

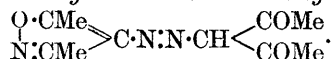
CLXXXI.—*Non-aromatic Diazonium Salts. Part VII.*  
*The Diazo-reaction in the isoOxazole Series.*

By GILBERT T. MORGAN and HENRY BURGESS.

4-AMINO-3 : 5-DIMETHYLISOXAZOLE has been shown recently (this vol., p. 697) to give rise to diazonium salts comparable in stability with those derived from aniline and its homologues. The reactions of 3 : 5-dimethylisooxazole-4-diazonium chloride have now been examined further with the object of ascertaining to what extent the isooxazolediazonium salts can be used as synthetic agents.

Non-aromatic azo-derivatives are obtainable by coupling the diazonium salt with the  $\beta$ -diketones and  $\beta$ -ketonic esters.

3 : 5-Dimethylisooxazole-4-azo-acetylacetone,

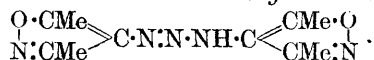


One gram of 4-amino-3 : 5-dimethylisooxazole in 5 c.c. of concentrated hydrochloric acid was cooled in a freezing mixture and diazotised by adding slowly 0.7 gram of sodium nitrite; the diazo-solution was then added to one gram of acetylacetone in 8 c.c. of 12 per cent. aqueous sodium hydroxide. The precipitation of the lemon-yellow azo-derivative was completed by salting out (yield 80 per cent.). After several crystallisations from alcohol, the compound was obtained in well-defined, yellowish-orange, hexagonal prisms melting at 115.5–116.5° (Found : N = 19.05.  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_3$  requires N = 18.83 per cent.).

3 : 5-Dimethylisooxazole-4-azo-acetylacetone was very soluble in cold aqueous caustic alkalis, hydrochloric acid, glacial acetic acid, and the ordinary organic media excepting light petroleum; it dissolved sparingly in hot water, but was insoluble in cold water. On warming, it reduced Fehling's solution and gave neither colour

reaction with ferric chloride nor copper salt with neutral copper acetate.

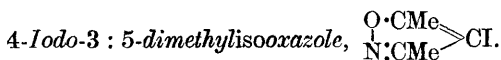
4-Diazoamino-3 : 5-dimethylisooxazole,



A diazo-solution prepared as above from one molecular proportion of the aminoisooxazole hydrochloride was added to an aqueous solution of the base (1 mol.) and sodium acetate (5 mols.). The pale brown product, precipitated completely by adding sodium chloride, was crystallised from a mixture of equal parts of acetone and light petroleum, from which solution the diazoamine first separated in colourless, transparent, hexagonal prisms which did not change if removed from the solvent. If left in contact with the mother-liquor, however, for several days, these prismatic crystals changed into small, opaque, white octahedra. Both forms of the diazoamine melted at 179—180° (Found : N = 29.93; C = 51.05; H = 5.70.  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_5$  requires N = 29.77; C = 51.02; H = 5.57 per cent.).

4-Diazoamino-3 : 5-dimethylisooxazole was soluble in the ordinary organic media excepting light petroleum; it dissolved in hot water or in aqueous caustic alkalis, and was reprecipitated from the latter by acids. It was very stable towards hydrolytic agents, and was not decomposed by cold concentrated hydrochloric acid.

*isoDiazo-reaction.*—A cold solution of 3 : 5-dimethylisooxazole-4-diazonium chloride (0.7 gram) was added slowly to 7 grams of sodium hydroxide in 6 c.c. of water. A reddish-pink precipitate appeared, but redissolved to a deep red solution, the temperature rising to 20°. This solution coupled with alkaline  $\beta$ -naphthol only in the course of several hours, but if first cautiously acidified it coupled immediately. The alkaline solution slowly lost its coupling power and on passing carbon dioxide into this solution a brown oil separated, which no longer coupled even after acidifying.

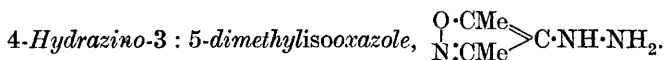


As the chloro- and bromo-isooxazoles appeared to be oily substances like the 4-triazo-compound (*loc. cit.*, p. 782), the iodo-derivative was prepared in order to demonstrate the replacement of the diazo-group by a halogen. The diazonium sulphate from 1 gram of aminodimethylisooxazole was added to 7 grams of potassium iodide in 10 c.c. of water. Rapid effervescence occurred

and a reddish-brown oil separated having an odour like that of iodoform, but more lachrymatory. After two hours, the mixture was distilled in steam and the distillate freed from iodine by sodium hydroxide.

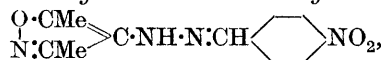
4-Iodo-3 : 5-dimethylisooxazole, when purified by repeated distillation in steam, separated in very pale yellow needles melting at 52·5—54° (Found : I = 57·47.  $C_5H_6ONI$  requires I = 56·93 per cent.).

This iodo-derivative was very soluble in ether, acetone, chloroform, or benzene, but less soluble in alcohol or hot water. It was extremely volatile, distilling in the vapour of acetone, and when left for four days over sulphuric acid about one-third of the preparation had volatilised. It was accompanied by a small amount of less volatile by-product separating in golden-yellow needles melting at 181—182° and containing no iodine. When pure, 4-iodo-3 : 5-dimethylisooxazole is only faintly odorous, although distinctly irritant to the eyes.



To a cold solution of 3 : 5-dimethylisooxazole-4-diazonium chloride prepared from 2 grams of the base were added 11 grams of stannous chloride dissolved in 8 c.c. of concentrated hydrochloric acid. A yellow, frothy precipitate, which first appeared, redissolved on stirring to a yellow solution, which was cooled to  $-5^\circ$ . The solution was made alkaline with sodium hydroxide and the hydrazine extracted with chloroform. This extract, when dried over sodium sulphate and evaporated at the ordinary temperature, left a pale green solid melting at 65—72° and having a strong odour resembling that of dimethylisooxazole. In subsequent experiments the viscous residue from the chloroform was dissolved in alcohol and warmed on the water-bath with *p*-nitrobenzaldehyde (1 mol.). The resulting hydrazone separated as a brick-red precipitate and was crystallised from alcohol in garnet-red, highly refractive prisms having a tough resinous fracture and melting at 183—184° (Found : N = 21·33.  $C_{12}H_{12}O_3N_4$  requires N = 21·53 per cent.).

4-*p*-Nitrobenzylidenehydrazino-3 : 5-dimethylisooxazole,



was soluble in ether, alcohol, chloroform, benzene, or acetone. A dilute solution of the hydrazone in the last of these solvents assumed an intense greenish-blue colour on the addition of concentrated aqueous sodium hydroxide; this coloration, which is

probably due to the formation of a highly coloured sodium salt of the type  $[\text{C}_5\text{H}_6\text{ON}]\cdot\text{NH}\cdot\text{N}:\text{C}:\text{C}_6\text{H}_4:\text{NO}\cdot\text{ONa}$ , is destroyed by acids and even by carbon dioxide or water.

Attempts to replace the diazonium group by ethoxyl or hydroxyl did not lead to the expected result. In the latter case about 20 per cent. of a solid product was obtained crystallising in colourless, transparent plates or lath-like needles melting at  $139\text{--}140^\circ$  (Found:  $\text{N} = 25.49$ ,  $25.56$  per cent.). This substance, which contains approximately the same amount of nitrogen as the original aminodimethylisooxazole, was also obtained in an attempt to replace the diazo-complex by a sulphinic group.

### Summary.

1. The foregoing experiments, in addition to those of the earlier communication (*loc. cit.*), show that the diazonium group, when attached to an isooxazole ring, is replaceable by the halogens and by the triazo-group, but not by hydroxyl, ethoxyl, or sulphinic groups.

2. In alkaline solutions an unstable isodiazo-compound is produced.

3. Reduction of the diazonium chloride leads to an unstable 4-hydrazinodimethylisooxazole.

4. isoOxazolediazonium salts couple with bases to form diazo-amino-derivatives and with phenols and  $\beta$ -diketones to yield mixed aliphatic-aromatic and non-aromatic azo-derivatives respectively.

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THE CHEMICAL DEPARTMENT,  
UNIVERSITY OF BIRMINGHAM,  
EDGBASTON.

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