CXIV.—*The Triazo-group. Part IV. Allylazoimide.*

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ATTENTION has been directed at various times to the facility with which the atoms composing the triazo-group part company, as testified by the following illustrations.

Benzylazoimide is resolved by acids into benzylideneimine and nitrogen (Curtius and Darapsky, *J. pr. Chem.*, 1901, [ii], **63**, 428):

Phenylazoimide under the influence of sodium ethoxide may be condensed with numerous esters, yielding triazole derivatives (Dimroth, *Ber.*, 1902, **35**, 1029, 4041; *Annalen*, 1904, **335**, 1):

Alkyl- and aryl-azoimides are transformed into diazoamino-compounds by the action of organo-magnesium derivatives (Dimroth, *Ber.*, 1903, **36**, 909; 1905, **38**, 670; 1906, **39**, 3906):

Potassium cyanide converts phenylazoimide into benzeneazocyanamide (Wolff and Lindenhayn, *Ber.*, 1904, **37**, 2374):

A trace of sodium ethoxide liberates two-thirds of the nitrogen from triazo-ketones (Forster and Fierz, *Trans.*, 1905, **87**, 826; this vol., pp. 72 and 669):

As an explanation of the last-named change, it has been suggested that, prior to elimination of nitrogen, the carbonyl group becomes saturated by the triazo-group, giving rise to an unstable cycloid which forthwith collapses.

The foregoing considerations, coupled with certain points of resemblance between diazomethane and the triazo-group,

led us to investigate the properties of allylazoimide, in which compound,

one might anticipate the display of some attraction on the part of the ethenoid linking for the highly active triazo-group; given a suitable environment, there should occur redistribution of affinities analogous to the interaction of ethylene and diazomethane, of which the outcome is pyrazoline (Azzarello, *Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 285):

On attempting to prepare allylazoimide from sodium azide and allyl chloride or iodide, interaction took place with moderate readiness, but it was noticed that, unless quickly removed, the triazo-derivative undergoes a profound change, in consequence of which we have never obtained yields exceeding 30 per cent. This is explained by the fact that allylazoimide, a liquid which boils at 76.5°, changes slowly, without external stimulus, into a crystalline, isomeric, diazoamino-compound, which melts at 192° and is very sensitive towards acids. Reflecting on the probable constitution of this compound, we were at first disposed to regard it as having a cycloid structure arising from allylazoimide by the following rearrangement:

Such a ring would be called dihydrotriazine, and represents, so far as we have been able to ascertain, a new type of cycloid; it is, in fact, a dihydrobenzene in which one-half of the molecule is replaced by the diazoamino(triazene)-group:

$\Delta^{2:5}$ -Dihydrobenzene.

Δ^5 -Dihydro-1:2:3-triazine.

In drawing this conclusion, we have not overlooked the possibility of secondary transformation into the isomeric methyl-1:2:3-triazole,

suggested by the recognition of the substance originally called dihydrotetrazine as 1-amino-3:4-triazole (Bülow, *Ber.*, 1906, **39**, 2618),

and of *N*-dihydrotetrazinedicarboxylic acid (bisdiazooacetic acid) as 1-amino-3:4-triazole-2:5-dicarboxylic acid, [View Article Online](#)

Our reason for preferring the hexacycloid representation is two-fold. Although the uncertainty hitherto prevailing as regards the constitution of bisdiazooacetic derivatives has been removed by the practical agreement with Bülow's views on the part of Curtius, Darapsky, and Müller (*Ber.*, 1907, **40**, 1470), all doubt as to the possibility of a tetrazine ring existing has been removed since the recent isolation of 1:2:4:5-tetrazine by the authors mentioned (*ibid.*, p. 84). In the second place, if the crystalline isomeride of allylazoimide were 4-methyl-1:2:3-triazole, it might be expected to resemble the triazolone described by Curtius and Thompson (*Ber.*, 1906, **39**, 4140) as arising from diazoacetamide by the action of baryta:

4-Methyl-1:2:3-triazole.

5-Triazolone.

Nevertheless, the two substances are distinguished sharply by their behaviour towards very dilute acids, which forthwith liberate two-thirds of the nitrogen from the compound under discussion, therein recalling the most conspicuous property of the aliphatic diazoamino-derivatives.

It has been mentioned that the transformed allylazoimide melts at 192°, a temperature which suggested a condition of polymerisation, and the elevation of boiling point in chloroform agrees with the formula $(\text{C}_3\text{H}_5\text{N}_3)_2$. This observation might perhaps invite consideration of such complex expressions as

or the possibility of polymerisation being due to change in valency on the part of nitrogen, developing the structure

but it seems to us more probable that the case under consideration is allied to that of *cyclopentadiene*, which has been shown by Krämer and Spilker (*Ber.*, 1896, **29**, 552) to undergo polymerisation with great facility, a change which they represent as follows:

Having in mind Thiele's theory of partial valency, and its application to *cyclopentadiene*, the alternative :

naturally suggests itself for the polymerised hydrocarbon, but the necessity of maintaining the diazoamino-structure in the transformed allylazoimide leads us to prefer the expression

for that substance.

EXPERIMENTAL.

Allylazoimide, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{N}_3$.

The interaction of sodium azide and allyl chloride or iodide was followed under various conditions in the hope of improving the unremunerative yields given by the earlier experiments, but we have had to content ourselves with interrupting the process at a point when the mixture of allylazoimide, its degradation products, and unchanged allyl haloid contains the maximum of triazo-hydrocarbon, which never exceeded 30 per cent. Allyl chloride is more profitable than the iodide, not only on account of initial cost, but also because the boiling point is below that of allylazoimide.

Fifty grams of allyl chloride and 100 c.c. of alcohol were heated under reflux on the water-bath with 50 grams of sodium azide in 150 c.c. of water during two hours, when nitrogen began to escape in small quantities from the faintly yellow liquid, through which a rapid current of steam was then passed; the distillate, diluted with much water, was extracted twice with ether, and the solvent, having been washed with dilute sulphuric acid to remove the basic products of transformation, was shaken several times with water and dried with calcium chloride. On fractionating with a long column of the rod-and-disk pattern, the temperature rose gradually to 76° , and the fraction passing over at $50\text{--}76^\circ$ gave, when twice distilled, a material which boiled steadily at 76.5° under 760 mm. pressure. Using the foregoing quantities, the yield amounted to 15 grams, but was greatly reduced by further distillation, each repetition diminishing the quantity of allylazoimide by about 15 per cent., owing to transformation into the isomeride and its products of change. Although seemingly an individual and free from chlorine, the analysis, for which we are indebted to Mr. Richmond, gave results several per cent. too low, and

this must be attributed to loss of nitrogen in the form of hydrazoic acid :

0.1544 gave 40.9 c.c. N_2 at 20.5° and 751 mm., along with 0.02371 of ammonia. $N = 30.4$ as gas, 15.4 as NH_3 ; total, 45.8.

$C_3H_5N_3$ requires $N = 50.6$ per cent.

Allylazoimide is a mobile, refractive liquid, having specific gravity 0.924 compared with water at 25° . The odour is allylaceous, but is less powerful and much sweeter than that of allyl chloride, more closely resembling that of chloroform, whilst the vapour, when inhaled, produces the characteristic throbbing sensation at the base of the forehead. Concentrated sulphuric acid decomposes the azide with vigour, but potash does not liberate gas, although stannous chloride sets free nitrogen immediately; the vapour of allylazoimide explodes when heated, but the detonation is mild.

$\alpha\beta$ -Dibromo- γ -triazopropane, $CH_2Br \cdot CHBr \cdot CH_2 \cdot N_3$.

On adding a solution of bromine in chloroform to a mixture of allylazoimide with the solvent, the calculated amount of halogen was decolorised without liberation of hydrogen bromide; after fifteen minutes at zero, the liquid was washed with sodium carbonate and distilled in steam, which separated the chloroform from the dibromide. The latter was distilled twice under 5 mm. pressure, boiling steadily at 87° :

0.3442 gave 29.55 c.c. N_2 at 18.7° and 754 mm., along with 0.01937 of ammonia. $N = 9.95$ as gas, 5.62 as NH_3 ; total 15.57.

$C_3H_5N_3Br_2$ requires $N = 17.28$ per cent.

Mr. Richmond, to whom we owe the analysis, reported difficulty in measuring the gas, on account of the mercurous bromide produced, and it is probable that a certain proportion of the nitrogen is lost in this way.

The Diazoamino-compound, $(C_3H_5N_3)_2$, from Allylazoimide.

Although a freshly-distilled specimen of allylazoimide undergoes no change with dilute acids, the substance acquires in the course of a few hours the property of effervescing when mixed even with acetic acid. The change on which this alteration of character depends is accelerated by warming the substance to about 50° , and after one or more days, according to circumstances, the liquid deposits large, lustrous, transparent crystals. Recrystallisation from benzene was first attempted, one gram requiring about 400 c.c. of the boiling solvent, but loss of material occurred, and the crystals deposited on cooling, although colourless, were found to retain a basic odour; purification

was effected by dissolving one gram in 30 c.c. of boiling chloroform to which 60 c.c. of petroleum (b. p. 60—80°) were then added. Snow-white, odourless plates were thus obtained, melting sharply and decomposing at 192°:

0.1846 gave 0.2955 CO₂ and 0.1045 H₂O. C = 43.65; H = 6.33.

0.1143 „ 49.3 c.c. N₂ at 16° and 767 mm. N = 51.42.

C₃H₅N₃ requires C = 43.37; H = 6.01; N = 50.62 per cent.

The analyses were somewhat complicated by the systematic appearance of nitrous fumes, but Mr. Richmond has confirmed the nitrogen percentage by his method:

0.0689 gave 20.1 c.c. N₂ at 15.7° and 746 mm., along with 0.01138 of ammonia. N = 33.76 as gas, 16.52 as NH₃; total, 50.28.

The diazoamino-compound dissolves more readily in acetone and in chloroform than in benzene, but it is sparingly soluble in ethyl acetate and insoluble in petroleum. Estimation of molecular weight based on the boiling point of chloroform solutions gave 172 and 170, the formula (C₃H₅N₃)₂ requiring 166. Hot alcohol and boiling water decompose the substance slowly, although definite products could not be obtained; the decomposition by dilute acids proceeds in a manner analogous to that in which the aliphatic diazoamino-compounds described by Dimroth are degraded, two-thirds of the nitrogen being set free:

0.1176 gave 34.6 c.c. N₂ at 19° and 748 mm. when treated with 5 per cent. hydrochloric acid. N = 33.85.

C₃H₅N₃ requires 2/3N = 33.75 per cent.

Several attempts have been made to isolate from the bright red solution definite products of this change, but the small quantity of material at our disposal has prevented a conclusion from being reached. The liquid reduced cold Fehling's solution and ammoniacal silver oxide immediately, the original compound being indifferent to these agents, but on evaporation the reducing properties disappeared, and the platinichloride prepared from the residue was found to be that of ammonium. As might be expected from these indications of its sensitive character, the product of decomposing the diazoamino-compound with acids did not form a stable salt with platinum tetrachloride, the yellow precipitate from which quickly became dark brown.

The power to combine with phenylcarbimide, usually possessed by diazoamino-compounds of this class, is not displayed by the transformed allylazoimide, which was heated with the agent during twenty-four hours. Furthermore, alcoholic ammoniacal silver oxide did not give an insoluble derivative.