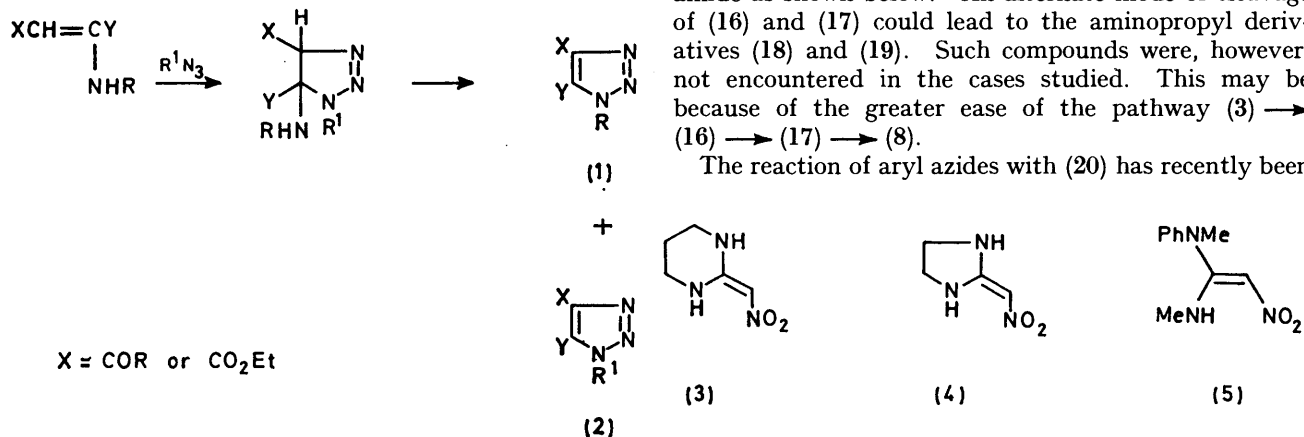


4-Nitro-1,2,3-triazoles from Nitro- $\alpha\beta$ -unsaturated *gem*-Diamines

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The reaction of nitro- $\alpha\beta$ -unsaturated *gem*-diamines (3)—(7) with *p*-chlorobenzenesulphonyl azide leads to the formation of the 4-nitro-1,2,3-triazoles (8)—(12).

THE reaction of β -amino- α,β -unsaturated ketones and esters with azides leads to the formation of two types of 1,2,3-triazoles (1) and (2) with or without a Dimroth rearrangement as shown in Scheme 1.¹⁻³



SCHEME 1

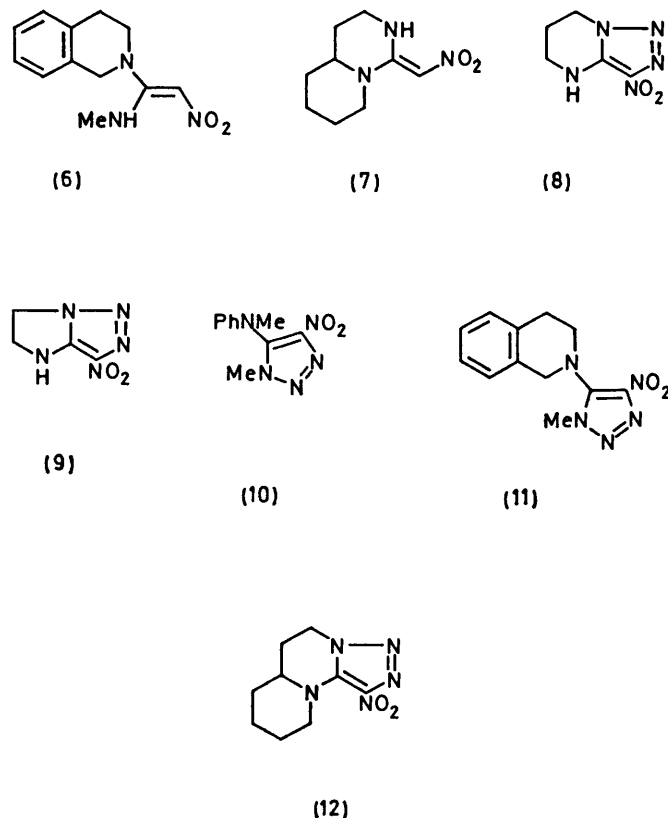
Because of the biological interest of nitro-heterocycles and the availability of nitro-enamines from work in our laboratory,⁴ we investigated the reaction of the following nitro- $\alpha\beta$ -unsaturated *gem*-diamines (3)—(7), which had at least one free NH group, with *p*-chlorobenzenesulphonyl azide. The starting materials were obtained by published procedures.⁴ The products, obtained in varying yields (Table), were identified as the 4-nitro-1,2,3-triazoles (8)—(12) respectively, corresponding to general structure (1; X = NO₂). This method can be used for the preparation of a variety of nitro-triazoles of potential interest as antiprotozoal agents. Such compounds would be difficult to obtain by other methods.

Previous syntheses of 4-nitro-1,2,3-triazoles by the azide route involve either the incorporation of the azide component *in toto* as in the formation of (13)^{5,6} or the elimination of the amine component as in the formation of (14) (see Scheme 2).⁷

The spectral characteristics of compounds (8)—(12) are in complete agreement with the structures assigned. The isomeric diazo-imine structures such as (15) [from (3)] are ruled out by the absence of i.r. absorption due to the C=N₂ group near 2100 cm⁻¹. Such diazo-structures may, however, be intermediates in the formation of the triazoles. The diazo-imines can be formed by the transfer of diazo-groups from the sulphonyl azide to the $\alpha\beta$ -unsaturated diamines. 1,3-Dipolar cycloaddition of the C=N₂ dipole across the azomethine bond can lead to the nitro-triazoles. Since basic conditions are needed for the

generation of the diazo-imines,⁸ the mechanism of formation of the nitro-triazoles is more likely to involve the Dimroth rearrangement of the triazolone adduct such as (16) to (17) followed by elimination of the arylsulphonamide as shown below. An alternate mode of cleavage of (16) and (17) could lead to the aminopropyl derivatives (18) and (19). Such compounds were, however, not encountered in the cases studied. This may be because of the greater ease of the pathway (3) \rightarrow (16) \rightarrow (17) \rightarrow (8).

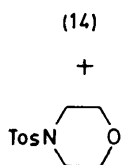
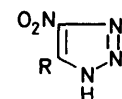
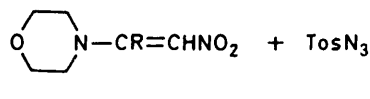
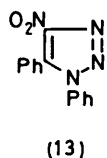
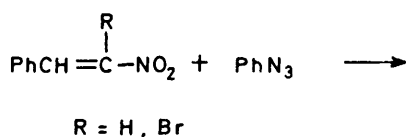
The reaction of aryl azides with (20) has recently been



4-Nitro-1,2,3-triazoles (8)–(12)

Comp.	Yield (%)	M.p. (solvent for recrystl.)	U.v. (EtOH) λ/nm ($\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$)	Mass spectrum M^+ , m/e	Molecular formula (mol. wt.)	Microanalyses (%)					
						Calculated			Found		
						C	H	N	C	H	N
(8)	35	218 (decomp.) (CH_2Cl_2 -MeOH)	224 (13 490) 343 (9 550)	169	$\text{C}_5\text{H}_7\text{N}_5\text{O}_2$ (169.2)	35.50	4.17	41.41	35.8	4.4	41.5
(9)	65	215 (decomp.) (MeCN)	225 (12 600) 332 (7 600)	155	$\text{C}_4\text{H}_5\text{N}_5\text{O}_2$ (155.1)	30.97	3.25	45.15	31.2	3.55	45.05
(10)	15	91 (Et_2O -hexane)	234 (17 380) 355 (1 620)	233	$\text{C}_{10}\text{H}_{11}\text{N}_5\text{O}_2$ (233.2)	51.49	4.75	30.03	51.7	4.8	30.3
(11)	12	151 (CH_2Cl_2 - Et_2O)	234 (12 900) 348 (2 300)	259	$\text{C}_{12}\text{H}_{13}\text{N}_5\text{O}_2$ (259.3)	55.59	5.05	27.02	55.8	5.4	27.2
(12)	75	163 (CH_2Cl_2 - Et_2O)	229 (22 000) 356 (10 100)	223	$\text{C}_6\text{H}_9\text{N}_5\text{O}_2$ (223.2)	48.42	5.87	31.38	48.6	6.25	31.25

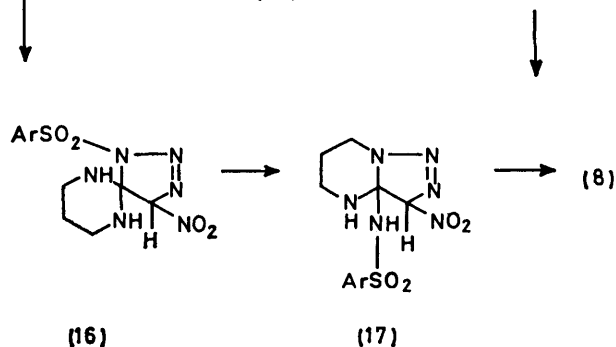
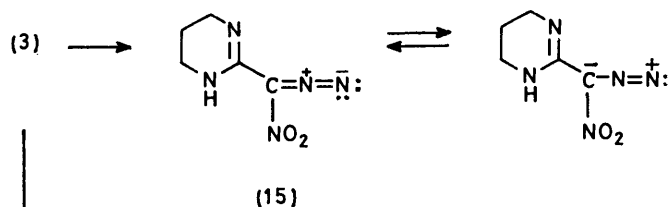
described.⁹ Unlike the cases reported above, the reaction yields the triazoline (21) which is deaminated with acetic acid to the aryltriazole (22) (see Scheme 3).



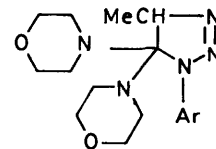
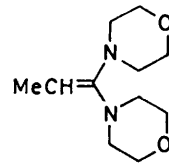
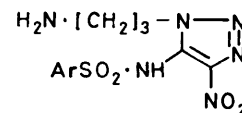
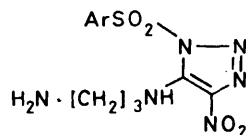
SCHEME 2

EXPERIMENTAL

Preparation of the 4-Nitro-1,2,3-triazoles.—In the case of the nitro- $\alpha\beta$ -unsaturated *gem*-diamines (3) and (4), the diamine (0.01 mol) was mixed with *p*-chlorobenzenesulphonyl azide (0.011 mol) in acetonitrile (200 ml) and then set aside

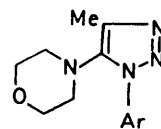


at room temperature for 7 days. In the case of (5), (6), and (7), the diamine (0.01 mol) was heated with the azide (0.011 mol) in dioxan (30 ml) at 80 °C for 15 h. In either case, the solvent was evaporated and the residue chromatographed over silica gel in chloroform, the column being eluted with chloroform containing gradually increasing amounts of



(20)

(21)



SCHEME 3

methanol. *p*-Chlorobenzenesulphonamide, m.p. 141 °C and *p,p'*-dichlorodiphenyl sulphone, m.p. 146 °C, were obtained as by-products.

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