CXXXIX.—*The Triazo-group. Part XVIII.*
 β -Triazoethylamine.

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AN inquiry into the possibility of producing triazomethylamine (Trans., 1910, **97**, 1056), although unsuccessful so far as the isolation of that base is concerned, led to the discovery that the association of a substituted amino-group with a triazotised carbon atom so weakens the attachment of the azoimide complex that the action of water is sufficient to eliminate hydrazoic acid. Triazomethylcarbimide, $N_3 \cdot CH_2 \cdot N : C : O$, phenyltriazomethylcarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot N_3$, and triazomethylcarbamide,

all parted with the triazo-group under the influence of water, thereby explaining the failure of attempts to prepare triazomethylamine from triazoacetamide by Hofmann's reaction.

It was not to be expected, however, that this disability would attend the derivatives of β -triazaoethylamine, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$, although, for another reason, this compound might prove to be unstable. It is well known from the work of Gabriel, that β -halogen substituted ethylamine, salts of which are produced when the respective phthalic derivatives are hydrolysed with hydrochloric and hydrobromic acids, cannot be maintained in the free state on account of their tendency to lose halogen hydride and undergo transformation into dimethyleneimine, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > NH$. In view of the

general resemblance between the triazo-group and the halogen atoms, therefore, it appeared probable that β -triazaoethylamine would be realised only in the form of salts, and that these would break up

into metallic azide and dimethyleneimine when treated with alkali. Actual experiment, however, has shown that β -triazoethylamine is a remarkably stable substance. We have isolated it in the form of a colourless liquid, which boils at $63.5^\circ/50$ mm., and may even be distilled from solid potassium hydroxide without undergoing change.

The early attempts to prepare β -triazoethylamine were unsuccessful. Following the lines of Gabriel's experiments in connexion with the corresponding derivatives of ethylamine, bromoethylphthalimide was converted into triazoethylphthalimide, but the temperatures at which this substance undergoes hydrolysis were too high to admit of its application. Triazoethyl iodide was then treated with alcoholic ammonia in the expectation that there would arise a mixture of bases from which the primary one might be isolated; it was found, however, that triazoethylamine derivatives are not produced, the effect of ammonia being similar to that of fixed alkali, namely, removal of hydrogen iodide and liberation of triazoethylene. Ultimately, the simplest possible process was found to be the most applicable; on heating β -bromoethylamine hydrobromide with excess of sodium azide in aqueous alcohol,

$\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HBr} + 2\text{NaN}_3 = 2\text{NaBr} + \text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HN}_3$,
and adding excess of alkali to the liquid, β -triazoethylamine was rapidly carried over by a current of steam. Some typical derivatives of the base have been prepared, but beyond its stability, its properties hardly call for comment, being those of a primary alkylamine; when it is remembered, however, that β -triazopropionic ester behaves towards alkalis exactly like the corresponding halogen derivatives, the tenacity with which the azoimide nucleus is retained in triazoethylamine is noteworthy.

EXPERIMENTAL.

β -Triazoethylamine, $\text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

Fifty grams of β -bromoethylamine hydrobromide dissolved in 120 c.c. of water were heated with 36 grams of sodium azide during six hours on the water-bath, when excess of 20 per cent. sodium hydroxide was added, and a current of steam passed through the liquid; the distillate was collected in dilute hydrochloric acid, and yielded about 20 grams of triazoethylamine hydrochloride on evaporation. In order to isolate the base, an aqueous solution of the hydrochloride was saturated with solid potassium hydroxide prior to extraction with ether, it having been found that the latter removes only a very small proportion of the base from a moderately alkaline aqueous solution. On distilling the residue from the

ethereal extract which had remained in contact with solid potassium hydroxide during some days, the triazoethylamine was found still to contain water ($N=63.33$; $C_2H_6N_4$ requires $N=65.09$ per cent.); it was accordingly redistilled from solid potassium hydroxide, boiling steadily at $63.5^\circ/50$ mm.:

0.0884 gave 47.7 c.c. at 14° and 779 mm. $N=65.10$.

$C_2H_6N_4$ requires $N=65.09$ per cent.

β-Triazoethylamine is a colourless, oily liquid, with a marked basic odour, and having $D_{1.0488/16^\circ}$; the effervescence with concentrated sulphuric acid is very vigorous.

Reduction to Ethylenediamine.—The relationship of triazoethylamine to ethylenediamine was established by adding 0.5 gram of the hydrochloride to 50 c.c. of dilute hydrochloric acid in which 0.5 gram of tin foil had been dissolved, agitating the cold solution until gas evolution ceased, and then, having made the liquid alkaline, shaking it with 2 grams of benzoyl chloride, when the product was identified with the dibenzoyl derivative of ethylenediamine.

The *hydrochloride*, prepared in the manner described above, crystallises in colourless, silky needles, melting at 72° :

0.0853 gave 33.8 c.c. N_2 at 18° and 766 mm. $N=46.13$.

0.2710 „ 0.3198 AgCl. $Cl=29.19$.

$C_2H_7N_4Cl$ requires $N=45.74$; $Cl=28.94$ per cent.

The salt is very hygroscopic, dissolving freely in water and alcohol; it effervesces when thrown into a solution of stannous chloride in hydrochloric acid.

The *benzoyl* derivative was prepared by the Schotten-Baumann process, and remained as a colourless oil, which did not crystallise:

0.1492 gave 38.3 c.c. N_2 at 18° and 759 mm. $N=29.61$.

$C_9H_{10}ON_4$ requires $N=29.47$ per cent.

The substance effervesces vigorously with concentrated sulphuric acid; when heated in alcohol with 30 per cent. sodium hydroxide it is hydrolysed slowly without losing the triazo-group.

Ten grams of bromoethylphthalimide in 25 c.c. of alcohol were heated with 3.5 grams of sodium azide dissolved in a few c.c. of water during five hours; alcohol was then evaporated, the residue being diluted with water and extracted with ether. The white solid deposited on evaporating the dried ether was recrystallised

from a small quantity of hot alcohol, from which there separated long, pale yellow needles, melting at 58° :

0.0916 gave 20.6 c.c. N_2 at 17° and 763 mm. $N=26.20$.

$C_{10}H_8O_2N_4$ requires $N=25.92$ per cent.

Attempts to hydrolyse this material to salts of β -triazoethylamine at moderate temperatures were unsuccessful.

p-Nitrobenzylidene- β -triazoethylamine,
 $NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot CH_2 \cdot N_3$.

An alcoholic solution of *p*-nitrobenzaldehyde was heated during two hours on the water-bath with the calculated amount of triazoethylamine hydrochloride neutralised with aqueous sodium carbonate; the oil which separated on dilution with water quickly solidified, and was recrystallised from hot petroleum (b. p. $60-80^{\circ}$):

0.0832 gave 22.8 c.c. N_2 at 19° and 777 mm. $N=32.33$.

$C_9H_9O_2N_5$ requires $N=31.96$ per cent.

The crystals of this derivative are hard, elongated, rectangular plates, melting at 71° ; they remain transparent in the mother liquor, becoming opaque on exposure to air. The substance is freely soluble in cold acetone, ethyl acetate, chloroform, ethyl alcohol, and benzene. The action with concentrated sulphuric acid is remarkably sluggish, liberation of gas taking place only on prolonged stirring; with stannous chloride and hydrochloric acid there is effervescence on warming.

p-Toluene- β -triazoethylsulphonamide,
 $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot N_3$.

Molecular proportions of *p*-toluenesulphonyl chloride and of β -triazoethylamine were dissolved separately in ice-cold pyridine, mixed together, and, after two hours, poured into water. The precipitated oil having remained viscous during two days, it was extracted with ether, and shaken with 10 per cent. sodium hydroxide; on saturating the latter with carbon dioxide, a solid was precipitated slowly, and was recrystallised from petroleum:

0.1524 gave 30.8 c.c. N_2 at 17° and 774 mm. $N=23.89$.

$C_9H_{12}O_2N_4S$ requires $N=23.35$ per cent.

The sulphonamide dissolves sparingly in hot petroleum, and crystallises in long, slender, lustrous needles, melting at 64° ; it is readily soluble in benzene and in other organic media. The liberation of gas with concentrated sulphuric acid is immediate, but takes place with stannous chloride only on warming.

β-Triazoethylcarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$.

Two grams of triazoethylamine hydrochloride and 2.6 grams of potassium cyanate were allowed to interact in a few c.c. of water, and left in a vacuum desiccator until dry. The residue was then extracted with absolute alcohol, and the filtered solution of triazoethylcarbamide evaporated to dryness, the final crystallisation being effected by hot benzene, from which it separates in lustrous, snow-white flakes, melting at 59° :

0.0878 gave 40.4 c.c. N_2 at 18° and 779 mm. $N=54.51$.

$C_3H_7ON_5$ requires $N=54.26$ per cent.

The carbamide is insoluble in boiling petroleum, but dissolves very freely in alcohol and in water, these solutions effervescing when heated with stannous chloride.

s-Phenyl-β-triazoethylcarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot C_6H_5$.

On mixing *β*-triazoethylamine (1 gram) and phenylcarbimide (1.4 gram), both diluted with benzene, the temperature rose, and snow-white needles began to separate after a few minutes; the crystals melted at 99° , and the point of fusion was not raised by recrystallisation from hot benzene:

0.1694 gave 0.3274 CO_2 and 0.0874 H_2O . $C=52.71$; $H=5.64$.

$C_9H_{11}ON_5$ requires $C=52.68$; $H=5.36$ per cent.

The substance dissolves readily in cold ethyl alcohol, ethyl acetate, chloroform, or hot benzene, but is sparingly soluble in boiling water or petroleum. Evolution of gas with concentrated sulphuric acid is very vigorous, but with stannous chloride takes place only when the liquid is heated.

s-Phenyl-β-triazoethylthiocarbamide, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

Although heat was developed on mixing triazoethylamine and phenylthiocarbimide in benzene solution, the product did not crystallise until sown:

0.1348 gave 36.0 c.c. N_2 at 15° and 776 mm. $N=31.95$.

$C_9H_{11}N_5S$ requires $N=31.69$ per cent.

The thiocarbamide dissolves sparingly in boiling water or petroleum, crystallising from the latter in long, narrow, rhomboidal plates, melting at 64° ; it is freely soluble in cold methyl alcohol, ethyl acetate, chloroform, acetone, and benzene.

β-Triazoethylquinolinium Iodide, $C_9H_7N \begin{smallmatrix} < \\ I \end{smallmatrix} CH_2 \cdot CH_2 \cdot N_3$.

Five grams of triazoethyl iodide and 3.2 grams of quinoline were mixed in a stoppered bottle and left in darkness; crystals began to separate in the course of a few days, and amounted to two grams at the end of three weeks, whilst a further quantity was deposited subsequently. The salt is readily soluble in hot alcohol, crystallising in transparent, golden-yellow prisms; it becomes suddenly deep red at 162° , and melts and decomposes at $162-164^\circ$:

0.2164 gave 32.0 c.c. N_2 at 18° and 759 mm. $N=17.06$.

0.2232 „ 0.1586 AgI. $I=38.42$.

$C_{11}H_{11}N_4I$ requires $N=17.18$; $I=38.94$ per cent.

In order to convert the quinolinium iodide into the platinichloride, an alcoholic solution was shaken with freshly precipitated silver chloride; it became colourless, and after filtration was treated with slight excess of platinic chloride, which gave a pale red precipitate:

0.1292 gave 15.6 c.c. N_2 at 19° and 745 mm. $N=13.63$.

0.1464 „ 0.0356 Pt. $Pt=24.31$.

$C_{22}H_{22}N_8Cl_6Pt$ requires $N=13.79$; $Pt=24.18$ per cent.

The *platinichloride* is insoluble in boiling alcohol, and requires a considerable proportion of boiling water for dissolution, separating in long, flat, pale brown needles; these melt with vigorous intumescence at 200° .

Attempts to prepare similar salts from methylaniline and dimethylaniline were unsuccessful, and the action of piperidine was found to resemble that of ammonia, causing a rapid separation of piperidine hydriodide.

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