LXXXVI.—*The Triazo-group. Part XIII. Triazomethylcarbimide (Triazomethyl isoCyanate).*

By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

THE present investigation was undertaken with the object of adding one more type to the series of simply constructed, aliphatic triazo-compounds which have been examined during the past three years. Triazomethylamine, it was thought, in view of its low molecular weight, its high percentage of nitrogen, and the theoretical possibility of converting it into the still more curious pentazomethane, $N_3 \cdot CH_2 \cdot N_2$, would prove to be a fertile subject for research.

The prospect of obtaining triazomethylamine by the action of alkaline hypobromite on triazoacetamide was not a favourable one, Hofmann having found that the application of his well-known reaction to chloroacetamide led to symmetrical chloromethylchloroacetylcarbamide (*Ber.*, 1885, **18**, 2375); the isolation of chloromethylamine, in fact, was not to be expected, because interaction between hydrogen and chlorine would be almost certain to follow association of the halogen with a carbon atom bearing the amino-group. The knowledge that derivatives of triazoacetic acid retain

the substituent more tenaciously than those of chloroacetic acid led us to attempt the Hofmann reaction with triazoacetamide, but nothing of a basic character besides ammonia was produced; the presence of alkali azide in the residual liquid, however, encouraged us to continue the investigation, as it pointed to behaviour on the part of the triazo-group quite distinct from that which characterises it in the original material.

Another mode of attacking the problem was accordingly sought, and, recalling the facility with which cinnamenylcarbimide may be obtained from cinnamoylazoimide (Forster, *Trans.*, 1909, **95**, 433), we prepared triazomethylcarbimide from triazoacetyl chloride and sodium azide, in the hope that by some process which would leave the azoimide complex undisturbed, the remaining nitrogen atom in triazomethylcarbimide, or in a carbamide derivative obtained from it by the action of bases, might be transformed into the amino-group:

It should be explained that when the description of cinnamenylcarbimide appeared in March, 1909, it was believed to be the earliest record of this process for obtaining *isocyanates*. An account of the formation of these compounds by removing nitrogen from acyl azoimides, published by G. Schroeter (*Chem. Zeit.*, 1908, **32**, 933), however, escaped our notice until June, 1909, when the detailed account of Schroeter's investigation appeared (*Ber.*, 1909, **42**, 2336). This publication led R. Stoermer (*Ber.*, 1909, **42**, 3133) to announce that the same reaction had been observed by him nearly nine years previously, but had remained unpublished excepting in dissertations.

The first step in the direction indicated demanded an improvement in the preparation of triazoacetyl chloride, which before had been obtained in small quantities only; this has been accomplished by heating triazoacetic acid with thionyl chloride, and distilling the triazoacetyl chloride from about 15 per cent. of triazoacetic anhydride produced along with it. Interaction between triazoacetyl chloride and sodium azide led at first to some very alarming explosions, but conditions of moderate safety have now been ascertained, and although the hazardous nature of our experiences led us finally to discontinue the investigation, enough has been learned concerning triazomethylcarbimide to warrant a description of the substance being presented.

Triazoacetyl azide, the compound intermediate between triazoacetyl chloride and triazomethylcarbimide, has not been isolated, and we believe it to be a very dangerous substance. The com-

paratively low temperature at which it suffers explosive decomposition precludes the possibility of preparing it from sodium azide and undiluted triazoacetyl chloride, and although the use of ether as diluent has led to the only satisfactory results which have been obtained, the course of the reaction is not altogether trustworthy. It sometimes happens that the double decomposition between the azide and the chloride is not complete before the conversion of the triazoacetyl azide into triazomethylcarbimide has begun, and as a more elevated temperature is required for the latter transformation, the former is liable to proceed beyond control, and an explosion follows. Moreover, the sensitive character of triazomethylcarbimide itself renders it necessary to carry through the twofold change within the shortest possible limits of time, and the difficulty of retarding the first change while accelerating the second one is considerable.

An examination of triazomethylcarbimide furnished an immediate explanation of the failure to prepare triazomethylamine by the Hofmann reaction, treatment with cold water being sufficient to remove the azoimide complex in the form of hydrazoic acid. The same change occurs when triazomethylcarbamide and phenyltriazomethylcarbamide are treated with warm water or cold alkali carbonates, and it is therefore not surprising that the action of alkali hydroxide on triazoacetobromamide should result in the production of alkali azide. It seems remarkable that the replacement of carboxyl in triazoacetic acid by the isocyanate or substituted amino-group should modify so profoundly the behaviour of the azoimide radicle. The description of triazomethane given by Dimroth and Wislicenus (*Ber.*, 1905, **38**, 1573) does not state whether the triazo-group is readily detached from carbon in that substance, but it was shown that in the case of 1 : 2-bistriazoethane this effect is produced only by continued action of hot alcoholic alkali (*Trans.*, 1908, **93**, 1070). Moreover, disruption between carbon and nitrogen in triazoacetic acid takes place only as a consequence of destroying the azoimide nucleus and the formation of an imino-compound (*loc. cit.*, 72). It is evident, therefore, that the union between a carbon atom and the triazo-group is rendered much less intimate by associating the carbon with another atom of nitrogen. In this connexion it is worth while to recall the fact that carbaminoiminoazoimide (Thiele, *Annalen*, 1892, **270**, 1) loses the triazo-group very readily to alkali, and in this compound, also, there is another atom of nitrogen associated by a single linking with the carbon which carries the triazo-group :

Carbaminoiminoazoimide. Triazomethylcarbimide. Phenyltriazomethylcarbamide.

It may be stated, in fact, that the behaviour of triazomethylcarbimide reveals the triazo-group in a condition of association with carbon which is even more easily dissolved than that prevailing in the acyl azides, since these are obtainable in aqueous systems.

One of our objects in preparing triazomethylcarbimide was to ascertain whether any atomic rearrangement would take place between the triazo-group and the unsaturated carbimide nucleus, for example:

Such a transformation might have been expected from the readiness with which the azoimide complex unfolds itself to take part in additive actions, but the inquiry in this direction has been hampered by the facility with which the carbimide undergoes conversion into the *isocyanurate*, a change common to *isocyanates* generally. The product being a white, odourless solid, we were prepared to find that the change represented above had actually taken place, but there seems little doubt that it consists of tris-triazomethyl *isocyanurate* on account of its behaviour towards weak alkali hydroxide, which resolves it into hydrazoic acid, cyanuric acid, and formaldehyde:

In this respect there is complete analogy between our polymeride and the substance obtained by Hofmann from trimethyl *isocyanurate* and phosphorus pentachloride (*Ber.*, 1886, **19**, 2088); the latter compound, trichloromethyl *isocyanurate*, should arise also by polymerisation of the chloromethylcarbimide recently described by Schroeter (*Ber.*, 1909, **42**, 3358).

Although the presence of the *isocyanate* group is associated in triazomethylcarbimide with transformations characteristic of that class, for instance, conversion into phenyltriazomethylcarbamide by aniline:

the unusually sensitive condition of the azoimide nucleus leads to complications when the substance is treated with ammonia or water. In the former reaction, there is produced, in addition to triazomethylcarbamide, a derivative of this which probably arises in the following manner:

When water acts on the carbimide, a liquid substance is produced

together with an insoluble solid, hydrazoic acid being set free; as the liquid is very explosive and contains more nitrogen than the original material, we regard it as triazomethylcarbamy azide, but it could not be purified. Since phenylcarbamy chloride and bromide arise by the action of halogen hydrides on phenylcarbimide, it seems reasonable that triazomethylcarbamy azide should be formed, in view of the large proportion of hydrazoic acid set free:

and the insoluble solid would be the product of the following changes:

There remains one point of general interest to be noted. When the derivatives of triazomethylcarbimide are heated with aqueous alkali hydroxide, the odour of formaldehyde quickly becomes perceptible, ammonia and hydrazoic acid being simultaneously produced. This is readily understood by recognising that exchange of the triazo-group for hydroxyl in such substances would lead to derivatives of hydroxymethylamine, the hypothetical formaldehyde-ammonia:

The liberation of formaldehyde is thus explained in conformity with the behaviour of α -amino-alcohols.

EXPERIMENTAL.

Attempt to Prepare Triazomethylamine, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{NH}_2$.

Our first experiment in the above direction consisted in applying to triazoacetamide that modification of Hofmann's original process which has been described by François (*Compt. rend.*, 1908, **147**, 680). Five grams of triazoacetamide were dissolved in 20 c.c. of water in which calcium carbonate was suspended, slowly treated with 9 grams of bromine, and mixed with ice-cold 30 per cent. potassium hydroxide as soon as effervescence had subsided. After two hours the temperature was raised to about 100° by passing the liquid through a narrow tube bent several times up and down in the manner described by François, the tube being immersed in boiling water. On subjecting the product to distillation in a current of steam, aqueous ammonia was condensed, and the residue in the flask contained potassium azide. This experiment, although

a failure, revealed the distinctive property acquired by the triazo-group when the atom of carbon to which it is attached becomes directly associated with another atom of nitrogen, because it has been shown that potassium azide is not produced when potassium triazoacetate is heated with excess of alkali. It indicated, further, the necessity of proceeding to triazomethylamine by an indirect method.

Preparation of Triazoacetyl Chloride.

The method by which triazoacetyl chloride was obtained on a former occasion (*Trans.*, 1909, **95**, 200) being unsuited to the production of large quantities, the following course was adopted. Triazoacetic acid from 100 grams of ethyl triazoacetate was heated at 60—70° during two hours under 2—3 mm. pressure in order to remove water, and transferred to a reflux apparatus connected with a tube containing calcium chloride; 87 grams of thionyl chloride were added, and the temperature slowly raised, when brisk evolution of sulphur dioxide and hydrogen chloride took place. Heating was continued, latterly on the water-bath, until the gases had been removed, when the residue was distilled under diminished pressure. The chloride boiled at 43—44°/14 mm., and had sp. gr. 1·3640/13°; with due observance of precautions in hydrolysing the ester and in the removal of alcohol from the solution of potassium triazoacetate, the yield of chloride is about 75 per cent. of that calculated from the weight of ester employed, the residue in the flask consisting of very impure triazoacetic anhydride from which a certain amount of triazoacetic acid may be recovered. Before applying the chloride to the preparation of triazomethylcarbimide, it is advisable to ensure the absence of thionyl chloride or products containing sulphur. A convenient way of doing this consists in treating a portion with a solution of stannous chloride in hydrochloric acid, and warming until nitrogen ceases to be liberated; on diluting with a considerable proportion of water, the liquid should remain colourless, presence of sulphur being indicated by darkening due to stannous sulphide.

Triazomethylcarbimide (Triazomethyl isoCyanate), $\text{N}_3\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{O}$.

The preliminary steps towards preparing this compound led to somewhat alarming occurrences. On adding 0·5 gram of sodium azide to 0·7 gram of triazoacetyl chloride, action began without delay, accompanied by vigorous effervescence, and culminating after fifteen seconds in a terrific explosion. The test was then repeated with rather smaller quantities, the containing vessel being surrounded with ice, but the detonation, although delayed perhaps

a few seconds, was just as imposing, and was accompanied by a flash of yellow light. It was therefore necessary to use a diluent.

Expecting that the boiling point of triazomethylcarbimide would approach 120° under atmospheric pressure, we aimed at selecting a solvent from which it might be distilled without carrying the medium, and accordingly added 3.5 grams of sodium azide to 5 grams of triazoacetyl chloride in twice its volume of *o*-nitrotoluene, but here again the outcome was astonishing, for an explosion occurred after a very short interval; these results must be attributed to a rise in the temperature of the liquid above the detonating point of triazoacetyl azide, because triazoacetyl chloride is a comparatively harmless material. The next attempt was made with a mixture of ether and benzene, but this experiment failed because the production and decomposition of the triazoacetyl azide was not complete within the period devoted to the trial, namely, three to four hours, so that although triazomethylcarbimide was certainly produced, it was mixed with a large proportion of triazoacetyl chloride. Substituting bromobenzene for benzene led to no more fortunate result, but we ultimately found that under certain conditions the *isocyanate* may be prepared by using ether alone.

Seven grams of sodium azide were added to a mixture of 10 grams of triazoacetyl chloride with 40 c.c. of ether (dried over sodium) in a flask connected with a reflux condenser and a tube of calcium chloride; action soon became evident from the ebullition of the solvent, and was allowed to proceed for about an hour. The flask was then warmed cautiously on a water-bath during three hours to complete the double decomposition between the chloride and the azide, after which the ether was gradually boiled away, and the residue heated alone for the last two hours of the seven occupied by the experiment. It was then evident from the odour of the product that transformation into *isocyanate* had been complete, because although the smell of this material is horribly pungent, that of triazoacetyl chloride is very penetrating, and has a distinctive quality which makes it perceptible in those cases when it is still present.

The combined product from two such experiments was then freed from ether under atmospheric pressure, and distilled with the aid of the pump, when the *isocyanate* passed over as a clear, colourless liquid at $44\text{--}45^{\circ}/32$ mm., $39^{\circ}/26$ mm., and $35.5^{\circ}/19$ mm.:

0.1483 gave 72.7 c.c. N_2 at 20° and 764 mm. $N=56.38$.

0.0818 „ 40.4 c.c. N_2 „ 20° „ 772 mm. $N=57.42$.

$C_2H_2ON_4$ requires $N=57.14$ per cent.

Although it would appear from this description that the preparation of triazomethylcarbimide is a simple one, a successful

result has been obtained in very few of the thirty or forty experiments which have been made. Moreover, the course of the reaction is so treacherous that after an alarming explosion which took place recently during the removal of the solvent, and which must have been due to imperfect decomposition of the triazoacetyl azide, although the action had apparently proceeded in the manner described, we have reluctantly abandoned the investigation of this interesting substance.

The vapour of triazomethylcarbimide exerts an overpowering effect on the mucous membrane of the eyes and nose, and the liquid produces painful sores if allowed to come in contact with the skin. The freshly distilled isocyanate has sp. gr. 1.2580/18°, and when covered with aqueous sodium carbonate quickly dissolves, yielding sodium azide. The action of concentrated sulphuric acid is violent, but not explosive, while effervescence with stannous chloride in hydrochloric acid is very brisk.

Action of Water.—Several grams of freshly distilled triazomethylcarbimide were covered with a few c.c. of cold water, and left in an open beaker during three to four weeks. Action took place immediately, hydrazoic acid passing into the water, and being easily recognised after a short interval by the powerful odour, while that of the isocyanate was destroyed in the course of a few hours. At the conclusion of the experiment a white solid remained suspended in the water, and a heavy, colourless oil, which did not appear to be undergoing any further change, was also observed. The solid was removed mechanically, being rather sticky, washed with ether, and extracted with hot acetone, which dissolved a small quantity of the polymeride, melting at 153°. The snow-white residue was insoluble in boiling chloroform or benzene, and in hot pyridine; it intumesced at 242°, forming a clear, yellow liquid a few degrees above this temperature. When heated with 20 per cent. aqueous potassium hydroxide, the substance did not dissolve, and but a moderate proportion of hydrazoic acid was eliminated; ammonia was set free, and the odour of formaldehyde became perceptible. It effervesced mildly with concentrated sulphuric acid:

0.1706 gave 57.6 c.c. N_2 at 22° and 764 mm. $N = 38.45$.

$C_5H_{10}O_4N_6$ requires $N = 38.53$ per cent.

The heavy oil from which the foregoing product had been separated was extracted with ether, and treated with animal charcoal and anhydrous sodium sulphate; on evaporating the filtrate in a vacuum, a viscous, odourless oil remained, and did not become solid during four months in the desiccator. The liquid was insoluble in dilute hydrochloric acid or sodium carbonate, but gradually changed under the influence of the latter into a white

solid, whilst hydrazoic acid was eliminated. The first attempt to estimate nitrogen resulted in a violent explosion:

0.1153 gave 65.5 c.c. N_2 at 18° and 768 mm. $N=66.32$.

$C_2H_3ON_7$ requires $N=69.50$ per cent.

The oil underwent violent decomposition with concentrated sulphuric acid, which developed the odour of hydrogen cyanide; when heated with 30 per cent. potassium hydroxide it gave formaldehyde, ammonia, and a large proportion of potassium azide.

Tristriazomethyl isocyanurate, $(N_3 \cdot CH_2 \cdot NCO)_3$.

On one occasion the distillation of the *isocyanate* was accompanied by a curious phenomenon. As the first few drops fell into the receiver, a particle of white solid was noticed in suspension, and as the operation proceeded this grew so rapidly that by the time the liquid had passed over, its transformation into the solid was almost complete. Some of this material afterwards appeared in the tube of the condenser, but we are still ignorant as to the cause of the change, which was not observed in any succeeding preparation; there was reason to think, however, that in this particular experiment the accompanying ether had been removed more thoroughly than usual.

The snow-white compound is odourless, and gives sluggish effervescence with concentrated sulphuric acid; it is insoluble in boiling alcohol, and only very sparingly soluble in hot chloroform and acetone. The substance dissolves somewhat readily in cold pyridine, however, separating in colourless needles on dilution with water, and melts, evolving gas, at 153° :

0.0670 gave 33.2 c.c. N_2 at 22° and 770 mm. $N=56.89$.

$C_2H_2ON_4$ requires $N=57.14$ per cent.

A 20 per cent. aqueous solution of potassium hydroxide dissolves the compound when gently warmed, developing the odour of formaldehyde; by the use of more dilute alkali the production of cyanuric acid was established, and acidification of the resulting liquid with dilute sulphuric acid gave hydrazoic acid. Thus the behaviour indicates a polymeride of the *isocyanate* rather than a simple transformation product in which the triazo-group has undergone rearrangement into a tetrazole derivative.

Phenyltriazomethylcarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot N_3$.

The calculated amount of freshly distilled aniline was mixed with three or four parts of ether (dried over sodium), cooled in ice, and slowly added to the *isocyanate* dissolved in the same proportion of ether. After a short interval, flat, lustrous, colourless needles

separated, and as the substance was found to undergo decomposition very rapidly in the dissolved state, especially if the solution is warmed, recrystallisation was effected by dissolving it in cold acetone, diluting with water, and filtering the felted mass of snow-white needles without delay:

0.1100 gave 35.7 c.c. N_2 at 23° and 766 mm. $N=36.88$.

$C_8H_9ON_5$ requires $N=36.65$ per cent.

Phenyltriazomethylcarbamide melts at 120° ; it is freely soluble in organic liquids excepting petroleum, which does not dissolve it on boiling. It is rapidly attacked by hot water, which eliminates the triazo-group in the form of hydrazoic acid. Brisk effervescence occurs with concentrated sulphuric acid, and gas is liberated also by stannous chloride in hydrochloric acid.

Action of Sodium Carbonate.—A freshly prepared specimen of the carbamide was covered with a dilute aqueous solution of the alkali, which at once converted it into a stiff paste; this quickly became hard again, and was then recrystallised from a small quantity of hot alcohol. Stellate aggregates of snow-white needles were deposited, melting at 147° with vigorous intumescence:

0.0391 gave 6.0 c.c. N_2 at 22° and 768 mm. $N=17.58$.

$C_8H_{10}O_2N_2$ requires $N=16.88$ per cent.

Absence of the triazo-group was indicated by the action of concentrated sulphuric acid, which merely dissolved the substance without evolving gas, and on examining the sodium carbonate from which the carbamide had been filtered, this was found to be rich in sodium azide.

Triazomethylcarbamide, $N_3 \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$.

Triazomethylcarbamide in ether (dried over sodium) was cooled with ice, and treated with a solution of ammonia in the same solvent until the odour of isocyanate was destroyed. White flocks appeared almost immediately, followed more slowly by clumps of long, lustrous, colourless needles. The solvent was decanted, the solid quickly drained on earthenware, and stirred with cold benzene to remove any unchanged isocyanate. After recrystallisation from a concentrated solution in dry acetone, which was allowed to evaporate in the desiccator, the substance melted at 56° :

0.0686 gave 35.9 c.c. N_2 at 22° and 776.5 mm. $N=60.55$.

$C_2H_5ON_5$ requires $N=60.87$ per cent.

Triazomethylcarbamide is freely soluble in cold acetone and insoluble in chloroform or benzene; cold water dissolves it readily, and the odour of hydrazoic acid becomes quickly noticeable on warming the solution. The substance froths vigorously with con-

centrated sulphuric acid, developing the odour of hydrogen cyanide; gas is liberated also by stannous chloride in hydrochloric acid. Hot aqueous 30 per cent. potassium hydroxide gives rise to ammonia, formaldehyde, and potassium azide.

A second product of the action of ammonia on triazomethylcarbimide was revealed on allowing the ether decanted from the foregoing compound to evaporate in a vacuum desiccator. The pasty residue had the odour of hydrazoic acid, and left a snow-white, crystalline mass when drained on earthenware, melting with decomposition at 227°

0.0999 gave 45.4 c.c. N_2 at 24° and 776.5 mm. $N=52.07$.

$C_4H_9O_2N_7$ requires $N=52.41$ per cent.

This compound was insoluble in cold acetone and water, but dissolved in the latter on warming, when hydrazoic acid was liberated. It effervesced with concentrated sulphuric acid, producing the odour of prussic acid; hot 30 per cent. potassium hydroxide resolved it into formaldehyde, ammonia, and hydrazoic acid. As already explained, we regard this substance as arising from the action of triazomethylcarbimide on the hypothetical aminomethylcarbamide resulting from replacement of the azoimide complex in triazomethylcarbamide by the amino-group.

We have pleasure in expressing our thanks to Mr. S. H. Newman for preparing a considerable quantity of triazoacetic acid and triazoacetyl chloride required as material for this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.