilines. The following investigation was undertaken to see whether the substitution of the methyl group in the nucleus affected the formation of diacetoxymercuri-compounds and of quinoneimides.

4-Nitro-*o*-toluidine on mercuration in alcoholic solution yields 5-acetoxymercuri-4-nitro-*o*-toluidine. The orientation is established by replacing the acetoxymercuri-group by bromine or iodine. When heated alone, with sodium hydroxide, or boiled with alcohol or water for a prolonged period, the compound is transformed into a quinoneimide.

The foregoing changes apply to all the following compounds. It was found impossible to introduce mercury into position 3 or 6 as well as into 5.

In 5-nitro-*o*-toluidine the amino- and the nitro-group are in the para-position, which corresponds to *p*-nitroaniline. The latter yields a mono- and a di-substituted mercury



compound, together with a quinoneimide, but 5-nitro-*o*-toluidine gives no diacetoxymercuri-compound, and the mercury enters the ring in position 3. The compound and its quinoneimide may be represented by (I) and (II) respectively. The product (II) may be again changed into (I) by treating it with glacial acetic acid.

6-Nitro-*m*-toluidine, which again has the amino- and the nitro-group in the para-position, behaves presumably in the same way as the 5-nitro-*o*-toluidine, the mercury entering the ring in position 4, *i.e.*, ortho to the amino-group. Since 5-bromo-6-nitro-*m*-toluidine is not obtained when the mercury derivative is treated with bromine in acetic acid, the mercury must be in position 4, but 4-bromo-6-nitro-*m*-toluidine is not described in the literature, so direct comparison cannot be made. The acetoxymercuri-compound was only obtained associated with a molecule of water, any attempt to remove the latter merely giving the quinoneimide.

The mercury derivative from 2-nitro-*p*-toluidine is mercurated in position 5, as it yields 5-chloro-2-nitro-*p*-toluidine on treatment with chlorine and calcium chloride in alcoholic solution.

Since no monohalogen derivatives of 3-nitro-*p*-toluidine are known, it is not possible to state definitely whether the mercury has entered position 5 or 6, but judging from the foregoing results it is most probably in position 5.

The chief difficulty encountered in the production of the above compounds has been the elimination of nitrotoluidines from the final products.

EXPERIMENTAL.

The amounts of reacting substances are shown in the following table. The nitrotoluidine was dissolved in the alcohol, the mercuric acetate in the water, and the respective solutions brought to their boiling points before mixing. The whole was then heated for the time shown.

No.	Nitrotoluidine, g.	Alcohol, c.c.	Mercuric acetate, g.	Water, c.c.	Time, mins.
1	1 : 2 : 4, 12.5	150	37	100	180
2	1 : 2 : 5, 25	300	75	200	75
3	1 : 3 : 6, 10	150	30	200	120
4	1 : 4 : 2, 10	150	30	200	270
5	1 : 4 : 3, 20	25	60	200	120

(1) The residue (13 g.) was boiled with a mixture of alcohol (75 c.c.) and glacial acetic acid (15 c.c.). The resulting *quinoneimide*, m. p. about 250°, was brownish maroon (Found: Hg, 57.2. $C_7H_6O_2N_2Hg$ requires Hg, 57.2%).

4-Nitro-5-acetoxymercuri-*o*-toluidine. The filtrate from the foregoing preparation was concentrated, and the sticky product solidified by agitation with alcohol. The solid was boiled with alcohol (80 c.c.) and glacial acetic acid (5 c.c.), and filtered off. The filtrate gave an orange precipitate on dilution with water. Repeated crystallisation from alcohol-acetic acid yielded orange crystals, m. p. 212° (Found: Hg, 49.1. $C_9H_{10}O_4N_2Hg$ requires Hg, 49.8%). The quinoneimide on recrystallising from glacial acetic acid gave the same product. Treatment with bromine in acetic acid gave 5-bromo-4-nitro-*o*-toluidine, m. p. 118—119° (Found: Br, 34.5. Calc. for $C_7H_7O_2N_2Br$: Br, 34.6%). 5-Iodo-4-nitro-*o*-toluidine, m. p. 109°, was also obtained, the yield in both cases being quantitative.

(2) 5-Nitro-3-acetoxymercuri-*o*-toluidine. The cooled filtrate gave a solid (12 g.) on treatment with water. This was boiled with alcohol (100 c.c.) containing acetic acid (3 c.c.); orange plates separated on cooling, m. p. 223° after sintering at 190° (Found: Hg, 49.0. $C_9H_{10}O_4N_2$ requires Hg, 48.8%).

The foregoing product (7 g.) was boiled with dilute sodium hydroxide solution, maroon metallic needles of the *quinoneimide* resulting, which darkened but did not melt at 300° (Found: Hg, 57.2. $C_7H_6O_2N_2Hg$ requires Hg, 57.2%). Replacement of the mercury by bromine gave 3-bromo-5-nitro-*o*-toluidine, m. p. 180.3—181.3°.

(3) 6-Nitro-4(?)acetoxymercuri-*m*-toluidine (13.2 g.) separated from the filtrate and was boiled with 200 c.c. of alcohol. The terra-cotta residue (9 g.) was dissolved in hot acetic acid, treated with water and slowly evaporated. Brownish-yellow needles separated, sintering at 280°, but unmelted at 300° (Found: Hg, 46.8. $C_9H_{12}O_5N_2Hg$ requires Hg, 46.8%).

The preceding compound (0.5 g.), when heated with 10*N*-sodium hydroxide, gave a crystalline maroon product (Found: Hg, 57.3. $C_7H_6O_2N_2Hg$ requires Hg, 57.2%).

(4) 2-Nitro-5-acetoxymercuri-*p*-toluidine. The clear solution gave an orange precipitate on standing; repeated crystallisation from a solution containing water (50 c.c.), alcohol (30 c.c.), and acetic acid (5 c.c.) yielded a high-melting solid (7.1 g.) (Found: Hg, 48.9. $C_9H_{10}O_4N_2Hg$ requires Hg, 48.8%).

The *quinoneimide* was a crystalline maroon compound, isolated by the aid of 10*N*-sodium

hydroxide (Found: Hg, 57.3. $C_7H_6O_2N_2Hg$ requires Hg, 57.2%). Chlorine in alcoholic calcium chloride converted it into 5-chloro-2-nitro-*p*-toluidine, m. p. 130°.

(5) 3-Nitro-5(?)-acetoxymercuri-*p*-toluidine was obtained when the quinoneimide was recrystallised from a little acetic acid, orange-yellow crystals separating (Found: Hg, 48.7. $C_9H_{10}O_4N_2Hg$ requires Hg, 48.8%).

The residue (10 g.) from the reaction mixture was boiled with water (250 c.c.) containing a few drops of acetic acid, and after filtration the hot liquid was treated with a little sodium hydroxide solution. The dark chocolate, crystalline precipitate was unmelted at 300° (Found: Hg, 56.9. $C_7H_6O_2N_2Hg$ requires Hg, 57.2%).

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