LXII.—C-*Phenyl-s-triazole*.

By GEORGE YOUNG.

IN a previous communication, in conjunction with Mr. Oates (Trans., 1901, **79**, 665), I described the preparation of 3-phenyl-1-methyl-5-

hydroxy-1 : 2 : 4-triazole, $\begin{smallmatrix} \text{N} \cdot \text{NMe} \\ | \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{Ph} \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{OH}$, and, on heating this substance

with phosphorus pentasulphide, a product was obtained, the empirical formula for which contained CH_2 less than that required for 3-phenyl-1-methyl-*s*-triazole. As this was in agreement with the experience of Andreocci (*Atti R. Accad. Lincei*, 1890, [iv], **6**, ii, 209), who

obtained 1-phenyl-3-methyl-1 : 2 : 4-triazole, $\begin{smallmatrix} \text{NPh} \cdot \text{N} \\ | \\ \text{CH} : \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{Me}$, by heating 1-phenyl-3 : 4-dimethyl-5-oxy-4 : 5-dihydro-1 : 2 : 4-triazole,

with phosphorus pentasulphide, we ascribed to our product the constitution of C-phenyl-*s*-triazole, $\begin{smallmatrix} \text{N} - \text{NH} \\ | \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{Ph} \cdot \text{N} \end{smallmatrix} \gg \text{CH}$. This view of the

constitution is now confirmed, as the product obtained on heating *C*-phenylhydroxy-*s*-triazole, $\begin{array}{c} \text{N}-\text{NH} \\ | \quad | \\ \text{CPh} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{OH}$ (Young and Witham, *Trans.*, 1900, **77**, 226), with pentasulphide is found to be identical with the substance obtained from 3-phenyl-1-methyl-5-hydroxy-1 : 2 : 4-triazole.

The term *s*-triazole is used in this paper to distinguish the triazole, which may be either $\begin{array}{c} \text{NH} \cdot \text{N} \\ | \quad | \\ \text{CH} : \text{N} \end{array} \gg \text{CH}$ or $\begin{array}{c} \text{N} \text{-----} \text{N} \\ | \quad | \\ \text{CH} \cdot \text{NH} \end{array} \gg \text{CH}$, from *v*-triazole, which may be $\begin{array}{c} \text{NH} \cdot \text{N} \\ | \quad | \\ \text{N} : \text{CH} \end{array} \gg \text{CH}$ or $\begin{array}{c} \text{N} \cdot \text{NH} \\ | \quad | \\ \text{N}-\text{CH} \end{array} \gg \text{CH}$.

It is worth noting that, whereas the melting point of 1-phenyl-1 : 2 : 4-triazole, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \quad | \\ \text{CH} : \text{N} \end{array} \gg \text{CH}$ (m. p. 47°; Andreocci, *Ber.*, 1892, **25**, 225), follows Wedekind's rule (*Ber.*, 1898, **31**, 949) for the effect of substitution on the melting points of carbon-nitrogen cyclic compounds, both *C*-phenyl-*s*-triazole, $\begin{array}{c} \text{N}-\text{NH} \\ | \quad | \\ \text{CPh} \cdot \text{N} \end{array} \gg \text{CH}$ (m. p. 119·5—120°; this paper), and 1-phenyl-1 : 3 : 4-triazole, $\begin{array}{c} \text{N} \text{-----} \text{N} \\ | \quad | \\ \text{CH} \cdot \text{NPh} \end{array} \gg \text{CH}$ (m. p. 121°; Pellizzari and Massa, *Atti R. Accad. Lincei*, 1901, [v], **10**, i, 363), melt at almost the same temperature as the parent substance, *s*-triazole (m. p. 120—121°; Andreocci, *loc. cit.*).

EXPERIMENTAL.

C-Phenylhydroxy-*s*-triazole (6 grams) was intimately mixed with phosphorus pentasulphide (15 grams) and the mixture heated in an oil-bath for 6 hours at 230—250°. The product was boiled with aqueous potassium carbonate in a reflux apparatus, and, after cooling, was extracted repeatedly with ether. The ethereal solution was then concentrated until crystallisation commenced, when, on cooling, the residual liquid crystallised to a mass of shining plates and needles, which melted at 119—120°.

0·1825 gave 0·4426 CO₂ and 0·0809 H₂O. C = 66·14; H = 4·92.

0·1740 „ 43·6 c.c. moist nitrogen at 18° and 761 mm. N = 28·96.

C₈H₇N₃ requires C = 66·21; H = 4·83; N = 28·97 per cent.

C-Phenyl-*s*-triazole was readily soluble in alcohol, warm ether, or benzene, and moderately so in hot water, but dissolved only to a slight extent in light petroleum; it crystallised from water in clusters of soft, matted needles, from a mixture of benzene and light petroleum in nodular aggregates of microscopic needles, and from dilute alcohol in slender needles. It melted at 119·5—120°, volatilised in shining

plates when heated over its melting point, and was slightly volatile in a current of steam.

A mixture of equal parts of the products obtained from 3-phenyl-1-methyl-5-hydroxy-1 : 2 : 4-triazole and from *C*-phenylhydroxy-*s*-triazole respectively melted at 119—119·5°.

Towards aqueous alkali hydroxides and towards silver nitrate, *C*-phenyl-*s*-triazole exhibited the behaviour characteristic of those triazoles in which the *N*-hydrogen atom is not substituted. It dissolved in dilute aqueous potassium hydroxide more readily than in water, and was reprecipitated from the alkaline solution on addition of ammonium acetate and expulsion of the liberated ammonia by gentle warming. When treated with silver nitrate in alcoholic solution, it formed the *additive* compound of silver nitrate and the silver derivative, $C_8H_6N_3Ag, AgNO_3, H_2O$, which was obtained as a white precipitate from which H_2O was driven off at 110°.

0·8184, at 110°, lost 0·0352 H_2O . $H_2O = 4·30$.

0·8184 gave 0·4024 Ag. Ag = 49·17.

$C_8H_6N_3Ag, AgNO_3, H_2O$ requires Ag = 49·34; $H_2O = 4·11$ per cent.

C-Phenyl-*s*-triazole dissolved readily in cold dilute or in warm concentrated hydrochloric acid. The *hydrochloride*, which crystallised in slender needles on cooling the solution in the concentrated acid, decomposed on drying or on treatment with water. On adding platinum chloride to the solution in warm concentrated hydrochloric acid and cooling, the *platinichloride*, $(C_8H_7N_3)_2, H_2PtCl_6, 3H_2O$, separated in yellowish-red plates containing 3 mols. of water of crystallisation, which were driven off at 110°. The anhydrous *platinichloride* melted and decomposed at 223°.

1·2298, at 110°, lost 0·0912 H_2O . $H_2O = 7·41$.

0·7730, dried at 110°, gave 0·2138 Pt. Pt = 27·66.

$(C_8H_7N_3)_2, H_2PtCl_6, 3H_2O$ requires $H_2O = 7·16$ per cent.

$(C_8H_7N_3)_2, H_2PtCl_6$ „ Pt = 27·86 „

When washed with water, the platinichloride lost 2 mols. of hydrochloric acid and was converted into the *derivative*,

which is of a lighter yellow colour. This salt lost $3H_2O$ at 110°, dissolved in aqueous potassium carbonate, and was precipitated unchanged from this solution on the addition of hydrochloric acid.

0·6007, at 110°, lost 0·0468 H_2O . $H_2O = 7·79$.

0·5561, dried at 110°, gave 0·1736 Pt. Pt = 31·22.

0·5433, precipitated from aqueous potassium carbonate and dried at 110°, gave 0·1699 Pt. Pt = 31·27.

$(C_8H_7N_3)_2, PtCl_4, 3H_2O$ requires $H_2O = 7·93$ per cent.

$(C_8H_7N_3)_2, PtCl_4$ „ Pt = 31·10 „

The *acetyl* derivative, $\text{C}_8\text{H}_6\text{N}_3 \cdot \text{C}_2\text{H}_3\text{O}$, was obtained by boiling *C*-phenyl-*s*-triazole with acetic anhydride and sodium acetate; it dissolved readily in alcohol, ether, benzene, or warm light petroleum; from its solution in the last solvent, it crystallised in feathery aggregates of slender needles. When recrystallised from dilute alcohol, it formed small, white needles which melted at 90° . It was easily hydrolysed by boiling aqueous potassium carbonate to *C*-phenyl-*s*-triazole melting at 119 — 120° .

0.2242 gave 43.2 c.c. moist nitrogen at 15° and 754 mm. $\text{N} = 22.38$.

$\text{C}_8\text{H}_6\text{N}_3 \cdot \text{C}_2\text{H}_3\text{O}$ requires $\text{N} = 22.46$ per cent.

The carbamido-derivative of *C*-phenyl-*s*-triazole, described in the previous paper (Trans., 1901, 79, 665), was also prepared by the action of potassium cyanate and hydrochloric acid on *C*-phenyl-*s*-triazole obtained from *C*-phenylhydroxy-*s*-triazole. After solution in benzene and precipitation by adding light petroleum, it melted at 147° . The analysis shows that it probably contained traces of unchanged phenyltriazole.

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0.1818 gave 0.3855 CO_2 and 0.0818 H_2O . $\text{C} = 57.83$; $\text{H} = 4.09$.

$\text{C}_8\text{H}_6\text{N}_3 \cdot \text{CO} \cdot \text{NH}_2$ requires $\text{C} = 57.44$; $\text{H} = 4.25$ per cent.

The carbamido-derivative was easily hydrolysed by boiling water or by cold dilute hydrochloric acid with evolution of carbon dioxide and formation of phenyltriazole, which melted at 119° .