

1-Methyl-1,2,3-benzotriazin-4(1H)-one

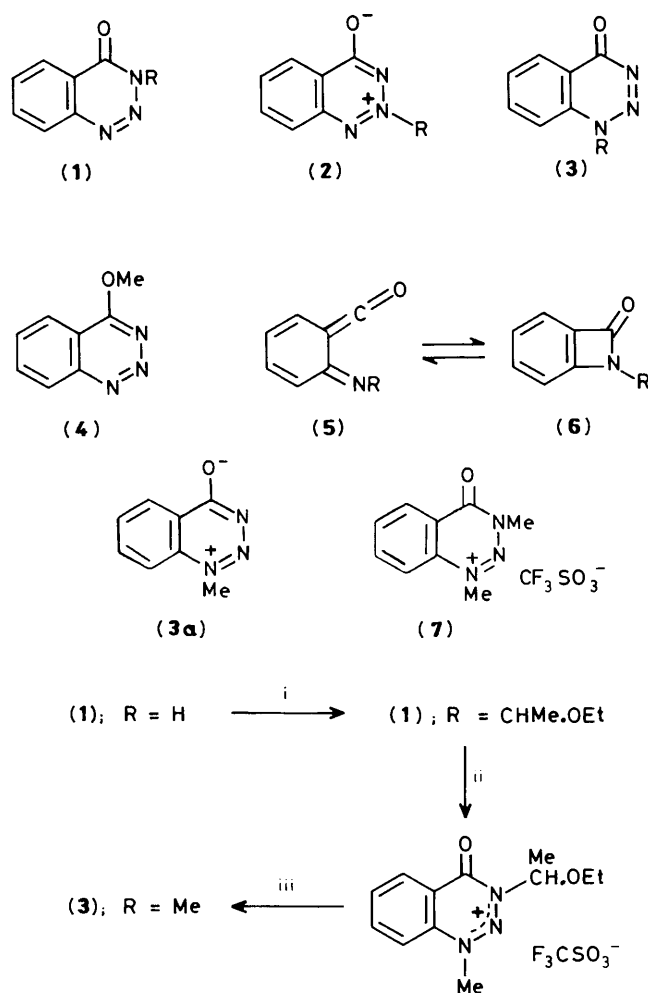
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The title compound is prepared by methylation of 1,2,3-benzotriazin-4(3H)-one, protected at the 3-position by a 1-ethoxyethyl substituent, followed by removal of the protective group; the unusual physicochemical properties of the compound are probably associated with a highly polar structure.

1,2,3-Benzotriazin-4-one has for long been known to exist in the 3H-form (**1**; R = H), as its predominant tautomer.¹ Many alkyl derivatives of the 3H-(**1**) and the zwitterionic 2H-(**2**) forms are known, but to date no representative of the 1H-series (**3**) has been reported. An early attempt to make the

1-methyl and 1-ethyl compounds was described by Finger,² who was the first to prepare the well-known parent compound (**1**; R = H). However, he found that the 2-(N-alkyl-N-nitrosoamino)benzamides did not cyclise to (**3**). Alkylation of 1,2,3-benzotriazinone, or its anion, has given the 2- or



Scheme 1. Reagents and conditions: i, $\text{EtO} \cdot \text{CH}=\text{CH}_2 / \text{TsOH}$, toluene, 2 h; ii, $\text{MeOSO}_2\text{CF}_3$, CHCl_3 , 12 h; iii, $\text{H}_2\text{O}/\text{H}^+$, CHCl_3 , stir 2 h at 20°C .

3-*N*-methyl, or the methoxy derivative (4), or mixtures of these, depending on the conditions and the reagent used.^{3,4}

At first sight, it might seem likely that derivatives of (3) could be too unstable to be isolated, since they have an apparently very simple mode of decomposition available, by

loss of dinitrogen and formation of the imino ketenes (5), the open-chain valence tautomers of benzotriazinones (6).⁵ However, we have found that 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (3; R = Me) can be made, in good yield, by the route shown in Scheme 1. It is a somewhat photosensitive, but apparently otherwise stable, white crystalline solid, which does not melt below 320°C .† Other properties which were noted are as follows: the mass spectrum (70v electron impact; source temperature 200°C) showed no sign of a parent ion (m/z 161), but gave a strong peak at m/z 133 ($M^+ - 28$), and also a small peak at m/z 266 [dimer of (5; R = Me)?]. The *N*-methyl signal appeared at δ 4.33 in the ^1H n.m.r. spectrum. The ^{13}C n.m.r. spectrum showed the C-4 (carbonyl) signal at δ 163.2, perhaps indicative, with the high melting-point, of a large contribution from the dipolar structure (3a) to the constitution of the molecule. For comparison, C-4 in (1; R = Me) absorbs at δ 155.2, that in (2; R = Me) at δ 167.7, and that in (4) at δ 160.7. However, both protonation and alkylation of (3; R = Me) take place at N-3, rather than at oxygen. In aqueous acid, the u.v. spectrum is not significantly different from that of the 1,3-dimethyl cation (7), or that of the 3-methyl compound (1; R = Me) in 50% H_2SO_4 . The 1-methyl compound is a stronger base ($\text{p}K_a$ ca. +0.8) than the 3-methyl ($\text{p}K_a$ ca. -2.7), as the tautomeric preference for the 3*H*-form (1; R = H) requires. Methylation ($\text{MeOSO}_2\text{CF}_3$) of (3; R = Me) provides the same product (7) as that formed from the isomer (1; R = Me).

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References

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† In bulk (ca. 0.5 mg in a melting-point tube), one sample decomposed vigorously at 150°C , but this may have been due to the presence of a catalytic impurity. Other similar samples, and isolated crystals on a Kofler hot-stage microscope, very slowly decomposed without melting, at the highest temperature the available apparatus would allow.