169. *Acetylene Reactions. Part IV. Formation of Trimethylvinyl- and Tetramethyl-ammonium Hydroxide from Acetylene and Aqueous Trimethylamine.*

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Interaction of aqueous trimethylamine and acetylene under pressure yields neurin (trimethylvinylammonium hydroxide) only if the reaction is carried out at or below 50°. At higher temperatures (50—100°) a mixture of neurin and tetramethylammonium hydroxide is formed, and, at temperatures above 100°, the latter is essentially the only product.

Recent information obtained from Germany (Rose, " Products formed by interaction of acetylene and amines," B.I.O.S. Final Report No. 359, Item No. 22) indicated that aqueous trimethylamine, when brought into reaction with acetylene under pressure, gave neurin (trimethylvinylammonium hydroxide). This appeared to be an attractive synthesis of a powerful organic base which should have many chemical and technological applications, and the reaction was studied as part of a general programme of work on the reactions of acetylene.

The apparatus used and precautions observed in this work have been described in Part I (this vol., p. 780).

The first experiment was done in the smaller (1·2-l.) autoclave (Part I, *loc. cit.*), using aqueous trimethylamine and an acetylene–nitrogen mixture at 250 ± 10 lb./sq. in., the partial pressure of the acetylene being of the order of 170 lb./sq. in. This experiment, carried out for 6·5 hours, yielded chiefly neurin, the conversion being 23%; the yield cannot be given, as the unchanged trimethylamine was not recovered.

A second experiment was carried out in the larger (8-l.) mild-steel rocking autoclave, and, owing to the relatively slower absorption of acetylene, was carried out for 30 hours by intermittent heating in four separate periods of 7·5 hours on each of four successive days. The main product from this reaction was tetramethylammonium hydroxide, identified by isolation of tetramethylammonium iodide and characterisation of this as the iododibromide (Chattaway and Hoyle, *J.*, 1923, 656).

					Composition of product:			
					$NMe_4{\cdot}OH$.		Neurin.	
Run.	Charge.	Acetylene–N_2, (2 : 1), lb./sq. in.	Time, hrs.	Temp.	% w./v.	wt., g.	% w./v.	wt., g.
1	NMe_3 (325 g.), H_2O (600 g.).	250±20	6·5	60—65°	?	?	24 [1]	132
2	NMe_3 (890 g.), H_2O (1685 g.).	250±20	30 [2]	60—65	20	286	8	114
3	NMe_3 (156 g.), H_2O (294 g.).	250±10	17	75	12·2	57·5	11·7	55
4	NMe_3 (156 g.), H_2O (294 g.).	250±10	4·5	75	5·8	19·8	10·2	37·5
5	NMe_3 (920 g.), H_2O (1600 g.).	250±10	15	104—106	30	390 [3]	—	—
6	NMe_3 (170 g.), H_2O (300 g.).	250±10	97	30±3	1·9%	6	16·9	53

[1] Chiefly neurin, but tetramethylammonium hydroxide not determined.

[2] Intermittent heating 4 × 7·5 hrs.

[3] No neurin detected.

A roughly quantitative method of analysis of mixtures of neurin and tetramethylammonium hydroxide was worked out, based on the high solubility of neurin iodide and the low solubility of tetramethylammonium iodide in water. The sample was acidified with hydriodic acid, the tetramethylammonium iodide collected, washed with alcohol, and dried, and a correction applied for the solubility of the iodide in the filtrate. The neurin content was calculated by difference from the total quaternary hydroxide (determined by titration) and the weight of tetramethylammonium iodide, calculated as hydroxide.

The results of various experiments on the interaction of trimethylamine, water, and acetylene are recorded in the table. Qualitatively, this table indicates that the formation of tetramethylammonium hydroxide is favoured by higher temperatures, and, at constant temperature (cf. runs 3 and 4), by longer reaction periods.

The spontaneous decomposition of neurin to tetramethylammonium hydroxide was demonstrated by heating a sample of neurin (17%) and tetramethylammonium hydroxide (1·9%) solution at 110—120°/5 hours. The tetramethylammonium hydroxide content increased to 6·1%. A similar sample, heated with the addition of trimethylamine showed a similar increase to 9·0% of tetramethylammonium hydroxide. In each case, a brown resin was formed which was insoluble in water and 2N-hydrochloric acid.

The mechanism of the formation of tetramethylammonium hydroxide is not clear. It is demonstrated that neurin, when boiled for 5 hours, evolves trimethylamine; the extent of this decomposition at 100° is about 10% in 5 hours, the neurin decomposed being equivalent, within the experimental error, to the trimethylamine evolved, and no tetramethylammonium hydroxide is formed. It appears, therefore, that the first stage is represented :

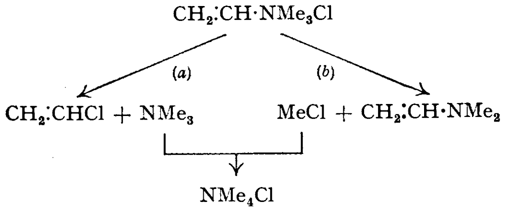
$$CH_2{:}CH{\cdot}NMe_3{\cdot}OH \longrightarrow NMe_3 + CH_3{\cdot}CHO(?).$$

No acetaldehyde was detected, but this is not surprising, as it could not be expected to survive the strongly alkaline conditions of the reaction. When the trimethylamine is continuously removed from the reaction mixture, no tetramethylammonium hydroxide is formed; when (as in the sealed tube experiments) the trimethylamine is retained, some " trans-methylation " mechanism must be assumed, as for example:

$$CH_2{:}CH{\cdot}NMe_3{\cdot}OH + NMe_3 \longrightarrow NMe_4{\cdot}OH + (NMe_2{\cdot}CH{:}CH_2).$$

The decomposition of neurin chloride was studied; this subject has been investigated by Meyer and Hopf (*Ber.*, 1921, **54**, 2277), who demonstrated that dimethylvinylamine was formed in very small yield. Our experiments confirm that the *isolated* yield of dimethylvinylamine is very small, but indirect evidence points to the formation of about 40% of this amine.

The decomposition of neurin chloride can proceed in two directions, (*a*) and (*b*).



By collecting the volatile constituents (trimethylamine and methyl chloride) of the decomposition products in a trap at −70°, and allowing these to recombine at room temperature, a yield of 38·5% of tetramethylammonium chloride was obtained, indicating that a decomposition had proceeded *via* route (*b*) to at least this extent. In agreement with Meyer and Hopf, we find that dimethylvinylamine is a very unstable substance, which polymerises readily and reacts violently with acidic reagents.

EXPERIMENTAL.

Trimethylvinylammonium Hydroxide.—Trimethylamine (325 g.) dissolved in water (600 g.) was enclosed in a stainless steel internally agitated autoclave. The air in the vessel was removed by pressing in nitrogen to 500 lb./sq. in., releasing, repressuring, and again releasing to leave a residual nitrogen pressure of 50 lb./sq. in. Acetylene was then added from a cylinder to give a total pressure of 150 lb./sq. in., and the autoclave heated to 61° during 2½ hours, by which time the total pressure had reached 250 lb./sq. in. Absorption started at 61°, and this temperature was maintained for 6·5 hours; the pressure, which fell steadily at 20 lb./sq. in./hr., was periodically restored with fresh acetylene.

The liquid product was a mixture of a dark aqueous fluid and a viscous black resin; the latter was removed with ether, and the aqueous layer shaken with active charcoal at room temperature and filtered to give a pale brown solution (550 c.c.) containing 24% wt./vol. (by titration) of trimethylvinylammonium hydroxide.

A sample (300 c.c.) of this solution was heated at 70°/15 mm. for 30 minutes to remove traces of dissolved trimethylamine, neutralised with 5N-hydrochloric acid (130 c.c.) to pH 8, evaporated at 40°/15 mm., and finally dried over phosphoric oxide in a high vacuum. Neurin chloride was obtained as white crystals (85 g.), m. p. 193—194°. The picrate formed yellow needles from water, m. p. 263—264° (decomp.) (Found: C, 42·25; H, 4·65; N, 17·6. Calc. for $C_{11}H_{14}O_7N_4$: C, 42·05; H, 4·5; N, 17·8%); Gulewitsch (*Z. physiol. Chem.*, 1898, **25**, 174) gives m. p. 264°. The iodide, formed by interaction of the chloride and potassium iodide, gave white crystals, m. p. 197°; Bode (*Annalen*, 1892, **267**, 276) gives m. p. 196°.

Trimethylethylammonium Hydroxide.—Aqueous neurin (45 c.c. of 24% wt./vol. solution) was hydrogenated over Raney nickel at ordinary temperature and 100-atm. hydrogen pressure. The resulting solution had a strong amine odour; it was filtered from catalyst and boiled. The vapours contained trimethylamine which was absorbed in water and identified as the picrate, m. p. and mixed m. p. with an authentic specimen, 216°. The residual solution contained trimethylethylammonium hydroxide (yield 50%), identified as the picrate, m. p. and mixed m. p. with an authentic specimen 299—301°.

Tetramethylammonium Hydroxide.—Trimethylamine (920 g.) and water (1600 g.) were charged into an 8-l. mild-steel autoclave, and the air was displaced by nitrogen and finally pressured to 150 lb./sq. in. with a 2 : 1 mixture of acetylene and nitrogen. The autoclave was heated and rocked at 104—106° for 15 hours, the acetylene pressure being periodically restored. The dark mixture of oil and aqueous base was extracted with ether, heated at 60°/15 mm. in a stream of nitrogen to remove trimethylamine, and clarified with carbon, yielding 1300 c.c. of 29·2% tetramethylammonium hydroxide.

A sample (100 c.c.) of the solution was neutralised with azeotropic hydriodic acid (45 c.c.) cooled to 12°, and the precipitated iodide collected, washed with alcohol, and dried. Yield 60 g. The filtrate (130 c.c.) contained 4·5 g. of iodide, as the solubility of tetramethylammonium iodide in water is 33 g./l. at 12°.

The tetramethylammonium iodide (Found: I, 63·1. Calc. for $C_4H_{12}NI$: I, 63·2%) was infusible at 330°, and was characterised by conversion into the iododibromide, m. p. 191—192° alone and in admixture with an authentic specimen prepared according to Chattaway and Hoyle (*loc. cit.*).

Analysis of Mixtures of Neurin and Tetramethylammonium Hydroxide.—The quaternary hydroxide was neutralised with azeotropic hydriodic acid cooled to 12°, the iodide filtered off, and the volume of filtrate measured. The iodide was pressed dry, washed with a little cold alcohol followed by ether, and dried to constant weight. To this weight is added a factor of 33 g./l. of filtrate as a correction for the solubility of the iodide in water at 12°; Walden (*Z. physikal. Chem.*, 1906, **55**, 708) gives 20·1 g./l. at 0°, 53·1 g./l. at 25°. The total hydroxide-ion content was determined by titration, and neurin calculated by difference.

In blank experiments with pure tetramethylammonium hydroxide, and mixtures of this with neurin, recovery of added tetramethylammonium hydroxide varied from 96 to 104%.

Formation of Tetramethylammonium Hydroxide from Neurin.—Neurin solution (20·5 c.c. of 17% w/v, containing 1·9% of tetramethylammonium hydroxide) was heated in a sealed tube at 110—120° for 5 hours. The contents of the tube, a mixture of a clear aqueous fluid and a brown resin, were extracted with ether, and the aqueous layer analysed as above. The tetramethylammonium hydroxide content was 6·1% w/v.

A similar experiment, in which 1·65 g. of trimethylamine were dissolved in the neurin–tetramethylammonium hydroxide solution, showed an increase in the tetramethylammonium hydroxide content to 9%.

Decomposition of Neurin.—A solution of neurin (50 c.c. of 17% w/v) containing 1·9% w/v of tetramethylammonium hydroxide was boiled gently under reflux in a stream of nitrogen, the vapours from the reflux condenser being led through two traps in series containing standard sulphuric acid. After 5 hours, the flask was allowed to cool for 30 minutes, the stream of nitrogen being continued. The residual neurin, and the trimethylamine absorbed in the sulphuric acid traps, were then determined by titration. The decrease of neurin content corresponded to a loss of 0·0092 g.-mol., whilst the trimethylamine evolved was 0·0106 g.-mol. There was no detectable increase in the tetramethylammonium hydroxide content.

In a control experiment with pure tetramethylammonium hydroxide solution, no trimethylamine was evolved in 5 hours.

Decomposition of Neurin Chloride.—Neurin chloride (75 g.) was distilled with a free flame in a current of nitrogen, the decomposition products being collected in a trap cooled with acetone–solid carbon dioxide. Distillation was continued until the vapour temperature was 95°. The total distillate (55 c.c.) was redistilled in nitrogen through a 3-in. column packed with Monel metal gauze spirals, giving 50 c.c. of a liquid, b. p. $<15°$; 1 g. of liquid, b. p. 31—33°, was collected which decolourised alkaline permanganate, reacted violently with 2 : 4-dinitrophenylhydrazine sulphate, and polymerised rapidly. The low-boiling fraction (50 c.c.; 40 g.) was sealed in a tube and set aside at room temperature. After 24 hours a white crystalline precipitate, m. p. $>300°$ (26 g.), of tetramethylammonium chloride was formed, identified as the picrate, m. p. and mixed m. p. with an authentic specimen 314° (decomp.) (Lossen, *Annalen*, 1876, **181**, 374, gives m. p. 312—313°).

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