Cycladdition of 1,2,3-Benzotriazines to Diphenylcyclopropenone

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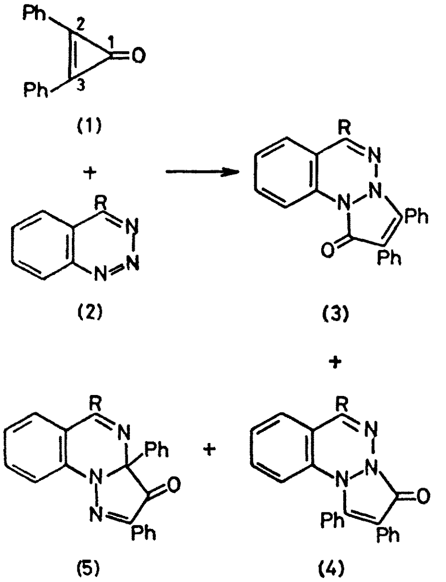
Summary With diphenylcyclopropenone, 1,2,3-benzotriazines give cycloadducts (**3**), (**4**), and (**5**), this last product requires rearrangement of a [2 + 3] cycloadduct resulting from addition of the triazine to the 2,3-bond of diphenylcyclopropenone, and conversion of the triazine into a diazine

REACTION of diphenylcyclopropenone (DPCP) (**1**) with 4-phenyl-1,2,3-benzotriazine[1] (**2**; R = Ph) in refluxing benzene gave the two isomeric, yellow 1 : 1-adducts (**3**; R = Ph) [m.p. 250—252 °C, ν_{max} (Nujol) 1642 cm^{-1}, 38%] and (**4**; R = Ph) (m.p. 203—204 °C, ν_{max} 1666 cm^{-1}, 8%) together with a red adduct (**5**; R = Ph) (m.p. 176—177 °C, ν_{max} 1730 cm^{-1}, 5%). In refluxing toluene the proportion of (**5**) was increased (39%) whereas at room temperature only (**3**) and (**4**) were observed. Control experiments showed that (**5**) did not arise by thermal rearrangement of (**3**) or (**4**). 4-Methylthiobenzotriazine (**2**; R = SMe),[2] in refluxing toluene gave an analogous red adduct (**5**; R = SMe) (m.p. 161—162 °C, ν_{max} 1745 cm^{-1}, 63%) but the only yellow adduct isolated was (**3**; R = SMe) (m.p. 166—168 °C, ν_{max} 1645 cm^{-1}, 26%).†

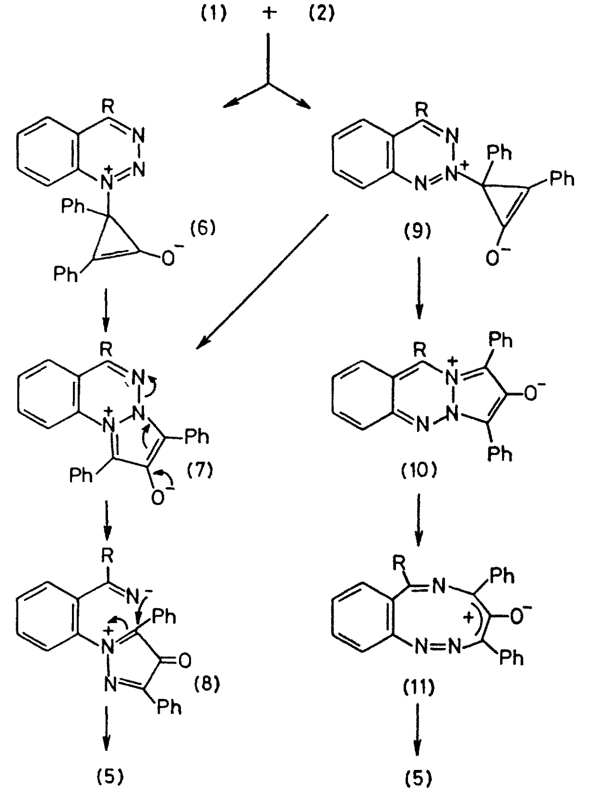


Structure (**3**; R = Ph) for the major yellow isomer was confirmed by *X*-ray crystallography, and the regioisomeric structure (**4**) for the minor adduct was assigned on the basis of the carbonyl absorption at 1666 cm^{-1} and the absence of any absorption due to an sp^3 carbon in the ^{13}C n.m.r. spectrum which rules out alternative structures arising from addition to the C=N of the triazine.‡ The ^{1}H n.m.r. spectra of compounds (**3**; R = Ph) and (**4**; R = Ph) both show low-field doublets, *J* = 8 Hz, assigned to 10-H, at δ 8·90 and 8·24 respectively. The sole yellow adduct isolated from methylthiobenzotriazine is closely analogous to (**3**; R = Ph) having a similar carbonyl absorption and a low field doublet at δ 8·86. The unexpected structure of the red adducts was revealed by an *X*-ray xtudy of (**5**; R = SMe). Both red adducts (**5**; R = Ph and SMe) showed a high-frequency carbonyl absorption in the infra-red and the sp^3 carbon was apparent [δ (CD_2Cl_2) 82·12 and 82·64 respectively] in their ^{13}C n.m.r. spectra.

Crystal data: crystals of (**3**) are monoclinic, a = 10·911(1), b = 18·394(1), c = 10·505(1) Å, β = 99·92(1)°, U = 2077 Å^3; space group $P2_1/a$, Z = 4. Those of (**5**) are monoclinic, a = 11·422(1), b = 15·030(1), c = 11·851(1) Å, β = 109·47(1)°, U = 1918 Å^3; space group $P2_1/c$, Z = 4. Data for both compounds were measured on a diffractometer using Cu-K_α radiation; 3098 independent reflections were measured for (**3**) and 2814 for (**5**). Both structures were solved by direct methods and refined to give current *R* values of 0·086 and 0·075 for (**3**) and (**5**) respectively.§

Formation of the yellow adducts (**3**) and (**4**) is not exceptional. This mode of addition involving cleavage of the 1,2-bond of DPCP (**1**) is observed with benzocinnoline and a number of azaheterocycles‡ and imines.[3,4] Adducts (**3**) could arise by nucleophilic attack of triazine N-1 on C-1 or of N(2) on C(2) of DPCP and collapse of the resulting zwitterions; formation of (**4**) would similarly involve attack of N(1) or C(2) or N(2) on C(1).

Formation of the red adducts (**5**) involves an unusual mode of addition[5] resulting in cleavage of the 2,3-bond of DPCP. Initial attack clearly must occur at C-2 of DPCP. Nucleophilic addition of N(1) would lead, *via* (**6**), to (**7**) which could undergo a 'Dimroth-type' rearrangement to



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† In refluxing benzene, 4-anisylbenzotriazine gave analogous adducts (**3** and **4**; R = p-MeOC$_6$H$_4$) but only a trace of (**5**; R = p-MeOC$_6$H$_4$); 4-methylbenzotriazine gave only (**3**; R = Me). All new compounds gave satisfactory analytical data.

‡ With pyridazine addition to the C=N rather than N=N was observed in contrast with our observations with benzotriazines. See ref. 4.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation to this communication.

give the observed product Alternatively, nucleophilic attack *via* N(2) would give (**9**) which could lead to (**5**) *via* (**10**) or (**7**) as shown (Scheme) Whether the increased proportion of (**5**) at higher temperature reflects the anticipated higher energy of activation for nucleophilic attack by N-2 or the differing energy requirements for C(1)–C(2) *vs* C(2)–C(3) cleavage in the zwitterions (**6**) and (**9**) is not yet clear

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[1] B M Adger, S Bradbury, M Keating, C W Rees, R C Storr, and M T Williams, *J Chem Soc , Perkin Trans* 1 1975 31

[2] B Stanovnik and M Tisler, *J Heterocycl Chem* , 1971, **8**, 785

[3] T Eicher and J L Weber, *Top Curr Chem* , 1975, **57**, 1

[4] J W Lown and K Matsumoto, *Can J Chem* , 1971, **49**, 1165

[5] Diels–Alder and 1,3-dipolar cycloadditions to the 2,3-bond of DPCP have been observed previously see ref 3 and K T Potts and J S Baum, *Chem Rev* , 1974, 189, H Matsukubo and H Kato *J Chem Soc , Perkin Trans* 1, 1975, 632 Precedent for the addition of a 2π-addend to the 2,3-bond is to be found with electron-rich alkenes and alkynes, J Sauer and H Krapf, *Tetrahedron Lett* , 1969, 4279, and references therein