

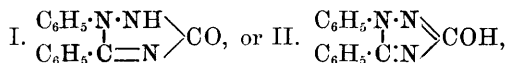
CXI.—*Synthesis of Diphenyloxytriazole.**

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In a preliminary notice previously communicated to the Society (Proc., 1894-95, 124), I described a reaction which resulted in the formation of 1 : 5-diphenyl-3-oxy-1 : 2 : 4-triazole. This substance is produced by the action of an oxidising agent on a mixture of benzaldehyde and α -phenylsemicarbazide, and its formation may be represented by the equation—



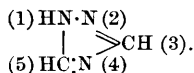
The product is a white crystalline substance which dissolves in warm concentrated hydrochloric acid and in dilute alkalis. Its alkaline solution has no action on Fehling's solution even on prolonged boiling. Heated with phosphorus pentasulphide, it undergoes Andreocci's reaction for oxytriazoles, being reduced to a weak base of the formula $\text{C}_{14}\text{H}_{11}\text{N}_3$. Its constitution must be either—



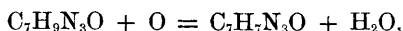
and the pronounced acid and extremely feeble basic character of the substance would seem to make Formula II the more probable.

As the 2 mols. of water formed in the reaction are different in their origin—the oxygen atom for the one molecule being supplied by the benzaldehyde, that for the other by the oxidising agent—it seemed probable that the action would take place in two stages. Some preliminary experiments showed that, if the conditions at all approach those under which the formation of the diphenyloxytriazole takes place, benzaldehyde and phenylsemicarbazide have, when all oxidising agents are carefully excluded, no action on each other. The intermediate product could therefore not be a benzyldene derivative of phenylsemicarbazide, and the action is not, as was first supposed, analogous to that by which Bladin (*Ber.*, 1889, 22, 796) prepared diphenylcyanotriazole from phenylhydrazine dicyanide and benzaldehyde. The first stage then must be an oxidation process. It might possibly have resulted in the formation of

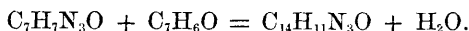
* The name triazole was given to the carbon nitrogen ring, $\text{C}_2\text{N}_3\text{H}_3$, by Bladin, who first described derivatives of it, and his nomenclature is adhered to in this paper, the position of substituting groups and the relative positions of the nitrogen atoms in the ring being shown according to the plan



a benzoylphenylsemicarbazide, $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NH}\cdot\text{CONH}_2 \\ | \\ \text{C}_6\text{H}_5\cdot\text{CO} \end{array}$, which, losing water in the second stage, would form the triazole ring; but this substance, when prepared by Widman (*Ber.*, 1893, **26**, 948) from benzoyl chloride and phenylsemicarbazide, resisted all inducements to the ring condensation. The failure of an attempt to produce the final product by the action of benzoic acid on phenylsemicarbazide, shut out the possibility that the first stage might consist in oxidation of the benzaldehyde. A more successful result was obtained by excluding the benzaldehyde from the first stage; the action then took place according to the equation—

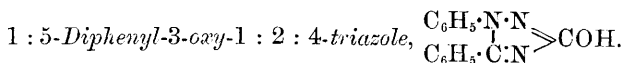


the product being phenylazocarbamide, $\text{C}_6\text{H}_5\text{N}\cdot\text{N}\cdot\text{CONH}_2$. This, when heated in alcoholic solution with benzaldehyde, condenses with it to diphenyloxytriazole.



These two equations represent the two stages of the reaction. It is true the condensation in the second stage takes place with more difficulty (see experimental details) when the intermediate product is first isolated, than when the two stages are allowed to proceed together; the ease with which the second stage takes place under the latter condition is probably due to the amount of heat which is evolved by the oxidation.

EXPERIMENTAL.



An alcoholic solution of benzaldehyde and phenylsemicarbazide was boiled for a few minutes, the alcohol evaporated over the water bath, and the residue extracted with boiling water to remove unchanged phenylsemicarbazide; the white, crystalline residue was purified by recrystallisation from alcohol. The long, white needles thus obtained, on analysis, gave figures agreeing with those required for the formula $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$. The yield by this method is extremely small, amounting to only 4 per cent. of that theoretically obtainable according to the equation $\text{C}_7\text{H}_5\text{N}_3\text{O} + \text{C}_7\text{H}_6\text{O} + \text{O} = \text{C}_{14}\text{H}_{11}\text{N}_3\text{O} + 2\text{H}_2\text{O}$. A much larger yield was obtained on adding an oxidising agent, and the following method was found to give the best results, yielding as much as 60 per cent. of the theoretical.

Phenylsemicarbazide* and benzaldehyde, in molecular proportion,

* The phenylsemicarbazide was prepared from phenylhydrazine and potassium

are dissolved in alcohol, and boiled for a few minutes, with the addition of an alcoholic solution of the necessary amount of ferric chloride (2 mol. FeCl_3). On adding water, diphenyloxytriazole is precipitated as a mass of brownish needles, which, after being collected and dried, are sufficiently pure for further use. The substance may be purified by crystallising it from boiling alcohol; as the solution cools, the diphenyloxytriazole is deposited as a mass of slender, white needles, which, when rapidly heated, melt at 288° , at the same time undergoing partial decomposition. If more slowly heated, diphenyloxytriazole sublimes in long needles at about 280° . Analysis of the substance recrystallised from alcohol gave results agreeing with the formula $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$.

- I. 0.1409 gave 0.3656 CO_2 and 0.0599 H_2O .
 II. 0.1381 „ 0.3583 „ „ 0.0577 „
 III. 0.2124 „ 32.8 c.c. moist nitrogen at 15.5° and 752 mm.

	I.	II.	III.	Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$.
C	70.76	70.75	—	70.88 per cent.
H	4.72	4.60	—	4.64 „
N	—	—	17.85	17.72 „

Specimen I was prepared by the first method, specimens II and III by the second method.

Diphenyloxytriazole is insoluble in cold water, only slightly soluble in boiling water, in cold alcohol, or boiling ether, but easily in boiling alcohol. It has very decided acid properties, its aqueous solution reddens blue litmus paper; it is easily soluble in dilute alkalis, and from the solutions thus obtained it is precipitated unchanged on the addition of hydrochloric acid. It dissolves, on being gently warmed, in a solution of sodium carbonate. The alkaline solution of diphenyloxytriazole has no action on Fehling's solution, even on prolonged boiling.

The silver derivative, $\text{AgC}_{14}\text{H}_{10}\text{N}_3\text{O} + \text{H}_2\text{O}$, is precipitated as a white, amorphous powder on adding silver nitrate solution to a neutral solution of diphenyloxytriazole in aqueous ammonia. The salt, if moist, gradually turns pink on exposure to light, but when washed rapidly with small quantities of alcohol and ether, and dried in a vacuum over sulphuric acid, it is stable. When heated at 110° , the salt gives up its molecule of water.

0.7234 lost, at 110° , $0.0366 \text{ H}_2\text{O} = 5.07$.

$\text{AgC}_{14}\text{H}_{10}\text{N}_3\text{O} + \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.97$ per cent.

cyanate according to the directions given by Widman (*Ber.*, 1893, **26**, 2613. Foot-note). From freshly prepared materials, an almost quantitative yield may be obtained.

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0.6675 of the dried salt gave $0.2686 \text{ AgCl} + 0.0078 \text{ Ag}$. $\text{Ag} = 31.46$.
 $\text{AgC}_{14}\text{H}_{10}\text{N}_3\text{O}$ requires $\text{Ag} = 31.39$ per cent.

Diphenyloxytriazole is also a weak base, as it dissolves easily in concentrated hydrochloric acid on warming, and the solution, on cooling, deposits small tufts of needles, which, when dried on a porous plate over caustic potash in a desiccator and analysed, gave figures agreeing with the formula $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O} \cdot \text{HCl} + 2\text{H}_2\text{O}$.

0.4672 gave 0.2186 AgCl . $\text{HCl} = 11.90$.

$\text{C}_{14}\text{H}_{11}\text{N}_3\text{O} \cdot \text{HCl} + 2\text{H}_2\text{O}$ requires $\text{HCl} = 11.79$ per cent.

The salt gives up the whole of its hydrochloric acid as well as the water of crystallisation when heated at 100° .

0.2949 lost, at 100° , 0.0680 . HCl and $2\text{H}_2\text{O} = 23.05$.

$\text{C}_{14}\text{H}_{11}\text{N}_3\text{O} \cdot \text{HCl} + 2\text{H}_2\text{O}$ requires $\text{HCl} + 2\text{H}_2\text{O} = 23.39$ per cent.

The hydrochloride is also easily dissociated by washing with water.

Acetyldiphenyloxytriazole, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}(\text{C}_2\text{H}_3\text{O})$.—The acetyl derivative was prepared by boiling the diphenyloxytriazole with acetic anhydride and fused sodium acetate for one hour, using a reflux condenser, dissolving the product in ether, washing several times with potassium carbonate solution, and finally with water. After drying the liquid with calcium chloride, the greater part of the ether was distilled off, and the remainder allowed to evaporate spontaneously, when the acetyl derivative was deposited in well formed prisms, melting at 133° .

0.2158 gave 28.6 c.c. moist nitrogen at 13° and 734.3 mm. $\text{N} = 15.12$.

$\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}(\text{C}_2\text{H}_3\text{O})$ requires $\text{N} = 15.05$ per cent.

Acetyldiphenyloxytriazole is easily soluble in alcohol and ether; on boiling with dilute potassium carbonate solution, it is rapidly hydrolysed to acetic acid and diphenyloxytriazole.

Benzoyldiphenyloxytriazole, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}(\text{C}_7\text{H}_5\text{O})$.—The benzoyl derivative, prepared by boiling the oxytriazole with a slight excess of benzoyl chloride, was isolated and purified in precisely the same way as the acetyl derivative. It crystallises in white, flat needles, melting at 134° . It was also prepared from the silver derivative of the oxytriazole by boiling it with an ethereal solution of benzoyl chloride, filtering, and distilling off the ether. It is sparingly soluble in hot water, easily in hot alcohol and in ether. It is easily hydrolysed by warming with potassium carbonate solution.

0.238 gave 25.6 c.c. moist nitrogen at 16° and 759.7 mm. $\text{N} = 12.53$.

$\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}(\text{C}_7\text{H}_5\text{O})$ requires $\text{N} = 12.31$ per cent.

Ethyldiphenyloxytriazole, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O} \cdot \text{C}_2\text{H}_5$.—This derivative was

prepared by heating molecular proportions of diphenyloxytriazole, potassium hydrate, and ethylic iodide (the last in slight excess) with a small quantity of ethylic alcohol in a sealed tube at 100° for one hour; it was also prepared by the action of ethylic iodide at the ordinary temperature on the silver derivative. Both methods gave the same substance. It is easily soluble in alcohol and ether, slightly so in boiling water, and, when recrystallised from dilute alcohol, forms tufts of delicate white needles, which melt at 92° .

Ethyldiphenyloxytriazole is not hydrolysed by boiling with alkalis or acids.

0.1981 gave 27.8 c.c. moist nitrogen at 16° and 761.5 mm. N = 16.38.

0.1924 gave 26.3 c.c. moist nitrogen at 15° and 759.4 mm. N = 16.16.

$C_{16}H_{15}N_3O$ requires N = 15.85 per cent.

Specimen I was prepared with potassium hydroxide, specimen II from the silver salt.

Phenylazocarbamide, $C_6H_5N:N\cdot CO\cdot NH_2$.

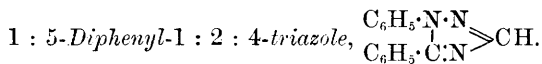
Five grams (1 mol.) of phenylsemicarbazide were suspended in cold water, and a cold aqueous solution of ferric chloride (2 mols. $FeCl_3$) slowly added, the mixture being well stirred. The solution was extracted by agitating with ether so long as the ether became coloured, the process being much shortened if the aqueous solution is saturated with ammonium sulphate. The ethereal solution when distilled on the water bath deposited long, silky, yellowish-red needles, melting at 114° ; yield, 4 grams.

0.1519 gave 38.4 c.c. moist nitrogen at 22° and 750.6 mm. N = 28.26.

$C_6H_5N_2\cdot CONH_2$ requires N = 28.18 per cent.

Widman (*Ber.*, 1895, **28**, 1925) has quite recently prepared the same substance from nitrosophenylsemicarbazide, and also by the oxidation of phenylsemicarbazide with potassium permanganate in dilute sulphuric acid. I find that the properties of the substance prepared as above agree with those quoted by Widman. I would add that the aqueous solution has a slight but decidedly acid reaction to litmus paper, and that the phenylazocarbamide is slightly volatile with steam. Phenylazocarbamide is slowly formed by the action of moist air on phenylsemicarbazide.

Phenylazocarbamide and benzaldehyde do not react in alcoholic solution at the boiling point, and the addition of ferrous chloride as a condensing agent is without effect; if, however, the alcoholic solution of the two be heated in a sealed tube at 120° for one hour, considerable quantities of diphenyloxytriazole are formed according to the equation $C_7H_7N_3O + C_7H_6O = C_{14}H_{11}N_3O + H_2O$. The yield is increased in this case by the addition of ferrous chloride.



This was prepared from the corresponding diphenyloxytriazole by the action of phosphorus pentasulphide according to Andreocci's method (*Real Accad. Lincei*, 1890, ii, 209). Six grams of diphenyloxytriazole were intimately mixed with 10 grams of phosphorus pentasulphide, and the mixture heated for six hours at 230–250°; the dark brown brittle mass thus obtained was boiled with potassium carbonate solution, using a reflux condenser, the solution extracted with ether, and the ethereal solution dried over calcium chloride. On distilling off the ether, a brown oil was left, which rapidly solidified; when recrystallised from water, it formed clusters of fine white needles melting at 91°. Six grams of diphenyloxytriazole yielded 2 grams of the pure product.

0.2145 gave 36.3 c.c. moist nitrogen at 16° and 742.1 mm. N = 19.25.
0.1572 gave 0.4372 CO₂ and 0.0723 H₂O. C = 75.84; H = 5.10.

C₁₄H₁₁N₃ requires C = 76.01; H = 4.97; N = 19.00 per cent.

Diphenyltriazole is easily soluble in ether and alcohol, moderately in boiling water, and is sufficiently soluble in cold water to repay extraction of the aqueous mother liquors with ether; it is moderately volatile with steam; as the substance crystallised from the steam distillate in thin, shining plates, it was necessary to ascertain its identity with the substance crystallising in needles, and with this object a nitrogen determination was made and the melting point observed; it melts at 91°.

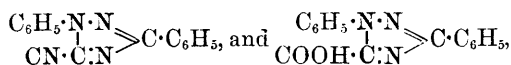
0.2215 gave 37.1 c.c. moist nitrogen at 12° and 738 mm. N = 19.29.

C₁₄H₁₁N₃ requires N = 19.00 per cent.

Subsequently the conversion of the one form into the other was noticed during recrystallisation.

Diphenyltriazole sublimes unchanged when heated above its melting point; it is a feeble base; its aqueous solution turns red litmus paper blue, and it forms a hydrochloride and a platinochloride, both of which are dissociated by water. Pinner (*Ber.*, 1894, **27**, 997), by heating benzoylbenzenylhydrazine, prepared an isomeric diphenyltriazole, $\text{C}_6\text{H}_5\cdot\text{C} \begin{array}{c} \text{NH}\cdot\text{N} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C}\cdot\text{C}_6\text{H}_5$, which he states to have no basic properties.

Bladin (*Ber.*, 1889, **22**, 801) by the action of benzaldehyde on phenylhydrazine dicyanide, hydrolysis of the resulting diphenylcyanotriazole, and elimination of carbon dioxide, prepared a diphenyltriazole, to which, considering phenylhydrazine dicyanide, to have the constitution $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NH}_2 \\ | \\ \text{CN}\cdot\text{C}\cdot\text{NH} \end{array}$, and the intermediate products to be



he assigned the constitution $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{N} \\ | \quad | \\ \text{HC} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{C}_6\text{H}_5$. It has been shown, however, by Bamberger and de Gruyter (*Ber.*, 1893, **26**, 2385) and by Widman (*Ber.*, 1893, **26**, 2617) that phenylhydrazine dicyanide has the constitution $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CN}) \cdot \text{NH}_2$, which would give with benzaldehyde, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{N} \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{CN}$, and the diphenyltriazole derived from this should be identical with that which I have described above. But the properties quoted by Bladin are entirely at variance with those I have found in my preparation. Bladin describes his substance as a yellow, hard glass, which, on analysis, gave $1\frac{1}{2}$ per cent. too little carbon, but could not be purified as it was not volatile with steam, and separated from the various solvents as an oil. It was, moreover, insoluble in water, soluble with difficulty in ether, and of an extremely feeble basic nature. I have therefore examined Bladin's compound. The diphenyltriazolecarboxylic acid, prepared according to Bladin's directions, was carefully purified, first by fractional precipitation by hydrochloric acid from the solution of its ammonium salt, and then by repeated recrystallisations from alcohol. The properties of the acid agreed with Bladin's description; it crystallised in hard, colourless, flat needles, which melted with effervescence at 176° (Bladin gives 172 — 182° C.), and lost 1 mol. alcohol of crystallisation at 100° .

0.3222 lost, at 100° , 0.0472. $\text{C}_2\text{H}_6\text{O} = 14.65$.

$(\text{C}_6\text{H}_5)_2\text{C}_2\text{N}_3 \cdot \text{COOH}$, $\text{C}_2\text{H}_6\text{O}$ requires $\text{C}_2\text{H}_6\text{O} = 14.79$ per cent.

0.2132, dried at 100° , gave 29.3 c.c. moist nitrogen at 16° and 756.5 mm. $\text{N} = 15.94$.

$(\text{C}_6\text{H}_5)_2\text{C}_2\text{N}_3 \cdot \text{COOH}$ requires $\text{N} = 15.84$ per cent.

The carefully purified acid was heated in a flask in an oil bath, the temperature of which was slowly raised until the substance began to melt. The temperature was then lowered to 160° , at which it was maintained so long as carbon dioxide was evolved. When cold, the light brown, viscid, syrupy product was treated with ether in the cold, in which the greater part dissolved; the residue was not crystalline. The ethereal solution was filtered and evaporated, and the oily residue extracted with boiling water; the aqueous solution, on cooling, deposited at first a considerable amount of uncrystallisable, tarry matter, and then, after standing for some hours in the cold, a small amount of white, needle-shaped crystals. These melted at 85 — 87° , and after recrystallisation from dilute alcohol at 90 — 91° .

The amount of substance thus obtained was too small for analysis, but the melting point, the solubility, and the appearance of the crystals deposited from dilute alcohol, leave no doubt of its identity with the diphenyltriazole prepared from phenylsemicarbazide.

Diphenyltriazole hydrochloride, $C_{14}H_{11}N_3.HCl + 2H_2O$.

Diphenyltriazole dissolves easily in warm concentrated hydrochloric acid; the addition of water to this solution precipitates the diphenyltriazole unchanged if the warm concentrated hydrochloric acid be allowed to cool, the hydrochloride is deposited in bunches of long thin prisms. The salt is easily dissociated by washing with water or by heating to 90° .

0.3241 gave 0.1579 AgCl. $HCl = 12.37$.

0.4623, at 90° , lost 0.1141. HCl and $H_2O = 24.68$.

$C_{14}H_{11}N_3.HCl + 2H_2O$ requires $HCl = 12.43$ and $HCl + 2H_2O = 24.69$ p.c.

Diphenyltriazole Platinochloride, $[C_{14}H_{11}N_3.HCl]_2PtCl_4 + 4H_2O$.

The platinochloride is thrown down as a yellow precipitate on adding platinum chloride solution to a solution of diphenyltriazole in concentrated hydrochloric acid. It is soluble in warm concentrated hydrochloric acid, and crystallises out, on cooling, in long, yellowish-red prisms, containing $4H_2O$, which are given up at 100° .

0.3009 gave 0.0625, Pt. $Pt = 20.80$.

0.2360, at 100° , lost 0.0191. $H_2O = 8.09$.

$(C_{14}H_{11}N_3.HCl)_2PtCl_4 + 4H_2O$ requires $Pt = 21.15$ and $H_2O = 7.78$ p.c.

Andreocci investigated the behaviour of the platinochlorides of phenyltriazole and phenylmethyltriazole when boiled with water, and when heated at temperatures from 150° to 220° (*Real Accad. Linc.*, 1891, ii, 157). He says that the platinochlorides of the pyro-diazoles (Andreocci's term for triazoles) resemble in their behaviour the platinochlorides of the pyridine series in that by the action of water, the salts, $R_2H_2PtCl_6$, are converted into compounds of the type R_2PtCl_4 , which are yellow powders. The platinochloride of phenylmethyltriazole, when heated to 205° , loses, besides its water of crystallisation, 4 mols. HCl (*loc. cit.*, p. 188); the phenyltriazole salt, on the other hand, loses its water of crystallisation at 100° , 2 mols. HCl when heated at 150 – 180° , and another 2 mols. HCl at 200 – 215° , but at this temperature undergoes partial decomposition. Widman, on reinvestigating the platinochloride of the same phenyltriazole, confirmed Andreocci's results. I have studied the behaviour of the platinochloride of diphenyltriazole under the conditions mentioned. When heated to 180° , the salt fused, became somewhat

paler in colour, and lost weight. When the weight remained constant, the loss was equal to 4 mols. HCl, plus the water of crystallisation, and an estimation of the platinum in the residue agreed with the formula $(C_{14}H_{10}N_3)_2PtCl_2$.

0.2360 at 180° lost 0.0567. HCl and $H_2O = 24.19$.

$[C_{14}H_{11}N_3HCl]_2PtCl_4 + 4H_2O$ requires $4HCl + 4H_2O = 23.58$.

0.2214, heated at 180° , gave 0.0619 Pt. Pt = 27.86.

$[C_{14}H_{10}N_3]_2PtCl_2$ requires Pt = 27.67 per cent.

The behaviour of diphenyltriazole platinochloride when heated to 180° corresponds with that of the platinochloride of phenyltriazole as described in Andreocci's paper.

The behaviour of the platinochloride of diphenyltriazole when treated with water is in agreement with the very feeble basic properties of the substance; when washed with cold water, the red colour slowly disappears, the final residue being a white powder. The same action takes place, only more quickly, when the platinochloride is boiled with water. In both cases platinum tetrachloride and free hydrochloric acid can be detected in the washings, and the white residue is diphenyltriazole, complete dissociation of the salt having taken place.

The reaction by which the diphenyloxytriazole is formed, is being extended to other aldehydes as also to other semicarbazides.
