13. *Preparation of Nitroethane.*

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A convenient method for the preparation of nitroethane on a laboratory scale is described.

Although nitroethane can be satisfactorily prepared on a technical scale by nitrating ethane (*e.g.*, Hodge, U.S. 2,150,120, 1939), nodetails have been recorded for its preparation in quantity on a laboratory scale by a relatively inexpensive method. The preparation from silver nitrite and ethyl iodide is obviously too expensive. The same drawback applies to the reaction between α-bromopropionic acid and sodium nitrite (50% yield), particularly since lactic acid was found by us to give only a 13% yield of α-bromopropionic acid on treatment with hydrogen bromide. Very little α-chloropropionic acid is produced by the action of hydrogen chloride on lactic acid.

Kaufler and Pomeranz (*Monatsh.*, 1901, **22**, 492) showed that methyl sulphate and aqueous potassium nitrite reacted to give a 25% yield of nitromethane. Walden (*Ber.*, 1907, **40**, 3214) obtained a 50—57% yield by a similar method, and stated that ethyl sulphate also reacted, but less energetically. However he gave neither yield nor details of the latter reaction. The reaction between aqueous sodium nitrite and ethyl sulphate has now been investigated in detail. In the procedure recommended, there is no loss due to the slight solubility of nitroethane in water. All the yields recorded below are based on the equation :

$$\mathrm{EtO{\cdot}SO_2{\cdot}OEt + NaNO_2 = EtO{\cdot}SO_2{\cdot}ONa + EtNO_2}$$

This raises the question of the utilisation of the sodium ethyl sulphate produced in the reaction. Krause (D.R.-P. 294,755, 1916) showed that this salt, when made into a cream with solid sodium nitrite, sodium carbonate, and a small quantity of water and distilled above 100°, gave a 35% yield of nitroethane. Accordingly the aqueous layer from reaction in the cold.(initial reaction) was refluxed for 30 minutes with sodium carbonate and then distilled, but very little nitroethane was obtained. However, after a series of runs in the cold, crystalline sodium ethyl sulphate separated from the standard solution, and could then be worked up according to the method of Krause. . In this way the yield of nitroethane was increased above the 65% recorded below.

A series of experiments was also carried out varying (*a*) the concentration of sodium nitrite solution used, (*b*) the actual amount of sodium nitrite used. It was found that, within limits, the more dilute the solution, the greater the production of nitrous fumes and ethyl nitrite at the expense of nitroethane. The optimum concentration was 75 g. of sodium nitrite dissolved in 100 c.c. of water. With concentrations greater than this (saturated solution plus solid) the yield was considerably reduced, probably because less water was used and therefore the surface area available for the reaction was less.

Experimental

Initial Run.—Into each of seven stoppered bottles was placed a mixture of ethyl sulphate (120 g.) and sodium nitrite solution (120 g. in 160 c.c. of water.) The bottles were shaken mechanically for 20 hours, the pressure being released at intervals. The contents were then poured into a separating funnel, and the upper layer separated, dried over calcium chloride, and distilled at 14 mm., the distillate up to 60° being collected (the residue, *ca.* 230 g., consisted of ethyl sulphate and was used again). The distillate was fractionated at atmospheric pressure, and the fraction of b. p. 114—116° collected. This was shaken with water, dried over calcium chloride, run through charcoal, and redistilled; b. p. 114—115·5°. Yield, 124 g. (31%, or allowing for recovered ethyl sulphate, 43·5%) (Found : N, 18·4. Calc. for $C_2H_5O_2N$: N, 18·7%).

Routine Run.—A second experiment was then carried out using the same quantities of ethyl sulphate as above. The recovered nitrite solution (lower layer) from the first run was concentrated by adding approximately 16 g. of sodium nitrite per 160 c.c. of solution. Yield, 185 g. (46%, or allowing for recovered ethyl sulphate, 65%).

For each additional subsequent run approximately 16 g. of nitrite per 160 c.c. of solution were added, although this represents a rather diminishing concentration in view of the increased yield of nitroethane.

The table summarises experiments carried out under various conditions.

Expt.	Et_2SO_4, g.	$NaNO_2$, g.	H_2O, c.c.	$NaNO_2$ per 100 g. Et_2SO_4.	C.c. H_2O per 100 g. Et_2SO_4.	Nitroethane, g.	Recovered Et_2SO_4, g.	Pressure.
Sat. $NaNO_2$ plus solid ...	100	100	50	100	50	4·89	72·5	Nil
Dilute $NaNO_2$	60	60	600	100	1000	2	8·6	Considerable
Excess conc. $NaNO_2$	100	150	187	150	187	11·5	56	V. small
Intermediate conditions	100	100	125	100	125	10	67	Small

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