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POLYNUCLEAR ISOXAZOLE TYPES—VI[1]

REACTION OF 3-PHENYL-4,5-DIAMINOISOXAZOLE: ISOXAZOLO [4·5-*b*][1·4] DIAZEPINES AND ISOXAZOLO [4·5-*d*] *v*-TRIAZOLES

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Abstract—The reaction of 3-phenyl-4,5-diaminoisoxazole with acetyl- and acetonyl-acetone is described: in the former case, through an open chain intermediate, 3-phenyl-5,7-dimethylisoxazolo [4·5-*b*] [1·4] diazepine was obtained, in the latter case a conjugated pyrrolo–isoxazole derivative was isolated and its structure elucidated. The chemical properties of these products were investigated. From the reaction of the same diaminoisoxazole with nitrous acid, through an intermediate diazo compound, derivatives of the new isoxazolo [4·5-*d*] *v*-triazole system are obtained and the triazole ring opening is elucidated.

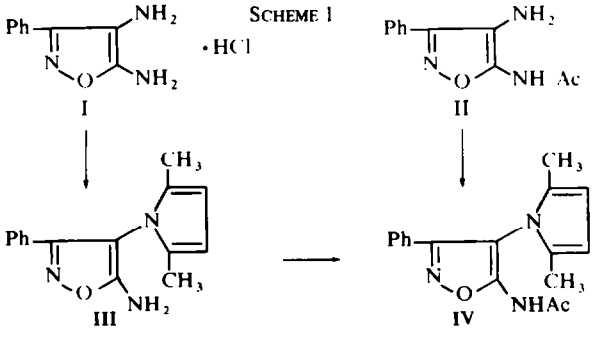
IN A recent paper[2] we have described the monohydrochloride of 3-phenyl-4,5-diaminoisoxazole (I) and its reaction with α-diketones, which represents a convenient route for the synthesis of isoxazolo [4·5-*b*] pyrazine derivatives.

In order to develop the study of the chemical properties of this molecule and to obtain new examples of a isoxazole ring condensed with other heterocyclic systems, we have investigated the behaviour of I toward various reactants.

With β- and γ-diketones, the nucleophilic attack was initially accomplished by only one amino group and a high degree of selectivity was shown: thus I reacted with acetonylacetone to give a product whose analysis was consistent with structure III. The presence in the IR spectrum of a set of bands between 3378 and 3130 cm^{-1} strongly suggested that only one of the amino groups had reacted to yield a pyrrole derivative in accordance with the well-known Paal–Knorr synthesis of this ring.

It can be easily demonstrated that the attack arose from the amino group at 4: thus (Scheme 1) from acetonylacetone and 3-phenyl-4-amino-5-acetylaminoisoxazole (II),[2] 3-phenyl-4[2,5-dimethyl-1-pyrryl]-5-acetylaminoisoxazole (IV) was obtained and the same product was also isolated from acetylation of III with Ac_2O: hence III must be 3-phenyl-4[2,5-dimethyl-1-pyrryl]5-aminoisoxazole.

SCHEME 1



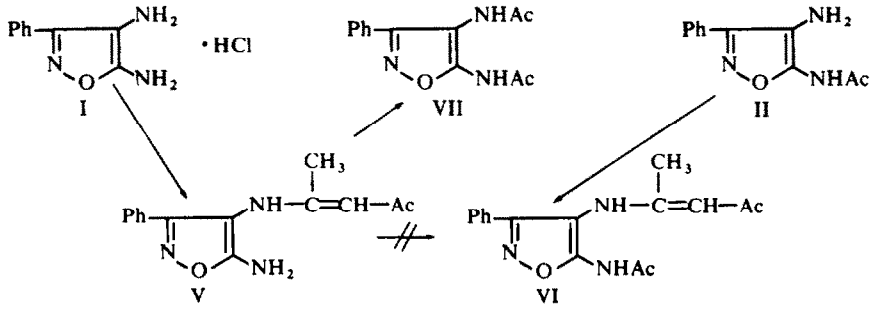
Similar results (but with lower yield) were obtained from the reaction of acetonylacetone with an ethereal solution of the free base of I.

Also with acetylacetone 3-phenyl-4,5-diaminoisoxazole gave only one product, analysed for an equimolar adduct minus one mole of water, and, since the IR spectrum shows a set of bands between 3370 and 3140 cm^{-1}, we can recognise the product as a Schiff base.

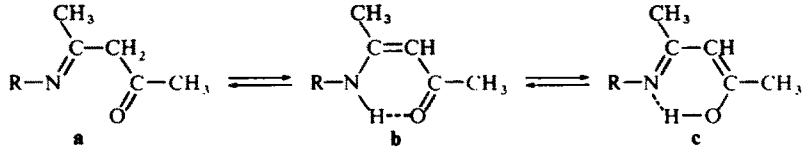
Unfortunately in this case the reactive group can be assigned only by analogy to the above described reaction, since an attempted structural demonstration resembling the one realized for III did not succeed. Although 3-phenyl-4-amino-5-acetylaminoisoxazole (II) yielded 2-[3'-phenyl-5'-acetylamino-4'-isoxazolyl]amino-2-penten-4-one (VI), every attempt to pass from V to VI by acetylation failed, since under mild conditions unchanged starting material was obtained whilst under conditions a little more severe 3-phenyl-4,5-diacetylaminoisoxazole[2] (VII) was isolated (Scheme 2). So if we assume that the reaction product arose from the attack of the amino group at 4, the structure of 2-[3'-phenyl-5'-amino-4'-isoxazolyl]amino-2-penten-4-one (V) can be assigned.

The identical product, but in lower yield and after a longer reaction time, is obtained also from an ethereal soln of the free base of I, again showing the main function of the acidic medium to be a catalyst in nucleophilic attack at carbonyl groups.

SCHEME 2



An interesting problem concerns the structure of V and VI: these compounds can exist in any of the three tautomeric forms: the Schiff base (**a**), the ketamine (**b**) and the enimine (**c**).



The NMR spectroscopic investigation of V (in DMSO d_6) shows two Me signals (singlets) at 1·68 and 1·97δ, an olefinic proton signal (singlet – 1H) at 5·27δ (which excludes the structure of a Schiff base), a singlet (2H) at 7·07δ ($-NH_2$), a multiplet centered at 7·5δ (five aromatic protons) and finally a singlet (1 amine proton) at 11·16δ, whose large paramagnetic shift clearly indicates the presence of an H-bonded chelate ring system.[3] Therefore it is possible to exclude the eniminic structure **c** and

also the *trans* configurations of **b** and **c**, which in the case of β-enaminoketones have been well studied[4] and also isolated.[5]

The IR spectrum (in $CHCl_3$*) in the 1600 cm^{-1} region, shows three characteristic bands, common to almost all β-enaminoketones, at 1658, 1615 and 1570 cm^{-1}; the small shift of these bands after deuteration† and the low HD ratio, suggest a strong coupling.[7]

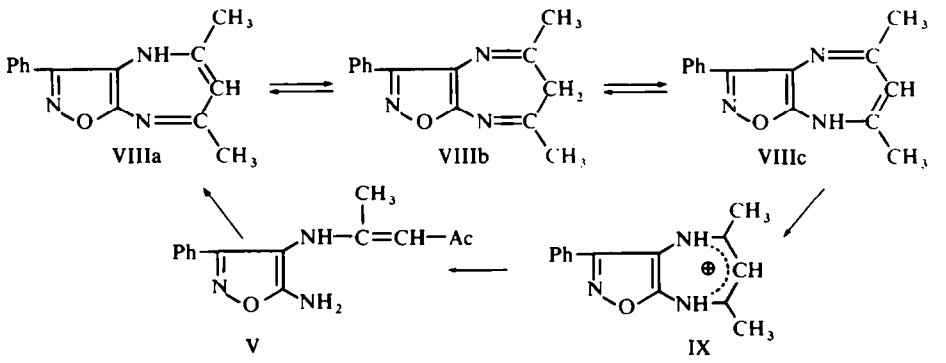
Cyclization to 3-phenyl-5,7-dimethylisoxazolo[4·5-*b*] [1·4] diazepine (VIII; Scheme 3) was achieved by treatment of V with organic bases.

The possible tautomeric equilibrium among the structures **a**, **b** and **c**, both in the solid state and in organic media, is almost completely shifted to the diiminic form **b** as following spectroscopic evidence shows:

(i) The IR spectrum, both in nujol mull and in CCl_4 soln, shows no NH absorption;

(ii) The NMR spectrum shows no trace of NH or olefinic proton signals, characteristic for the structures **a** or **c**, but presents (in $CDCl_3$) two singlets (3H + 3H) at 2·30 and 2·37δ (Me groups in 5 and 7), a sharp singlet (2H) at 3·07δ (methylene at 6) and a multiplet (5H) at 7·3–8·2δ (aromatic protons). Although the isoxazolo–diazepinic ring system is not planar, thus rendering the methylene protons at 6 non-equivalent, the signal of these protons at room temp is not split: clearly the two conformers are in a mobile equilibrium, which is too fast to discriminate the equatorial and the axial proton. Decreasing the temperature the signal is modified and at −70°‡ it becomes a very broad band between 3·2 and 3·6δ (the Me signals now occurs at 2·40 and 2·46δ).

SCHEME 3



The cyclization is reversed with acids (Scheme 3) and the hydrolytic cleavage of the ring occurs via an intermediate isoxazolo–diazepinium cation (IX), whose structure was determined by spectroscopic methods. In an acidic methanolic soln of VIII a

* In order to exclude the formation of dimers, it must be remembered that our concentration (0·001M) is much lower than the concentration of about 0·05M in which association occurs only in small degree.[6]

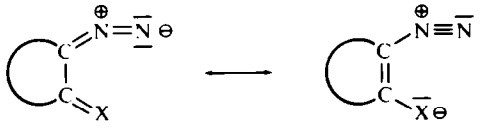
† The deuterated material was obtained as follows: the undeuterated ketamine (V) was dissolved in boiling anhydrous dioxane and an excess of 99·9% deuterium oxide (20 times more than the theoretical quantity) was added. After cooling the crystalline separated product was dried, redissolved and reprecipitated as above. The deuteration ratio was controlled by NMR spectroscopy.

‡ The variable temperature spectra were performed on a Perkin–Elmer R10 spectrometer at the School of Chemical Sciences of East Anglia University (Norwich—England) by Mr. P. Lehman whom we gratefully acknowledge.

deep violet-blue colour developed and a maximum at 548 mμ was obtained in the visible spectrum, not far from the value found for the analogous benzodiazepinium cation;[8] the colour soon paled and from the colourless solution V precipitated. The isoxazolo–diazepinium cation (IX) was also isolated as the hydrochloride, which precipitated from an ethereal soln of VIII with dry gaseous hydrochloric acid. Its IR spectrum (nujol mull) showed a broad band at 3250 cm^{-1}, while the NMR spectrum was recorded after addition of trifluoroacetic acid to a solution of VIII in $CDCl_3$: it shows two singlets (3H + 3H) at 1·64 and 1·74δ (two $-CH_3$), a singlet (1H) at 3·90δ (vinylic proton at 6), a broad band (1H) at about 9·1δ (protonated nitrogen); unfortunately the signal of the second NH is masked by the absorption of the acid. No evidence of a dication, even in strong protonating media, was observed, though this has been observed for benzodiazepine.[9]

Furthermore we have investigated the reaction of 3-phenyl-4,5-diaminoisoxazole (I) with nitrous acid as the most convenient route to isoxazole–triazoles, a system hitherto almost unknown, excepting a report[10] on isoxazolo[3·4-*d*]*v*-triazole derivatives.

While an attempt with aqueous nitrous acid was unsuccessful, treatment of I with isoamyl nitrite easily gave a product, whose IR spectrum shows a strong band at 2175 cm^{-1}, a value intermediate between those of a diazo group and of a diazonium salt, but in accordance with the value of most α,β-unsaturated diazocompounds.[11] As known, the real structure of compounds such as α-diazoketones must be considered as the result of resonance between two mesomeric forms: a diazo-compound (**a**) and an internal diazonium salt (**b**).

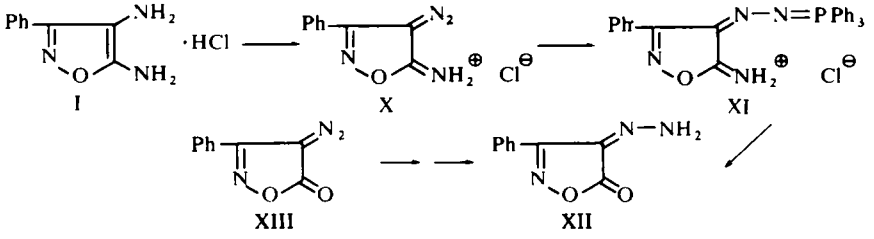


a **b**

The absence of any absorption from NH or NH_2 groups in the IR spectrum of our product, together with its elementar analysis, indicates that the residual amino group should be present in the molecule as hydrochloride.

Chemical evidence was obtained to assure the initial site of attack by nitrous acid (Scheme 4).

SCHEME 4



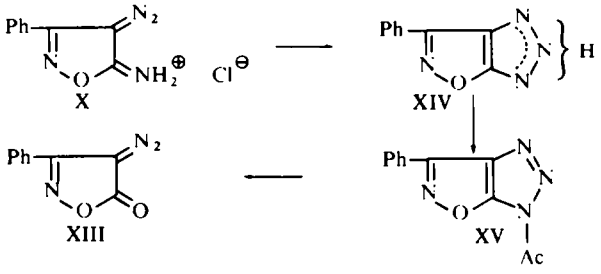
The diazo-compound (X), in the presence of triphenylphosphine, gave a highly unstable phosphazine (XI), whose IR spectrum lacks both diazo and NH or NH_2 bands, thus showing, together with elementar analysis, that the compound is still a hydrochloride.

Acidic hydrolysis cleaved the phosphazine (XI), giving high yields of the 4-hydrazone of 3-phenyl-4,5-dioxo-2-isoxazoline (XII) along with ammonium hydrochloride and triphenylphosphine oxide. Since the same hydrazone has also been obtained[12] by hydrolytic cleavage of the phosphazine of 3-phenyl-4-diazo-5-isoxazolone (XIII),[13] the original diazotation of I must have occurred at the 4-position, more easily available for electrophilic attack.

Every attempt to obtain the free base from its hydrochloride (X) was unsuccessful, since in aqueous mild basic conditions the immediate closure between the diazo group and the neighbouring amino group with formation of a triazole ring occurred. 3-Phenylisoxazolo[4·5-*d*]*v*-triazole (XIV) was obtained: its IR spectrum lacks the diazo group absorption band and shows a broad band at 3100 cm^{-1}, which has to be ascribed to the triazolic NH, largely bonded.

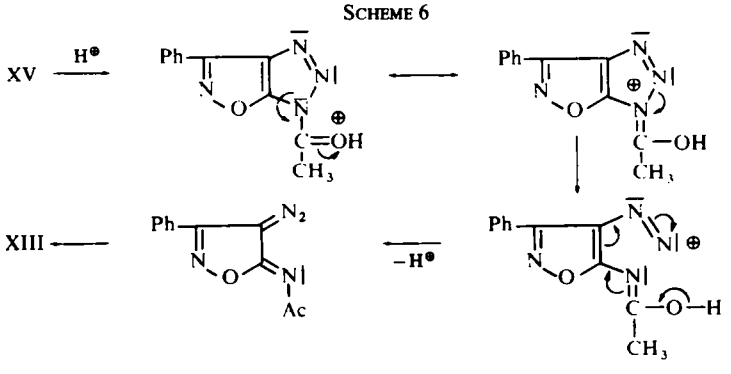
The isoxazolo–triazole ring system is relatively stable and was acetylated under mild conditions. After careful isolation we could obtain a monoacetylderivative, to which the structure of 3-phenyl-6-acetylisoxazolo[4·5-*d*]*v*-triazole (XV) was assigned. This compound, homogeneous at TLC under a variety of conditions, was assumed to be a single isomer, owing to its NMR spectrum, which shows only a multiplet (5H) at 7·6–8·2δ (aromatic protons) and one sharp singlet (3H) at 2·91δ (CH_3-CO). When this unstable acetylderivative was treated with acetic acid, a fast cleavage of the triazole ring occurred with subsequent formation of 3-phenyl-4-diazo-5-isoxazolone (XIII) (Scheme 5) as the exclusive reaction product.

SCHEME 5



Since the triazole (XIV) is stable under the same experimental conditions, the following mechanism, involving at first a Dimroth-like rearrangement,[14–16] is conceivable (Scheme 6).

SCHEME 6



The proton attack at the oxygen of the acetyl group promotes the ring opening to an α-diazoacetiminoderivative, which is then easily hydrolyzed to XIII.

EXPERIMENTAL

TLC: kieselgel plates with UV indicator; eluant: cyclohexane-AcOEt (70:30). All m.ps are uncorrected. IR spectra: Perkin–Elmer 257 spectrophotometer; UV spectra: Perkin–Elmer 137; NMR spectra: run by Mr. A. Arnone on a Varian A-60 spectrometer at the Istituto di Chimica Generale del Politecnico (Milano—Italy); Microanalyses: by Dr. Lucia Maggi Dacrema; UV spectra: by Dr. Maria De Bernardi.

3-*Phenyl*-4[2,5-*dimethyl*-1-*pyrryl*]5-*aminoisoxazole* (III)

(a) To a magnetically stirred soln of I (0·6 g) in water (50 ml), freshly distilled acetonylacetone (0·5 g) was added under a slow N_2 flow. After a few min a white ppt separated and, after standing some hr at room temp, III (0·7 g; 98·5%) was filtered off and crystallized as ivory small prisms; m.p. 126–127° (cyclohexane). (Found: C, 71·41; H, 6·17; N, 16·73. Calc for $C_{15}H_{15}N_3O$: C, 71·12; H, 5·97; N, 16·59%); UV (EtOH): λ_{max} 229, 275 mμ (log ε 4·35, 3·56).

(b) The same product III (0·3–0·4 g; 40–55Π) was obtained from an ethereal soln of the free base of I and acetonyl-acetone (0·5 g) after 2 days stirring at room temp.

3-*Phenyl*-4[2,5-*dimethyl*-1-*pyrryl*]5-*acetylaminoisoxazole* (IV)

(a) A soln of freshly distilled acetonylacetone (0·4 ml) in EtOH (3·0 ml) was added under a vigorous stirring and a slow N_2 flow to a soln of II (0·4 g) in EtOH (6·0 ml). After 3 days removal under vacuum of the solvent left a yellow oily residue, which, diluted with water, gave IV (0·5 g; 91·6%); recrystallization from MeOHaq gave white soft needles m.p. 203–204°. (Found: C, 67·22; H, 5·92; N, 13·91. Calc for $C_{17}H_{17}N_3O_2 \cdot 1/2\,H_2O$: C, 67·09; H, 5·96; N, 13·81%).

IV was dried under vacuum at 150° and then sublimed (120° and 0·05 mm Hg). (Found: C, 68·84; H, 6·09; N, 14·51. Calc for $C_{17}H_{17}N_3O_2$: C, 69·13; H, 5·80; N, 14·23%); IR (nujol mull): 3240 (NH); 1690 (CO); UV (EtOH): λ_{max} 231 mμ (log ε 4·30).

(b) A suspension of III (0·2 g) in Ac_2O (2·0 ml) was warmed at 60° over a steam bath; the soln slowly darkened and became off-black. TLC showed, beside the starting product III and the acetylderivative IV, the presence of some decomposition by-products, whose structures were not investigated. After 30 hr the starting material disappeared and the reaction mixture was poured onto ice. The crude dark product, filtered off and dried (0·2 g), was chromatographed on preparative TLC plates (cm 20 × 20–1 mm kieselgel with UV indicator); after elution the strip at R_f 0·5 was collected and eluted with MeOH yielding IV (0·11 g) absolutely identical in m.p., m.m.p. and IR spectrum with a sample obtained as described under (a).

2-[3'-*Phenyl*-5'-*amino*-4'-*isoxazolyl*]*amino*-2-*penten*-4-*one* (V)

(a) A soln of acetylacetone (1·0 ml) in water (5·0 ml) was added to an aq soln of I (0·5 g) under magnetical stirring. After a few minutes a white solid started to separate and the precipitation was accomplished in 3 hr; V (0·5 g; 88%) was filtered off and crystallized as colourless small prisms m.p. 195° dec (MeOH). (Found: C, 65·37; H, 6·17; N, 16·37. Calc for $C_{14}H_{15}N_3O_2$: C, 65·35; H, 5·88; N, 16·33%); UV (EtOH): λ_{max} 231·5, 306·5 mμ (log ε 4·45, 4·40).

(b) The same product V (0·4 g; 70Π) was obtained from an ethereal soln of the free base of I (about 0·4 g) and acetyl-acetone (1·0 ml) after 2 days stirring at room temp.

2-[3'-*Phenyl*-5'-*acetylamino*-4'-*isoxazolyl*]*amino*-2-*penten*-4-*one* (VI)

To a stirred soln of II (0·3 g) in EtOH (10·0 ml) a mixture of acetylacetone (0·3 ml) and EtOH (2·0 ml) was added dropwise. After 24 hr standing at room temp VI (0·12 g; 30%) as colourless prisms was filtered, m.p. 203–205° (MeOH). (Found: C, 63·83; H, 5·14; N, 14·03. Calc for $C_{16}H_{17}N_3O_3$: C, 64·20; H, 5·12; N, 14·04%); UV (EtOH): λ_{max} 234, 307 mμ (log ε 4·22, 4·21).

Acetylation of V. A suspension of V (1·5 g) in Ac_2O (15·0 ml) was heated at 60° over a steam bath for 6 hr. After decomposition in iced water a white solid (1·2 g) was isolated, which crystallized from MeOH as needles m.p. 202–203°, undepressed in mixture with a sample of 3-phenyl-4,5-diacetylaminoisoxazole (VII):[2] IR spectra were also superimposable. An identical result was obtained from a reaction mixture left 5 days at room temp.

3-Phenyl-5,7-dimethylisoxazolo[4·5-b] [1,4] diazepine (VIII)

An ethanilic soln of V (0·2 g) and Et_3N (0·1 ml) was gently refluxed for 4 hr. Removal under vacuum of the solvent left a yellowish oily residue which, after grinding, solidified as a white solid which recrystallized from diisopropyl ether as colourless small needles (0·1 g; 54·5%) m.p. 118–119°. (Found: C, 70·06; H, 5·21; N, 17·72. Calc for $C_{14}H_{13}N_3O$: C, 70·27; H, 5·48; N, 17·56%); UV (EtOH): λ_{max} 228, 241 (sh), 293 mμ (log ε 4·17, 4·16, 3·90).

Hydrolytic cleavage of VIII. To a soln of VIII (0·1 g) in MeOH (5·0 ml) HCl aq 5% (1·0 ml) was added and a violet colour developed, which slowly disappeared. After 12 hr standing at room temp, small colourless prisms (0·07 g) were collected m.p. 194–195° dec identical in every respect (m.p., m.m.p. and IR spectrum) with a sample of V.

3-Phenyl-4-diazo-5-iminoisoxazole hydrochloride (X)

A mixture of isoamyl nitrite (1·8 ml) was added dropwise to a soln of I (3·0 g) in THF (100 ml) under magnetical stirring and cooling with an ice bath. After a few min a white ppt started to separate. Stirring and cooling was continued for 3 hr, then X was collected (3·0 g; 97%) and purified by dissolving at 0° in a few drops of MeOH and adding diisopropyl ether until the soln became cloudiness. After cooling light yellow needles were collected m.p. 160° dec. (Found: C, 48·87; H, 3·36; N, 25·05; Cl, 15·46. Calc for $C_9H_7N_4OCl$: C, 48·84; H, 3·17; N, 25·07; Cl, 15·70%); UV (EtOH): λ_{max} 267 mμ (log ε 4·18).

3-Phenyl-4-triphenylphosphinazo-5-iminoisoxazole hydrochloride (XI)

When X (0·44 g) was added to a soln of triphenylphosphine (0·52 g) in DMSO (5·0 ml) it immediately dissolved developing a deep yellow colour. Anhydrous ether was added to the soln and a yellow oil separated, which solidified after washing with large volumes of anhyd ether. The yellow crystalline solid thus obtained (0·95 g; 99%) was purified by dissolving it in a few drops of cold dry EtOH and adding an excess of anhyd ether. After cooling overnight at 0° XI separated as bright yellow platelets m.p. 145° dec. (Found: Cl, 6·82. Calc for $C_{27}H_{22}N_4POCl$: Cl, 7·34%). Storage in a cool dry atmosphere preserved for about 48 hr this product, which readily decomposes at room temp.

Hydrolytic cleavage of XI. When conc HCl (0·4 ml) was dropped into a soln of XI (0·6 g) in MeOH (4·0 ml) the soln turned deep red. After a few hr standing, tufts of red needles (0·18 g; 77%) were obtained which after recrystallization from MeOH gave the 4-hydrazone of XII m.p. 168–170°. (Found: C, 57·03; H, 3·78; N, 22·45. Calc for $C_9H_7N_3O_2$: C, 57·14; H, 3·73; N, 22·21%); IR (nujol mull): 3320, 3130 (NH_2); 1735 (CO). This product was identical (m.p., m.m.p. and IR spectrum) with a sample obtained from an independent route.[12] Colourless crystals of NH_4Cl were separated from the acidic mother liquors concentrated to a small volume. After dilution with water the mother liquors were extracted with ether; the organic layers, washed with $NaHCO_3$ and then with water, dried and evaporated, gave a solid residue (0·15 g). Chromatography through a silicagel column (eluant: cyclohexane–AcOEt 3:2) afforded a second portion of XII (0·05 g; tot 0·23 g; 83%) and then a white solid (0·14 g; 39%) m.p. 156–157° (from diisopropyl ether) undepressed in admixture with a sample of *triphenylphosphine oxide.*

3-Phenylisoxazolo[4,5-d]v-triazole (XIV)

(a) X (0·2 g) was dissolved at room temp in 5% aq NaOH (2·0 ml); the clear yellowish soln was acidified with 20% aq H_2SO_4 and XIV (quantitative yield) was collected: colourless platelets (from benzene) m.p. 150° dec. (Found: C, 58·06; H, 3·33; N, 30·06. Calc for $C_9H_6N_4O$: C, 58·06; H, 3·25; N, 30·10%); IR (nujol mull): broad band at 3100 (ass. NH); UV (EtOH): λ_{max} 268 mμ (log ε 4·15).

(b) The same product was also obtained in quantitative yield on dissolving X in EtOH and adding a large amount of water; after standing a few hr XIV separated as colourless crystals.

3-Phenyl-6-acetylisoxazole[4,5-d]v-triazole (XV)

A suspension of XIV (0·1 g) in Ac_2O (0·5 ml) was heated on a steam bath at 70° for 10 min and then immediately cooled; XV separated from the yellow reddish soln as small colourless prisms (0·08 g; 65%) m.p. 98–100° (from diisopropyl ether). (Found: C, 57·79; H, 3·65; N, 24·90. Calc for $C_{11}H_8N_4O_2$: C, 57·89; H, 3·53; N, 24·55%). The compound is unstable when exposed to atmospheric moisture at room temp, converting into a glassy product, and must be kept in a dry cool place.

Dimroth rearrangement of XV. XV (0·10 g) was dissolved in AcOH (1·0 ml) and heated over a steam bath at 70°. After one min TLC showed no trace of the starting product at R_f 0·22 and the presence of a single new product at R_f 0·44. The excess solvent was removed and the residue (0·07 g; 85%) crystallized from cyclo-

hexane as beautiful light yellow needles m.p. 80°. The product is identical with a sample of XIII prepared by an independent route.[12]

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