2,5-Dihydro-1,2,3-triazine Derivatives from attempted 1,3-Dipolar Cycloaddition of 1,2,3-Triazole *N*-Oxides with Dimethyl Acetylenedicarboxylate: A New Ring Expansion

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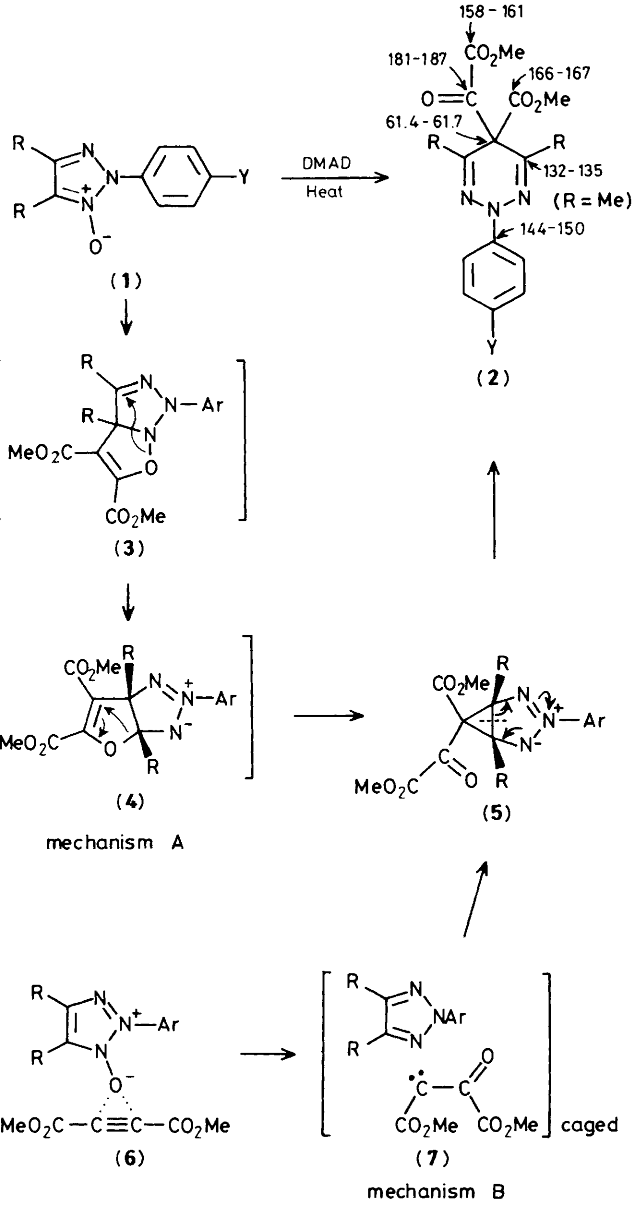
A new route to substituted 2,5-dihydro-1,2,3-triazine derivatives is described along with an *X*-ray crystal structure determination of one of these compounds.

1,2,3-Triazines are relatively rare and are by far the least studied of the triazine class.[1,2] Most of the known compounds are fused benzo-derivatives and new reactions which give high yields of monocyclic 1,2,3-triazine derivatives are of particular interest.[3—6] There is a paucity of detailed structural data on dihydro-derivatives of 1,2,3-triazines[1] but the *X*-ray structure of the parent 1,2,3-triazine has been described recently.[5] Herein we describe an interesting reaction which gives high yields of the dihydro-1,2,3-triazine derivatives (**2**) and we report the *X*-ray crystal structure of one of these.



Scheme 1. ^{13}C N.m.r. shift range for the dihydrotriazines (2) ($CDCl_3$) shown.

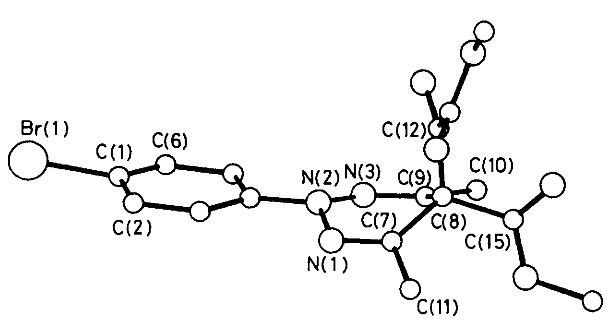


Figure 1. *X*-Ray crystal structure of compound (**2d**). Bond lengths, (Å) and angles (°): Br(1)–C(1) 1.916(10); N(1)–N(2) 1.372(10); N(2)–N(3) 1.364(10); N(3)–C(9) 1.302(12); C(7)–C(11) 1.505(14); C(8)–C(12) 1.505(13); C(9)–C(10) 1.487(14); N(1)–C(7) 1.265(11); N(2)–C(4) 1.433(12); C(7)–C(8) 1.529(13); C(8)–C(9) 1.489(13); C(8)–C(15) 1.534(14); C(7)–N(1)–N(2) 115.9(8); C(4)–N(2)–N(1) 116.7(8); C(9)–N(3)–N(2) 116.0(8); C(11)–C(7)–N(1) 117.2(9); C(9)–C(8)–C(7) 105.3(7); C(12)–C(8)–C(9) 109.9(8); C(15)–C(8)–C(9) 113.1(9); C(8)–C(9)–N(3) 119.7(9); C(10)–C(9)–C(8) 122.1(9); N(3)–N(2)–N(1) 121.2(7); C(8)–C(7)–N(1) 120.3(8); C(11)–C(7)–C(8) 122.5(8); C(12)–C(8)–C(7) 111.1(8); C(15)–C(8)–C(7) 111.4(8); C(15)–C(8)–C(12) 106.1(8); C(10)–C(9)–N(3) 117.9(9).

Table 1. Preparation of the dihydrotriazines (**2**).

	Compound R	Y	M.p., *t*/°C	Yield, % Toluene	Yield, % *o*-Xylene
(**2a**)	Ph	H	139—141[a]	72	18
(**2b**)	Ph	NO_2	173—175[a]	57	44
(**2c**)	Me	NO_2	142—144[b]	78	52[d]
(**2d**)	Me	Br	88—89[c]	40	—

[a] From diethyl ether. [b] From *p*-xylene. [c] From EtOH. [d] Yield in benzene, 44%.

When the compounds (**1**) were heated† with dimethylacetylene dicarboxylate (DMAD) in toluene good yields of the unexpected products (**2**) were obtained (Table 1). The reaction occurred also in benzene and *p*-xylene as solvents but the yields were lower. The structures of the products were established from the *X*-ray crystal structure‡ of compound (**2d**) (Figure 1) and were confirmed by ^{13}C and ^{1}H n.m.r. spectra for the series. It is likely that the species (**5**) (Scheme 1) is a key intermediate in this reaction. This could arise through a cycloaddition–rearrangement sequence in which case the mechanism (A) involving 1,3-dipolar cycloaddition of DMAD giving the precursory intermediates (**3**) and (**4**) is the most likely. This route is an oxygen analogue of the comparable reaction[7] of triazolium imides (**1**, N^-–Ar for O^-) which stops at the stable product (**4**, N-Ar for O). An alternative type of mechanism (B) could involve O transfer to the alkyne generating an acyl carbene. Attempts to trap intermediates

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† Typically, a solution of compound (**1c**) (0.88 mmol) in toluene (10 ml) was treated with DMAD (3.3 mmol), and the mixture stirred under reflux for 28 h, cooled to ambient temperatures, and treated with diethyl ether (10 ml) whereupon compound (**2c**) separated. Successive crops were collected by fractional evaporation of the filtrate (isolated yield, 78%). The final residue contained small quantities of starting materials and some further crude (**2c**), not included in the quoted yield, along with a trace quantity of a dark brown oil.

‡ *Crystal data:* $C_{14}H_{10}BrN_3O_5$, monoclinic, space group $P2_1/c$, a = 9.996(2), b = 12.851(2), c = 14.139(3) Å, β = 102.5(2)°, Z = 4, U = 1773.28 Å^3; Mo-K_α radiation (λ = 0.71069 Å), μ = 22.51 cm^{-1}. Data were collected on a Hilger and Watts Y290 diffractometer in the θ–2θ mode in the range 22° > θ > 2°. The structure was solved by direct methods (SHELX) and refined using full matrix least squares (SHELX), to final values of R = 8.28% and R_w = 8.99% with 1432 unique reflections having $I > 3\sigma(I)$ and 106 parameters. Hydrogen atoms were included in calculated positions and the maximum and minimum features in the final difference map were 0.25 and −0.18 e/Å^3. The maximum shift/e.s.d. for any parameter was <0.0009. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

with additives such as cyclohexene, stilbene, and nitriles were unsuccessful and the reaction occurred in their presence. Attempts to achieve other comparable oxygen transfers from the substrates (**1**) were also unsuccessful but oxygen transfers from amine oxides to the carbon of metal carbonyl complexes are known.[8—10] The structure of the dihydrotriazine ring is shown in Figure 1. Of interest is the planar symmetrical nature of the atoms comprising the C–N–N–N–C system in which the N(1)–N(2)–N(3) and C–N–N bond angles of 121 and 116° respectively contrast with the buckled saturated nature of the C–C–C region with almost normal single C–C bond lengths and tetrahedral bond angles.

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