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Rearrangement of 4-Phenylazo-5-hydroxy-1,2,3-triazoles to Amides of 2-Phenyl-5-carboxytetrazole

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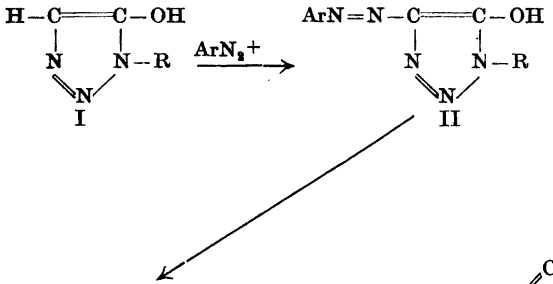
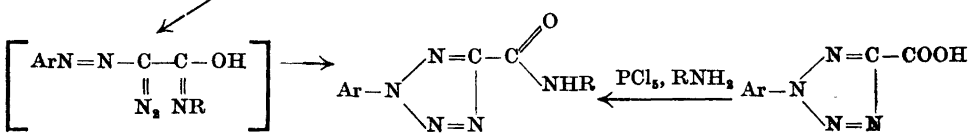
4-Phenylazo-5-hydroxy-1,2,3-triazoles (II), unsubstituted or substituted with methyl-, phenyl-, and benzyl- in position 1, have been prepared. It has been shown that II, when heated in glacial acetic acid, rearrange to amides of 2-phenyl-5-carboxytetrazole (IV). The rearrangement is believed to take place through an intermediate, aliphatic diazocompound (III).

Dimroth [1] and Curtius [2] have shown that 5-hydroxy-1,2,3-triazoles (I) couple with diazonium salts in alkaline solution with formation of 4-arylazo-5-hydroxy-1,2,3-triazoles (II).



	R—	Ar—
a	C_6H_5—	C_6H_5—
b	H—	C_6H_5—
c	CH_3—	C_6H_5—
d	$C_6H_5CH_2$—	C_6H_5—
e	—CH_2CONH_2	*p*-$CH_3C_6H_4$—

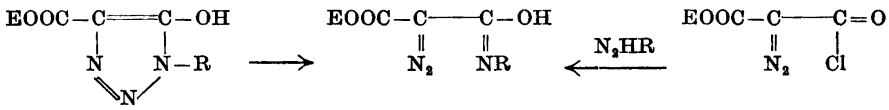


III IV VII

It was reported by Dimroth [1] that the orange-coloured 1-phenyl-4-phenylazo-5-hydroxy-1,2,3-triazole (IIa), on recrystallization from glacial acetic acid, rearranged to an isomeric, colourless compound which, as opposed to IIa,

had no acidic properties *. In the same way Curtius and Thomson [2] obtained a colourless isomer of IIe. No attempt has been made to find the structures of the two colourless compounds.

A number of esters of 4-carboxy-5-hydroxy-1,2,3-triazoles (V) were prepared by Dimroth and he showed that these compounds can isomerize to amides of diazomalonic ester (VI) when heated, alone or dissolved in water or organic solvents [3a-d]. When 1-*p*-nitrophenyl-4-ethoxycarbonyl-5-hydroxy-1,2,3-triazole was recrystallized from glacial acetic acid it gave the corresponding diazocompound (VI, R = *p*-nitrophenyl-) in quantitative yield [3c]. The mechanism of this reaction has been reinvestigated in more recent papers [4,5].



V VI VIII

In view of this it would be reasonable to assume that compounds of type II can also isomerize to aliphatic diazocompounds with the structure III. Compounds of type III will probably undergo a spontaneous ring closure with formation of amides of 2-aryl-5-carboxytetrazole (IV), in analogy with the preparation of 2,5-disubstituted tetrazoles by reaction of amidrazones with nitrous acid where intermediates with structure similar to III are likely to be formed [6,7]. This means that Dimroth's colourless isomer, formed by rearrangement of IIa, should be 2-phenyltetrazole 5-carboxanilide (IVa).

To prove this IVa was prepared by an unambiguous method, starting with the known 2-phenyl-5-carboxytetrazole (VII), which was made according to Bladin [6]. The acid (VII), *via* the chloride, gave the anilide (IVa) which had the same melting point and infrared spectrum as the rearrangement product from II and thus proving the structure of the latter.

To test the generality of this rearrangement it was tried in three other cases, starting with 5-hydroxy-1,2,3-triazoles, unsubstituted or substituted with methyl- and benzyl- in position 1. The coupling with phenyldiazonium chloride was done in 2 N sodium hydroxide and gave the 4-phenylazo-5-hydroxy-1,2,3-triazoles (Table 1). The latter, when boiled in glacial acetic acid solution for a few minutes, gave the corresponding tetrazoles (IV) in good yields (Table 2). The authentic tetrazoles, prepared from 2-phenyl--carboxytetrazole, all had melting points and infrared spectra completely identical with the tetrazoles prepared by rearrangement.

The 4-hydroxy-1,2,3-triazole (Ib) was prepared from ethyl diazomalonate monochloride (VIII) which with ammonia gives the monoamide (VI, R = H) [8]. VI was rearranged to 4-ethoxycarbonyl-5-hydroxy-1,2,3-triazole (V, R = H) with ethanolic potassium hydroxide. Saponification and decarboxylation of V

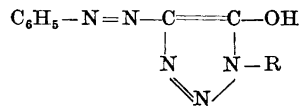
* Dimroth[1] thought that he obtained the coloured isomer (IIa)by coupling in 20 % sodium carbonate and the colourless isomer in weak basic solution, but according to our experience the coloured isomer is formed in both cases and the rearrangement takes place on recrystallization from acetic acid.

yielded 4-hydroxy-1,2,3-triazole [3c]. The 1-methyl-5-hydroxy-1,2,3-triazole was prepared in the same way.

The colourless isomer which Curtius and Thomsen [2] obtained from 1-carboxamidomethyl-4-*p*-tolylazo-5-hydroxy-1,2,3-triazole (IIe) on recrystallization from glacial acetic acid has not been included in the present investigation, but there can hardly be any doubt that it is also a tetrazole derivative and has the structure IVe.

Dimroth [1,3] showed that the rearrangement of V to VI takes place in a number of different solvents. Whether the rearrangement of II to IV can be effected in solvents other than glacial acetic acid has not been tried extensively, but prolonged heating of compounds of type II in ethanolic solution gave oily decomposition products with a strong smell of *iso*cyanides. Boiling in acetonitrile or dimethyl formamide also caused decomposition.

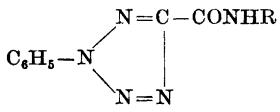
Table 1. 1-Substituted-4-phenylazo-5-hydroxy-1,2,3-triazoles (II).



R—	Yields %	M. p.°	Formula	Analyses					
				Carbon		Hydrogen		Nitrogen	
				Found	Calc.	Found	Calc.	Found	Calc.
H—	93	155—156	$C_8H_7N_5O$	50.65	50.80	3.72	3.76	37.20	37.00
CH_3—	59	156—157	$C_9H_9N_5O$	53.70	53.30	4.61	4.47	34.68	34.50
C_6H_5—	83	142—143*	$C_{14}H_{11}N_5O$	63.60	63.50	4.22	4.18	26.66	26.42
$C_6H_5CH_2$—	68	150—151	$C_{15}H_{13}N_5O$	64.65	64.60	4.51	4.69	25.23	25.05

* Dimroth[1] reported m.p. 131—132°.

Table 2. 2-Phenyl-5-carboxamidotetrazoles.



R—	Yields %	M. p.	Formula	Analyses					
				Carbon		Hydrogen		Nitrogen	
				Found	Calc.	Found	Calc.	Found	Calc.
H—	79(76)[a]	167—168*	$C_8H_7N_5O$	50.70	50.80	3.97	3.76	36.84	37.00
CH_3—	77(40)[b]	141—142	$C_9H_9N_5O$	53.20	53.30	4.35	4.47	34.30	34.50
C_6H_5—	78(83)[c]	160—161	$C_{14}H_{11}N_5O$	63.30	63.50	4.14	4.18	26.58	26.42
$C_6H_5CH_2$	63(50)[a]	108—109	$C_{15}H_{13}N_5O$	64.75	64.60	4.81	4.69	25.05	25.05

* Reported m.p. 167.7—168.5[6].

Solvents used for recrystallization: a) ethanol, b) light petrol (b.p. 100/140°), c) glacial acetic acid. Yields given in brackets refer to preparation of authentic tetrazoles.

EXPERIMENTAL

Melting points are uncorrected.

5(4)-Hydroxy-1,2,3-triazoles

4-Hydroxy-1,2,3-triazole. Ethyl diazomalonate monochloride [8] (8.5 g) was added during 5 min to 30 ml of ice-cold, stirred, 25 % ammonia. Stirring and cooling was continued for 30 min. The cream-coloured ethyl diazomalonate monoamide was filtered off and washed with water. Yield 6.2 g (81 %), m. p. 142—143° (reported [3c,8] m. p. 142° and 143°.)

The monoamide (4.15 g) was dissolved in 40 ml of hot absolute ethanol and the solution added to 4.45 g (3 moles) of KOH in 50 ml of hot ethanol. The potassium salt of 4-ethoxycarbonyl-5-hydroxy-1,2,3-triazole precipitated immediately, causing the mixture to solidify. After 10 min the ethanol was removed *in vacuo*, 25 ml of water was added and the resulting solution refluxed for 1 h. The solution was then acidified with conc. HCl (pH should be 3—4; excess of acid decomposes the 4-hydroxytriazole and a product results which is very difficult to purify) and boiled for 1—2 min to complete the decarboxylation. The mixture was evaporated to dryness *in vacuo* and the residue extracted with boiling absolute ethanol (3 × 15 ml). The ethanolic solution was evaporated to dryness and the residue extracted 7—8 times with 25 ml portions of boiling ether; the ether solution was concentrated to ca 50 ml and the 4-hydroxytriazole precipitated with light petrol. Yield 1.60 g (70 %), m. p. 126—128°. A sample was recrystallized twice from ethyl acetate and finally sublimed *in vacuo* (0.1 mm) at 110°. M. p. 130—132° (reported [3c,2] m. p. 130° and 135°). (Found: C 28.15; H 3.63; N 49.29. Calc. for $C_2H_3N_3O$: C 28.20; H 3.55; N 49.40.)

1-Methyl-5-hydroxy-1,2,3-triazole. Ethyl diazomalonate monochloride in ether was treated with dry methylamine; the methylamine hydrochloride was filtered off and the ether removed *in vacuo* leaving ethyl diazomalonate monomethylamide as a yellow oil, which could not be induced to crystallize. The crude oil was treated in the same way as above and gave 1-methyl-5-hydroxy-1,2,3-triazole in 65 % yield. The product was recrystallized from ethanol, m. p. 168—170°. (Found: C 36.45; H 5.00; N 42.48; Calc. for $C_3H_5N_3O$: C 36.30; H 5.08; N 42.40.)

1-Phenyl-5-hydroxy-1,2,3-triazole was prepared according to Dimroth [1].

1-Benzyl-5-hydroxy-1,2,3-triazole. 1-Benzyl-4-ethoxycarbonyl-5-hydroxy-1,2,3-triazole [9] was saponified and decarboxylated in the same way which Gompper [10] used for the methylester. Yield 85 %, m. p. 157—158°.

4-Phenylazo-5-hydroxy-1,2,3-triazoles

4-Phenylazo-5-hydroxy-1,2,3-triazole. A phenyldiazonium chloride solution, prepared from 0.54 ml of aniline in 15 ml N HCl and 0.41 g (1 mole) of sodium nitrite, was added during ca 5 min with stirring and ice cooling, to a solution of 4-hydroxy-1,2,3-triazole (0.5 g, 1 mole) in 15 ml 2N NaOH. The orange solution was kept for 1 h at 0°. Acidification with conc. HCl gave 4-phenylazo-5-hydroxy-1,2,3-triazole as a yellow precipitate which was filtered off and washed with water. Yield 1.03 g (93 %), m. p. 151—153°. After two recrystallizations from ethanol the substance was pure, forming yellow needles.

The same product was obtained when 4-carboxamido-5-hydroxy-1,2,3-triazole was used, the carboxamido group being split off during the reaction. With the same conditions as above the yield of azocompound was 96 %.

1-Methyl- and *1-benzyl-4-phenylazo-5-hydroxy-1,2,3-triazole* were prepared in the same way from 1-methyl- and 1-benzyl-5-hydroxy-1,2,3-triazole, respectively. They were both recrystallized from ethanol. Properties are given in Table 1.

1-Phenyl-4-phenylazo-5-hydroxy-1,2,3-triazole was prepared according to Dimroth [1] by coupling in 20 % Na_2CO_3. When 2N NaOH was used the product was very impure. The product was recrystallized from methanol; prolonged heating should be avoided during the recrystallization to avoid decomposition.

Rearrangement of 4-phenylazo-5-hydroxy-1,2,3-triazoles

2-Phenyltetrazole-5-carboxanilide. 1-Phenyl-4-phenylazo-5-hydroxy-1,2,3-triazole (1.2 g) was dissolved in 10 ml of boiling glacial acetic acid and the solution was boiled for 5 min. The orange colour of the azocompound disappeared almost immediately. On cooling the tetrazole crystallized; it was filtered off and washed with ether. Yield 0.75 g, m. p. 159–161°.

In the other three cases the rearrangement was done in the same way. If the product did not crystallize on cooling of the acetic acid solution it was precipitated with ether or light petrol. Their properties are given in Table 2.

Preparation of authentic tetrazoles

2-Phenyltetrazole-5-carboxanilide. Dried 2-phenyl-5-carboxytetrazole [6] (0.5 g) and phosphorus pentachloride (0.6 g, 1.1 mole) were mixed and heated for a few minutes until the vigorous reaction had ceased. Phosphorus oxychloride and excess of phosphorus pentachloride were then removed *in vacuo* at 100°. The crude chloride, which formed a solid, was cooled in ice and treated with excess aniline dissolved in ether. The mixture was stirred and the lumps were broken with a glass rod to complete the reaction. The solid was then collected by filtration and washed with diluted HCl and water.

The three other tetrazoles were prepared in the same way, IVb and IVc with 25 % aqueous ammonia and methylamine, respectively, and IVd with benzylamine in ether. Yields are given in brackets in Table 2. They were all analysed but the values are not given here; the analyses in Table 2 are those of the rearrangement products.

The infrared spectra were taken on a Beckman I.R.2 in strument using the KBr-disk technique.

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