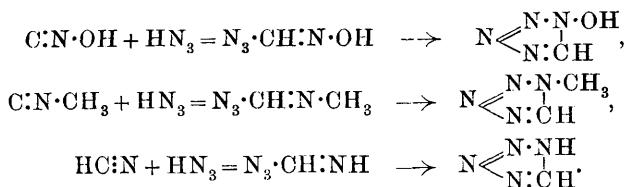CCLXIII.—*The   Triazo-group.   Part   XV.   Triazo-ethylene   (Vinylazoimide)   and   the   Triazoethyl Halides.*

By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

MANY cases have now been placed on record in which the atoms composing a triazo-group in the neighbourhood of an unsaturated linking have lent themselves to the formation of a cycloid, owing to a change involving saturation of this linking by the members of the azoimide nucleus.   As recent examples of this principle may be quoted the spontaneous transformation of allylazoimide into an isomeric diazoamino-compound (Trans., 1908, **93**, 1174), whilst an attempt to prepare benzhydroximic azide by interaction of the chloride and sodium azide led to 1-hydroxy-5-phenyltetrazole (Trans., 1909, **95**, 183; compare also Wieland, *Ber.*, 1909, **42**, 4199).

In the cases mentioned above, and in others which might be indicated, the environment favourable to the display of additive functions on the part of the triazo-group is intramolecular. Whether it is necessarily so cannot be stated with confidence, because, although striking examples of apparently intermolecular addition have been furnished quite recently by Palazzo and Oliveri-Mandalà (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 218, 228), who found that hydrazoic acid converts fulminic acid and methyl-carbylamine into 1-hydroxytetrazole and 1-methyltetrazole respectively, whilst Dimroth and Fester (*Ber.*, 1910, **43**, 2219) showed that tetrazole itself is obtainable by the interaction of hydrazoic and prussic acids, it is nevertheless possible that these changes actually depend on preliminary addition of H and N_3 to unsaturated atoms, and that it is the resulting triazo-compound which undergoes intramolecular rearrangement, as follows:

$$\mathrm{C\colon N\cdot OH + HN_3 = N_3\cdot CH\colon N\cdot OH} \quad \dashrightarrow \quad \mathrm{N}{\mbox{\large$<$}}^{\mathrm{N\cdot N\cdot OH}}_{\mathrm{N\colon CH}},$$

$$\mathrm{C\colon N\cdot CH_3 + HN_3 = N_3\cdot CH\colon N\cdot CH_3} \quad \dashrightarrow \quad \mathrm{N}{\mbox{\large$<$}}^{\mathrm{N\cdot N\cdot CH_3}}_{\mathrm{N\colon CH}},$$

$$\mathrm{HC\colon N + HN_3 = N_3\cdot CH\colon NH} \quad \dashrightarrow \quad \mathrm{N}{\mbox{\large$<$}}^{\mathrm{N\cdot NH}}_{\mathrm{N\colon CH}}.$$

In addition to the experiment just mentioned, Dimroth and Fester caused hydrazoic acid to act on acetylene, and although 1 : 2 : 3-triazole was obtained therefrom, they do not classify this change with the foregoing ones, as depending on the intermediate formation of vinylazoimide,

$$\mathrm{HC\colon CH + HN_3 = N_3\cdot CH\colon CH_2} \quad \dashrightarrow \quad \mathrm{N}{\mbox{\large$<$}}^{\mathrm{N-NH}}_{\mathrm{CH\colon CH}},$$
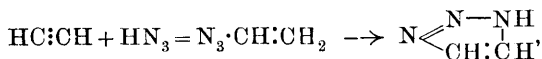
because phenylazoimide is converted into 1-phenyl-2 : 3-triazole by the action of acetylene. As we have been engaged for some time in experiments leading to the preparation of vinylazoimide, we think it may be of interest to put forward a description of this substance, which was isolated with the object of studying its tendency to undergo the above rearrangement.

The first experiments in the direction indicated were begun more than two years ago in continuation of the work on allylazoimide. Attempts were made to bring vinyl bromide into double decomposition with sodium azide, but there was not any evidence of the change having taken place; in spite of the readiness with which usually the triazo-group may be substituted for halogen in aliphatic compounds, the failure was not surprising, as it is well known that halogen attached to unsaturated carbon takes part in such reactions with the greatest difficulty. The preparation of triazoethyl alcohol (Trans., 1908, **93**, 1865), however, suggested the possibility of arriving at triazoethylene (vinylazoimide) by the withdrawal of halogen hydride from a triazoethyl halide. Accordingly, triazoethyl alcohol was converted into triazoethyl bromide by the action of phosphorus tribromide, and then by double decomposition with sodium iodide, triazoethyl iodide was prepared from the bromide; on acting with alcoholic potassium hydroxide on these compounds, they were readily deprived of halogen hydride without affecting the triazo-group.

Triazoethylene is a pale yellow liquid, heavier than water, boiling at 26°, and having an odour suggesting that of ethylene itself. It decolorises bromine water without delay, forming a heavy, oily dibromide. At one time we entertained the hope that it might be possible to withdraw the elements of hydrogen bromide from this substance in such a way as to produce triazoacetylene, the copper

derivative of which would probably rank among violent explosives, but it was soon found that the dibromide itself is a dangerous material, and, moreover, breaks up in an interesting manner under the influence of water. When suspended therein, the oil rapidly disappears, hydrobromic and hydrazoic acids being set free, whilst bromoacetaldehyde remains dissolved:

$$CH_2Br \cdot CHBr \cdot N_3 + 2H_2O = HBr + HN_3 + CH_2Br \cdot CH(OH)_2 \ - \rightarrow$$
$$CH_2Br \cdot CH:O + H_2O.$$
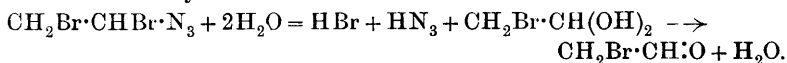
So far as we know, the dibromide of triazoethylene is the first compound in which a triazo-group is attached to an atom of carbon which carries also a halogen, and its peculiar susceptibility towards water explains the subsidiary decomposition which has always been observed to accompany the production of a bistriazo-compound from the double decomposition of sodium azide and a dihalogen derivative of the aliphatic series in which both halogen atoms are attached to the same atom of carbon (Trans., 1908, **93**, 1070; also this vol., pp. 126 and 1360). We have not attempted to isolate and distil the substance, because a brief experience of $\alpha\alpha$-bistriazoethane, which exploded with great violence at the laboratory temperature, apparently spontaneously, renders it most probable that $\alpha\beta$-dibromo-α-triazoethane would behave in the same way. This seems the more likely to take place in view of the possibility that the decomposition of triazoethylene dibromide might follow a different course in absence of water, leading to bromoazoimide:

$$CH_2Br \cdot CHBr \cdot N_3 \ -\rightarrow \ BrN_3 + CH_2Br \cdot CH \ -\rightarrow \ CHBr:CH_2.$$
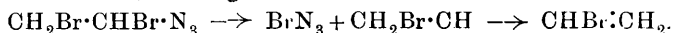
Since Raschig has shown (*Ber.*, 1908, **41**, 4194) that chloro-azoimide is frightfully explosive, the foregoing possibility is discouraging to a further investigation of $\alpha\beta$-dibromo-α-triazoethane.

The original purpose with which triazoethylene was prepared, namely, to illustrate its transformation into triazole:

$$CH_2:CH \cdot N {<}{\overset{N}{\underset{N}{\|}}} \ \rightarrow \ {\overset{CH:CH \cdot N}{\underset{NH-----N}{}}},$$
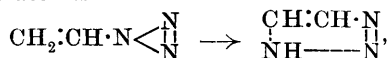
has not been fulfilled, the substance having shown itself to be surprisingly stable. After being heated with dilute alcohol under reflux during twelve hours, a considerable proportion was found to have survived, and although the remainder had changed into a dark brown substance, the presence of triazole could not be established. Furthermore, on heating an alcoholic solution in a sealed tube during twelve hours at 100—110°, there was produced a dark brown liquid having the odour of a carbylamine, and giving a precipitate with mercuric chloride, but again it was not found possible to recognise triazole.

The pale yellow colour of triazoethylene is an interesting feature of the compound, and appears to be a genuine property, because

it has been noticed in every specimen, whether prepared from triazo-ethyl iodide or bromide. It is doubtless due to the concentration of unsaturated atoms in a small molecule, and although not so intense as that of diazomethane, it is nevertheless quite distinctive. The comparatively high boiling point was not expected, because the recorded boiling points of vinyl chloride and of vinyl bromide are $-15°$ and $+16°$ respectively, and without having made a study of the subject, we were under the impression that, whilst the boiling point of an aliphatic chloro-derivative is unquestionably lower than that of the corresponding triazo-compound, the latter would be more volatile than the brominated substance. As it is often a matter of considerable practical importance to be able to predict, roughly, the boiling point of a new triazo-compound from that of its haloid parent, we have taken afresh the boiling point of several typical aliphatic azoimides described in previous papers, side by side with those of the corresponding bromo-derivatives. The results show conclusively that the triazo-group exerts an elevating effect on the boiling point greater than that of the bromine atom.

		B. p.	Mm.
Vinyl bromide	$CH_2{:}CHBr$	$16°$	750
Vinylazoimide	$CH_2{:}CHN_3$	26	760
Ethylene dibromide	$CH_2Br{\cdot}CH_2Br$	37	20
Triazoethyl bromide	$CH_2Br{\cdot}CH_2N_3$	49	20
Ethyl α-bromopropionate	$CH_3{\cdot}CHBr{\cdot}CO_2Et$	61	16
,, α-triazopropionate	$CH_3{\cdot}CHN_3{\cdot}CO_2Et$	70	16
,, α-bromoisobutyrate	$CBr(CH_3)_2{\cdot}CO_2Et$	62	16
,, α-triazoisobutyrate	$CN_3(CH_3)_2{\cdot}CO_2Et$	71	16
,, α-bromoisovalerate	$CH(CH_3)_2{\cdot}CHBr{\cdot}CO_2Et$	79	16
,, α-triazoisovalerate	$CH(CH_3)_2{\cdot}CHN_3{\cdot}CO_2Et$	82	16

The relationship between the triazo-group and the chlorine atom as regards their effect on the boiling point is revealed by the following data:

		B. p.	Mm.
Vinyl chloride	$CH_2{:}CHCl$	$-15°$	760
Vinylazoimide	$CH_2{:}CHN_3$	26	760
β-Chloroethyl alcohol	$CH_2Cl{\cdot}CH_2{\cdot}OH$	44	20
β-Triazoethyl ,,	$CH_2N_3{\cdot}CH_2{\cdot}OH$	73	20
Ethyl chloroformate	$Cl{\cdot}CO_2Et$	93	760
,, triazoformate	$N_3{\cdot}CO_2Et$	114	769
,, chloroacetate	$CH_2Cl{\cdot}CO_2Et$	52	20
,, triazoacetate	$CH_2N_3{\cdot}CO_2Et$	70	20
Methyl α-chloromethylacetoacetate	$CH_3{\cdot}CO{\cdot}CCl(CH_3){\cdot}CO_2Me$	76	13
,, α-triazomethylacetoacetate	$CH_3{\cdot}CO{\cdot}CN_3(CH_3){\cdot}CO_2Me$	76	0·66

We have not, as yet, been very successful in attempts to utilise triazoethyl iodide as a triazo-ethylating agent. Triazoethyl chloride has been obtained by heating the iodide with dry mercuric chloride, and in this connexion it is worth noting that the bromide remains unchanged when treated with the mercury salt under similar conditions. isoNitrosocamphor was transformed into an oily triazo-

ethyl derivative when heated with triazoethyl iodide and silver oxide in dry ether, but an attempt to prepare bistriazoethyl ether by heating a mixture of triazoethyl alcohol and iodide with dry silver oxide on the water-bath led to the recovery of unaltered triazoethyl alcohol after five days. This is the more curious because the action of ethyl iodide on triazoethyl alcohol in presence of silver oxide leads without difficulty to triazoethyl ether, $C_2H_5 \cdot O \cdot CH_2 \cdot CH_2N_3$. Lastly, we have not been able to produce triazoethylcarbimide by the action of triazoethyl iodide on lead or silver cyanate, whilst the interaction of triazoethyl iodide and silver cyanide, although producing an odour of carbylamine, was too far from complete to admit of isolating any definite products.

<center>EXPERIMENTAL.</center>

<center>*Triazoethylene* (*Vinylazoimide*), $CH_2 \colon CHN_3$.</center>

The alcoholic potassium hydroxide used for withdrawing halogen hydride from the triazoethyl halides was a solution of 5 grams in 20 grams of water, mixed with 25 grams of absolute alcohol. This was heated on steam in a generating flask, into which was fitted a dropping-funnel and a reflux double-surface condenser; from the latter, connexion was made to a small, dry flask, thence to a U-tube filled with calcium chloride, and finally to a large test-tube surrounded by a freezing-mixture. The temperature of the water in the condenser having been adjusted to 30°, 5 grams of triazoethyl iodide was admitted drop by drop into the alcoholic potassium hydroxide at the temperature of boiling alcohol, when a pale yellow liquid gradually accumulated in the small flask between the generator and the U-tube. All the iodide having been added, the liquid was boiled during fifteen minutes, when it was found that the cooled tube also contained some yellow liquid, and this, being presumably free from alcohol and water, was regarded as pure triazoethylene, and found to boil at 26°/760 mm. Although this experiment has been made several times, and triazoethyl bromide has been substituted for the iodide, it has always been observed that the liquid in both condensing vessels is pale yellow, and that the colour does not vary in depth; it therefore seems safe to conclude that this feature is not due to some impurity. Reference has been made to the absence of any conclusive evidence that triazoethylene changes into triazole; in addition to the experiments towards this end which have been already described, a solution of triazoethylene in petroleum was left in a stoppered vessel exposed to light during many days without giving the faintest indication of triazole; on allowing the solvent to evaporate, the odour of a carbylamine was noticeable.

The *dibromide* of triazoethylene was prepared by adding ice-cold bromine water to a well-cooled suspension of the substance in water, the colour of the halogen being immediately destroyed, whilst the limpid vinylazoimide changed to a heavy, viscous oil.   It is necessary to be most cautious in adding the halogen, because on one occasion a drop of bromine was admitted by accident to the vessel containing the triazo-compound, and led to a violent explosion, although the amount of material involved could not have exceeded 1 gram, and this was diluted with 20 c.c. of water.   On allowing the dibromide to remain in contact with water, it rapidly disappeared, and the liquid was found to contain hydrazoic and hydrobromic acids; moreover, it restored the colour to Schiff's reagent, and when mixed with ammoniacal silver oxide and filtered, the liquid quickly deposited silver on warming.   In order to make sure that the decomposition of triazoethylene dibromide by water does not follow the possible alternative course, that, namely, leading to bromoazoimide and vinyl bromide, a specimen of vinylazoimide was converted into the dibromide with a deficit of bromine, and at once treated with dilute sodium hydroxide, in the expectation that if bromoazoimide is formed, it would behave towards alkali in the manner that characterises chloroazoimide, and that alkali hypobromite would be produced; we were able to show that hypobromite is not formed, and therefore conclude that the decomposition proceeds only in the direction of hydrobromic and hydrazoic acids along with bromo-acetaldehyde.

The interaction of triazoethylene and concentrated sulphuric acid is mild, gas being evolved slowly, but brisk effervescence occurs with a solution of stannous chloride in hydrochloric acid.   The conclusion that alcoholic potassium hydroxide is without action on the substance may be drawn from the fact that on evaporating to dryness the liquid contained in the generating flask, no trace of alkali azide was to be found.

β-Chloro-α-triazoethane (*Triazoethyl Chloride*), $N_3 \cdot CH_2 \cdot CH_2Cl$.

The first attempts to prepare this material were made by adding triazoethyl alcohol dissolved in absolute ether to the calculated amount of phosphorus pentachloride covered with the same solvent; considerable action took place, and was increased by heating under reflux, but the yield of triazoethyl chloride, being only 2 grams from 20 grams of the alcohol, was too disappointing to encourage the adoption of this method.   Thionyl chloride acts vigorously on triazoethyl alcohol, but, as might be expected, gives a product which appears to be triazoethyl sulphite, and triazoethyl chloride could not be detected, whilst the effect of passing dry hydrogen chloride

into a suspension of anhydrous zinc chloride in triazoethyl alcohol
was to liberate hydrazoic acid. It was not until triazoethyl iodide
became available that the preparation of the chloride was possible.

Twenty grams of triazoethyl iodide, mixed with 32 grams of
dried mercuric chloride, were heated at 100° during three hours in
a small distilling flask, from which the product was then boiled
under 25 mm. pressure, 10 grams, or 90 per cent. of the theoretical
amount, being obtained; on re-distillation under the same pressure,
the substance boiled steadily at 45° :

0·0874 gave 30·9 c.c. N_2 at 24° and 751 mm. $N = 39·16$.

0·2709   ,,   0·3642 AgCl. $Cl = 33·25$.

$C_2H_4N_3Cl$ requires $N = 39·81$; $Cl = 33·65$ per cent.

The substance is limpid and colourless, having a pleasant odour
suggesting that of chloroform; the density is $1·2885/24°$.   The
action with a solution of stannous chloride in hydrochloric acid is
sluggish, gas being evolved only on warming the liquids; the
effervescence with concentrated sulphuric acid becomes brisk on
stirring, but the triazo-group appears to be indifferent towards
alkalis, which only liberate triazoethylene.   The chloride does not
lose its halogen completely when heated with boiling alcoholic silver
nitrate, as is the case with the other triazoethyl halides, and the
above estimation of chlorine was made by heating in alcohol with
30 per cent. aqueous potassium hydroxide, followed by precipitation
with silver nitrate in the solution acidified by nitric acid.

When thrown on a hot plate, the substance decrepitates, and
burns with a violet flame.

β-Bromo-α-triazoethane (Triazoethyl Bromide), $N_3 \cdot CH_2 \cdot CH_2Br$.

Although triazoethyl bromide has been obtained by the action of
bromine on triazoethyl alcohol in presence of amorphous phosphorus,
this is not the most convenient method of preparation, the inter-
action of phosphorus tribromide and the alcohol, when moderated
by a diluent such as ether or petroleum, leading to more satisfactory
results.   One hundred grams of triazoethyl alcohol, covered with
100 c.c. of petroleum (b. p. 40°) in a flask surrounded with melting
ice, were treated slowly with 112 grams of phosphorus tribromide
in 250 c.c. of the same petroleum, the mixture being shaken
vigorously   after   each   portion   was   added;   phosphorous   acid
separated, and a heavy, pale brown, viscous oil, insoluble in
petroleum, constituted a large proportion of the product.   After
three hours on the water-bath under reflux, the less dense liquid
was decanted, and the viscous residue shaken several times with
small quantities of petroleum, which were added to the decanted
solution of triazoethyl bromide ; any excess of phosphorus tribromide

was destroyed by agitation with small quantities of water, and the liquid having been treated with ignited sodium sulphate, petroleum was boiled away, and the residue distilled under diminished pressure. The best yield obtained by this process was only 58 grams, representing about 34 per cent. of the amount anticipated:

0·0641 gave 15·9 c.c. N_2 at 24° and 765 mm.　$N = 28·00$.

0·4942　„　0·6198 AgBr.　$Br = 53·38$.

$C_2H_4N_3Br$ requires $N = 28·02$; $Br = 53·33$ per cent.

Triazoethyl bromide is a colourless liquid, having the odour of ethylene dibromide, and rapidly becoming yellow when exposed to light; it boils at 49°/20 mm., and has the density 1·6675/19°. Action with concentrated sulphuric acid and with a solution of stannous chloride in hydrochloric acid resembles that of the chloro-compound, but hot alcoholic silver nitrate leads more readily to the elimination of halogen than in the case of that substance, and the above determination of bromine was carried out by this agent. The bromide does not become ignited when thrown on a hot plate, merely decrepitating mildly.

Attempts have been made to identify the viscous, brown oil which accompanies triazoethyl bromide when prepared by the foregoing method, so far without success. It is the production of this substance which is responsible for the disappointing yield, and is particularly inconvenient because triazoethyl bromide is the starting material for the chloride and the iodide. The presence of phosphorus, bromine, and the triazo-group suggested that the substance might be the bromide of bistriazoethylphosphorous acid, $(N_3·CH_2·CH_2·O)_2PBr$, but the bromine content was much too low; it may be a mixture of this substance with triazoethyl phosphite, $(N_3·CH_2·CH_2·O)_3P$, but an attempt to recover triazoethyl alcohol from it by hydrolysis was not successful.

β-Iodo-α-triazoethane (Triazoethyl Iodide), $N_3·CH_2·CH_2I$.

The method employed for this preparation was the one recently described by Finkelstein (*Ber.*, 1910, **43**, 1528), and was found to be expeditious and economical. Fifty-eight grams of triazoethyl bromide were added to a solution of 60 grams of sodium iodide in 400 c.c. of dry acetone, sodium bromide being precipitated immediately; the mixture having remained at the ordinary temperature during the night, action was completed by heating under reflux, when about two-thirds of the solvent was distilled off, and the residue poured into water contained in a separating funnel, from which the heavy, dark brown liquid was then tapped. This was mixed with the ether used for extracting the triazoethyl iodide from the aqueous acetone, and shaken vigorously with a little mercury

in order to remove dissolved iodine, the residue from the dried
ether being then distilled under diminished pressure, yielding 43
grams:

0·0814 gave 15·5 c.c. N_2 at 23° and 764 mm. $N = 21·58$.
0·4270   ,,   0·5063 AgI. $I = 64·12$.
$C_2H_4N_3I$ requires $N = 21·32$; $I = 64·45$ per cent.

Triazoethyl iodide boils at 68°/20 mm., and when freshly distilled
is colourless, but quickly becomes pale red; the odour resembles
exactly that of ethyl iodide. It has the density 1·9154/25°, and
is able to dissolve mercuric iodide, a property brought to light by
the fact that a specimen which had been decolorised by agitation
with mercury left a considerable residue of the salt on redistillation.
The action with stannous chloride in hydrochloric acid is more
brisk than in the case of the other triazoethyl halides, which the
iodide resembles, however, in regard to interaction with concentrated
sulphuric acid.   Behaviour on the hot plate is similar to that of
triazoethyl chloride.

It was hoped that a variety of interesting substances might be
obtainable from typical compounds containing replaceable hydrogen
by triazo-ethylation, but hitherto we have not been successful in
this direction.   *p*-Nitrophenol, for instance, when heated in dry
benzene with silver oxide and triazoethyl iodide, gave a brown oil
which did not invite further examination.   *iso*Nitrosocamphor also
gave an oil, remaining liquid during four months, and containing
22·35 per cent. of nitrogen ($C_{12}H_{18}O_2N_4$ requires $N = 22·4$ per cent.).
Silver and lead cyanates were heated in ether and in benzene at
the boiling points of these with triazoethyl iodide during many
hours, but triazoethylcarbimide could not be recognised, although
in absence of a diluent, some action takes place at about 100°, as
indicated by a mild explosion which occurred.   Silver   cyanide
developed the carbylamine odour when heated with triazoethyl
iodide during two days on the water-bath, but the proportion of
material remaining unchanged at the end of the experiment was
too large to hold out any prospect of success.   Bistriazoethyl sulphate
appears to be formed when triazoethyl iodide is heated in dry
benzene with silver sulphate, production of silver iodide being
clearly indicated; the residue left by the solvent on evaporation
did not distil at 140°/1 mm., but when hydrolysed with 30 per
cent. potassium hydroxide, the liquid contained potassium sulphate,
unmixed with iodide.

An attempt was made to prepare bistriazoethyl ether by heating
5 grams of triazoethyl alcohol and 11·3 grams of triazoethyl iodide
with 15 grams of dry silver oxide on the water-bath during five
days, but the entire product distilled at 85°/35 mm., weighed

5 grams, and contained 48·3 per cent. of nitrogen; this is the amount required by triazoethyl alcohol itself, whilst bistriazoethyl ether contains 53·8 per cent., from which it would appear that in the above experiment the triazoethyl alcohol remained unchanged, whilst the triazoethyl iodide was transformed into triazoethylene and diffused out of the apparatus.

$$\beta\text{-}Triazoethyl\ Ether,\ N_3\text{·}CH_2\text{·}CH_2\text{·}O\text{·}C_2H_5.$$

Twenty grams of triazoethyl alcohol and 50 grams of ethyl iodide were allowed to remain in darkness with 50 grams of dry silver oxide during two days, being then heated on the water-bath with occasional addition of small quantities of ethyl iodide. After one week, the liquid was separated and distilled under diminished pressure:

0·1057 gave 33·5 c.c. N_2 at $21°$ and 763 mm. $N = 36·39$.

$C_4H_9ON_3$ requires $N = 36·51$ per cent.

The substance is a colourless liquid, boiling at $49°/25$ mm., and having the density $0·9744/24°$. The odour resembles that of chloro-ether, and in steam is pungent and sweet. With concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid, there is a vigorous effervescence, but hot concentrated alcoholic potassium hydroxide appears to be without action on triazoether, the azoimide nucleus remaining intact. Triazoethyl ether does not explode when thrown on a hot iron plate. the vapour burning with a luminous, white flame.

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