CCLVII.—*Nitration of β-Naphthyltrimethylammonium Nitrate.*

By BERTRAM HOBART INGHAM.

IT has been shown by Vorländer and Sieberts (*Ber.*, 1919, **52**, 283) that in simple benzene derivatives the positively charged ammonium group in immediate proximity to the nucleus has an almost exclusive meta-orienting effect. This is a particular example of the generalisation, first enunciated by Robinson, that a positively charged group in immediate proximity to the nucleus always conduces to the formation of a high proportion of meta-substitution products. The former authors showed that on nitration of phenyltrimethylammonium nitrate or bromination of the bromide the corresponding meta-derivatives were produced, whilst *o*-, *m*-, and *p*-tolyltrimethylammonium nitrates yield, on nitration, 5-nitro-2-tolyl-, 4-nitro-3-tolyl-, and 3-nitro-4-tolyl-ammonium nitrates respectively. The so-called " effect " of this group is therefore strongly opposed to that of hydroxyl or methoxyl. In β-naphthol and its methyl ether the positions most readily substituted are precisely those which may be deduced from the simplest application of the rule of alternation, namely 1, 8, 6, and 3, and on such grounds it must be inferred that substitution at these positions in β-naphthyltrimethylammonium salts will occur less readily than in the corresponding positions in naphthalene itself. The simple rules of alternation, however, give no clue as to which of the remaining positions, namely, 7, 5, or 4, will be most readily attacked. It is well known that, in the naphthalene series, substitution occurs preferentially in the α-positions, and therefore positions 5 and 4 are more probable points of substitution than position 7. There remains yet a choice to be made between positions 5 and 4. If the action of the "meta-directive" group is to assist in the process of substitution in any way, then, other things being equal, the nucleus containing the directive group should be the more susceptible to substitution (as is the case with the two naphthols, for example). On the contrary, if its influence be inhibitory, and if the inhibition applies not only to the ortho- but also to the meta-position (to a smaller extent), then such influence should be most effective in the nucleus to which the group is attached, and position 5, being less affected than position 4, should be the more susceptible to substitution.

The author's experiments emphatically support the latter view, which, moreover, is entirely consistent with the results obtained in the schools of H. E. Armstrong and of A. F. Holleman. The product obtained on nitration of β-naphthyltrimethylammonium nitrate was nearly pure 5-nitro-β-naphthyltrimethylammonium nitrate in almost theoretical yield.

EXPERIMENTAL.

β-Naphthyltrimethylammonium iodide was prepared by a method similar to those of Bamberger (*Ber.*, 1889, **22**, 1306) and of Morgan (J., 1900, **77**, 882), but it was found to be unnecessary to heat the reactants in a sealed tube, refluxing for 3½ hours (in a copper flask) and allowing the crude product to stand over-night before purification being found to give practically as good a yield (approx. 60%). The substance was purified by extraction with and crystallisation from water, followed by recrystallisation from alcohol; it was thus obtained in colourless, hexagonal plates, m. p. 193° (decomp.).

The *nitrate* and the *picrate* were obtained by double decomposition from the iodide with silver nitrate and with picric acid, respectively; they crystallised from water, the nitrate in colourless, rectangular plates, m. p. 190° (decomp.), and the picrate in golden-yellow needles, m. p. 194—195° (decomp.).

Nitration of β-Naphthyltrimethylammonium Nitrate.—The salt was dissolved in three times its weight of 99% nitric acid (*d* 1·52) with water-cooling, a vigorous momentary reaction taking place. After having stood at room temperature for 2 hours, the solution was poured on 1½—2 times its weight of ice, and the product made almost neutral * with (solid) sodium bicarbonate, separation of the

---

* The substance acts as its own indicator, any alkalinity (even that of sodium bicarbonate) producing an intense red colour.

nitro-compounds proceeding with the neutralisation. The yield was almost theoretical. After two crystallisations from water and one from aqueous alcohol, a *mononitro-β-naphthyltrimethylammonium nitrate* was obtained in orange-yellow, rectangular prisms, m. p. 231° (decomp.) (Found: C, 52·5; H, 5·6; N, 14·4. $C_{13}H_{15}O_5N_3$ requires C, 53·2; H, 5·1; N, 14·3%). The nitrate was homogeneous, for when it was subjected to fractional crystallisation and subsequent conversion into the iodide, followed by refractionation, no difference in melting point or in appearance under a polarising microscope of any of the fractions could be detected.

The *iodide* was obtained from water in golden-yellow, rectangular prisms, m. p. 194° (decomp.) (Found: I, 35·9. $C_{13}H_{15}O_2N_2I$ requires I, 35·5%). The *picrate* was obtained from aqueous acetone in canary-yellow, rectangular prisms, softening from 248°, m. p. 254° (decomp.).

Unsuccessful attempts were made to determine the constitution of this nitration product of β-naphthyltrimethylammonium nitrate by oxidation, and also by treatment with concentrated aqueous solutions of alkalis, which caused the substance to undergo a peculiar and complicated change. In the circumstances, it was decided to proceed by synthesis as described below.

Methylation of 5-Nitro-β-naphthylamine.—5-Nitro-β-naphthylamine (Friedländer and St. Szymanski, *Ber.*, 1892, **25**, 2076) (1 mol.) in benzene (15 parts by weight) and methyl sulphate (4 mols.) in benzene (4 parts) were mixed and refluxed for 6½ hours, a dirty-white solid gradually separating. Next day, the precipitate was collected, washed with benzene, and boiled with water (100 parts), and the aqueous extract was cooled and made alkaline with ammonia, whereby the methylated bases were precipitated. The filtered solution, which contained 5-nitro-β-naphthyltrimethylammonium methosulphate, was divided into two portions, one of which was converted into the *iodide* (Found by micro-analysis: N, 8·4. $C_{13}H_{15}O_2N_2I$ requires N, 7·8%) and the other into the *picrate* by means of sodium iodide and picric acid, respectively.

Comparative and mixed m. p. tests showed that the nitration product of β-naphthyltrimethylammonium nitrate was 5-nitro-β-naphthyltrimethylammonium nitrate (see table).

As the yield of the quaternary salt obtained in the methylation experiment was very small, and also for comparative purposes, it was considered desirable to methylate the 8-nitro-isomeride and thereby furnish conclusive proof that the above quaternary salt was derived from 5-nitro-β-naphthylamine, and not from any impurity in it. The methylation was performed in the same way as that of the 5-isomeride.

Melting points of Nitro-β-naphthyltrimethylammonium Salts.

	5-Isomeride.	8-Isomeride.	Corresponding salt (X) from nitration product.	5-Isomeride mixed with X.	8-Isomeride mixed with X.
Iodide (1st sample)	189°	180°	192°	190°	180°
(2nd sample)	190	—	191	191	—
Picrate (1st sample)	254*	221—223	254*	254*	212—218
(2nd sample)	254*	221—223	254*	254*	212—229

* With softening from approximately 248° in each case.

The discrepancies of one or two degrees between some of the melting points given in the table and those of the corresponding substances given hitherto are due to the rate of heating; the m. p.'s in the table are strictly comparable, for they were taken simultaneously in the same bath.

The author wishes to express his thanks to Professor Lapworth for his interest in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, July 6th,* 1927.]