A Ring Closure of Methyl α-(2,4-Dinitrophenylamino)acrylate

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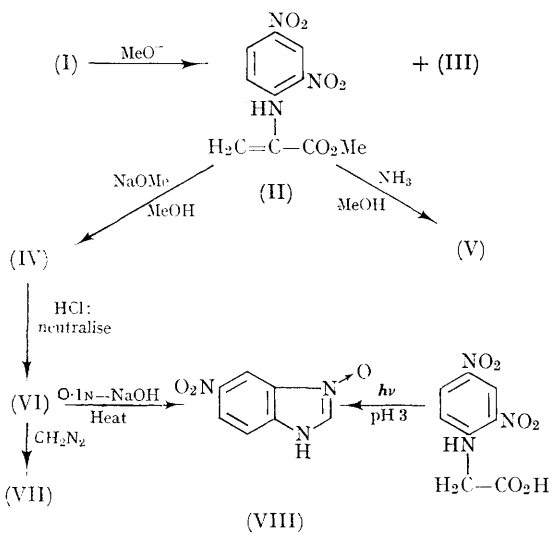
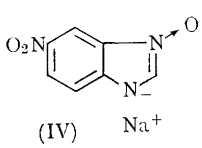
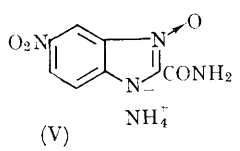
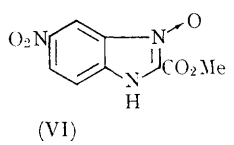
BASE-CATALYZED hydrolysis of 3-*O*-(2-acetamido-3,-4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-*N*-2,-4-dinitrophenyl-L-serine methyl ester (I) yields rapidly in the cold methyl α-(2,4-dinitrophenylamino)acrylate (II) and 2-acetamido-2-deoxy-D-glucose (III).[1] Under the basic elimination conditions (MeONa or NH_3 in anhydrous methanol), (II) was rapidly converted into (IV) as the sodium salt (in NaOMe–MeOH) or (V) as the ammonium salt carboxyamide (in NH_3–MeOH).

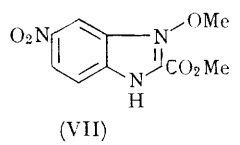


Upon neutralization of (IV) (dilute HCl) light cream-coloured needles (VI) were obtained from methanol, m.p. 205—206° (decomp.); $[\alpha]_D^{25}$ 0·00 (*c*, 0·3; $HCONMe_2$); λ_{max} (KBr) 3·80—4·00 (broad), 5·85 (CO_2Me), 6·22, 6·60 (NO_2), 7·30 (NO_2), 7·70, 7·98, 8·81, 9·47, 11·41, 13·63 (C–N–O) μ; nuclear magnetic resonance spectroscopy data: τ 0·98, 1·15, 1·30, 1·43, 1·60 (aromatic);[2] 5·93;[3] λ_{max} (EtOH) 252, 298 mμ; The compound (VI) was yellow in base and colourless in acid. Methylation of (VI) with diazomethane afforded a crystalline colourless methyl derivative (VII), m.p., 187—188°; λ_{max} (KBr) 5·78 (CO_2Me), 6·60 (NO_2), 6·70, 6·95, 7·34, 7·45 (NO_2), 7·97, 8·23, 8·85, 9·49, 10·48, 11·25, 12·15, 13·64 (–C–N–O) μ; λ_{max} (EtOH) 250, 298 mμ; nuclear magnetic resonance spectroscopy data[4]: τ 1·27, 1·45, 1·60, 1·88, 1·95, 2·52 (3 H); 5·78 (3 H); molecular weight (Rast), 221. Mild basic hydrolysis of (VI) (0·1 N-NaOH at 100° for 2 hrs.) afforded a pale yellow crystalline product (VIII) from









ethanol, m.p., 273—274°, λ_{max} (KBr) 3·80—4·30 (broad), 5·70 (broad), 6·20, 6·63 (NO_2), 7·72, 7·82, 8·26, 8·90, 9·52, 11·24, 12·43, 13·57 (–C–N–O) μ; λ_{max} (EtOH) 240, 283 mμ. The melting point, mixed melting point, chromatographic mobility (Silica Gel G, BuOH : H_2O : HOAc, 3 : 1 : 1), and infrared spectrum of (VIII) were identical in all

respects with those of 5-nitrobenzimidazole 3-oxide synthesized by photolysis of *N*-2,4-dinitrophenylglycine.[5-8] From these data it is concluded that (IV) is a product of ring closure of (II) with loss of the elements of formaldehyde. The structure assigned to (VI) is 2-methoxycarbonyl-5-nitrobenzimidazole 3-oxide. The synthesis of (II) was easily provided through the elimination in mild base of the *O*-toluene-*p*-sulphonate of *N*-2,4-dinitrophenyl-DL-serine methyl ester. A mechanism for ring closure of (II) to (IV) (salt of the *N*-oxide) is being investigated in these laboratories. The great reactivity of α-aminoacrylic acids is suggested in the ease of oxazoline ring formation in the presence of *N*-carbonyl blocking groups on αβ-unsaturated amino-acids.[9]

(*Received, March* 15*th*, 1966; *Com.* 157.)

[1] J. R. Vercellotti and A. E. Luetzow, *J. Org. Chem.*, 1966, **31**, 825.
[2] Dimethyl sulphoxide solution with tetramethylsilane internal reference. Varian Associates A-60 spectrometer.
[3] Pyridine solution with tetramethylsilane internal reference.
[4] Deuterochloroform solution with tetramethylsilane internal reference.
[5] S. Takahashi and H. Kano, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 282.
[6] R. J. Pollitt, *Chem. Comm.*, 1965, 262.
[7] D. W. Russell, *Chem. Comm.*, 1965, 498.
[8] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389.
[9] S. Ginsberg and I. B. Wilson, *J. Amer. Chem. Soc.*, 1964, **86**, 4716.