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CYCLOHEPTATRIENE FURANONES AND BICYCLO[5.3.0]DECATRIENONE; UNUSUAL CYCLOADDITION WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE (PTAD)

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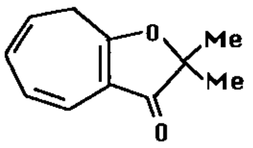
Abstract - Cycloheptatriene furanones (1), (2), (3) and bicyclo[5.3.0]decatrienone (4) react with PTAD to afford the formal (4+2) or (6+2)-tropilidene cycloadducts in contrast with other substituted cycloheptatrienes which give only norcaradiene type adducts.

The cycloaddition of PTAD and other dienophiles to cycloheptatrienes is useful in understanding the relative reactivity and equilibrium between the norcaradiene and the tropilidene valence tautomers.[1] It is well known that PTAD and most other dienophiles give exclusively cycloaddition to the norcaradiene tautomer.[2] Here we report the reaction of PTAD with bicyclo[5.3.0]decatrienone and cycloheptatriene furanones, a class of fused, hetero-substituted cycloheptatrienes whose reactivity toward dienophiles was previously unknown and which show unusual behavior.

The required substrates 1-4 were prepared by selective intramolecular cycloaddition of the carbenoid species derived from catalytic decomposition of α'-branched-α'-phenoxy-α-diazo ketones[3] and ω-phenyl-1-diazo-2-butanone.[4]



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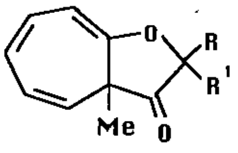
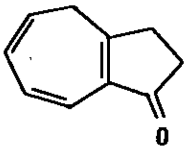


2 $R = R^1 = Me$

3 $R = H \quad R^1 = Ph$



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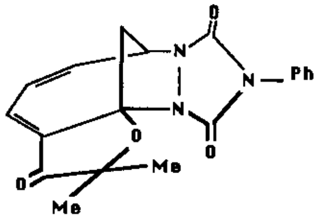
Dropwise addition of a dichloromethane solution of PTAD to a cooled and stirred solution of 2,2-dimethyl-2,8H-cyclohepta[b]furan-3-one (1) in the same solvent showed instantaneous decoloration of the brick-red colour of PTAD even at -58 °C (higher temperatures led to production of polymers). The resulting 1 to 1 adduct 5 was purified by silica gel column chromatography eluting with a mixture of dichloromethane-ethyl ether 8:2 and recrystallizing from ethanol (mp 182-183 °C).^{5} The structure of the formal (6+2)-cycloadduct 5 was assigned to the product on the basis of elemental analysis and ^{1}H nmr spectroscopy. Particularly diagnostic is the presence of three olefinic resonances at 5.63, 6.30, 6.70 ppm and of a well resolved AB pattern at 2.87 and 3.28 ppm ($\underline{J}$= 19.2 Hz) which was attributed to the methylenic protons. The structure assignment was substantiated by decoupling experiments and by the absolute value of the coupling constants which were in good agreement with literature data^{1c,d,2d,6} and with the dihedral angles expected on the basis of Dreiding models.



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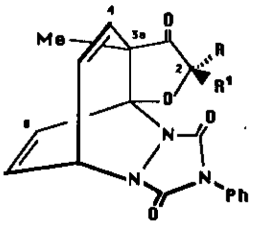
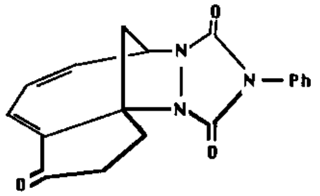


6 $R = R^1 = Me$

7 $R = H$ (or Ph) $R^1 = Ph$ (or H)



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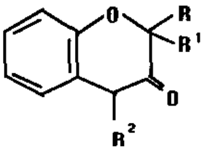
Cycloaddition to both 2,2,3a-trimethyl-2(3aH)-cyclohepta[b]furan-3-one (2) and 2-phenyl-3a-methyl-2(3aH)-cyclohepta[b]furan-3-one (3) occurred in dichloromethane at room temperature, showing a comparatively lower reactivity than 1. The formal (4+2)-cycloadducts 6 (mp 165-166 °C from AcOEt) and 7 (mp 154-155 °C from EtOH) were obtained after similar work-up and purification in 74 and 76 % yields, respectively. The structure assignments were again attributed on the basis of their ^{1}H nmr spectral data. Four distinct olefinic resonances are present at 6.03, 6.13, 6.49 and 6.56 ppm for 6 and at 6.04-6.06 (3 H included benzylic hydrogen), 6.55 and 6.69 ppm for 7, thus excluding norcaradiene and (6+2)-tropilidene type products. Good correlation with literature data^{1c,d,2d,6} and between the absolute magnitude of the coupling constants with the dihedral angles expected by analyses of the Dreiding models, were observed. To determine the configuration of carbon 3a,^{7} recourse was made to nuclear Overhauser effect (n.O.e.) experiments. In compound 6, irradiation of the three methyl resonances at 1.40, 1.59 and 1.62 ppm brought about a positive effect on the two olefinic protons in 4 and 8 (6.56 and 6.49 ppm) only for the first peak, showing it to be placed between the two unsaturated bridges. The assignment of the signal at 1.40 ppm to the 3a methyl is based on the large value of the n.O.e. (which would not be expected for the geminal methyl in 2 due to the larger distance) and because irradiation on at least one signal (the 3a methyl) had to show a n.O.e. effect with the hydrogen in 4.

The cycloaddition to 3 (two stereoisomer in a ca. 3:2 ratio) was assumed to give a similar stereoisomer with respect to the 3a carbon, while the configuration of carbon 2 is assumed not to change during the cycloaddition. The 3,4-dihydro(2H)azulenone 4, afforded under similar reaction conditions (dichloromethane, 0 °C) the (6+2)-tropilidene cycloadduct 8 (mp 167-168 °C from EtOH), whose structure was assigned as before and in analogy to adduct 5.[8]

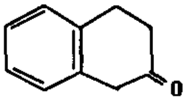
Other dienophiles such as maleic anhydride, tetracyanoethylene, dimethylacetylenedicarboxylate and other ones did not react under the same conditions. Upon increase of the reaction temperature, only rearrangement of the substrates to the aromatic isomers 9-12 was observed.



9 $R = R^1 = Me \quad R^2 = H$

10 $R = R^1 = R^2 = Me$

11 $R = H \quad R^1 = Ph \quad R^2 = Me$



12

The formation of the observed PTAD cycloadducts can be rationalized assuming the intervention of dipolar intermediates[9] but, at the present stage of the work, we cannot provide an unifying mechanistic picture.

ACKNOWLEDGEMENTS

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3. A. Pusino, V. Rosnati, and A. Saba, Tetrahedron, 1986, 42, 4319.

4. L.T. Scott, M.A. Minton, and M.A. Kirms, J. Am. Chem. Soc., 1980, 102, 6311.

5. All new compounds presented correct composition by elemental analysis and spectral data in accordance with the proposed structure.

6. *See for example:* *G.R. Krow, R. Rodebaugh, M. Grippi, G. DeVicaris, C.* Hyndman, and J. Marakowski, J. Org. Chem., 1973, 38, 3094; K. Harano, M. Yasuda, and K. Kanematsu, ibid., 1982, 47, 3736.

7. For sake of simplicity the carbon numbering of the adducts has been referred to that of the substrate, i.e., the numbering of the cyclohepta[b]furan-3-one skeleton.

8. Photooxygenation of 4 has been reported to afford the two possible (4+2)-tropilidene endoperoxides: L.T. Scott and C.M. Adams, J. Am. Chem. Soc., 1984, 106, 4857.

9. Cycloadditions of PTAD occurring via a dipolar intermediate are well known. See for example: W. Adam, O. De Lucchi, and I. Erden, J. Am. Chem. Soc., 1980, 102, 4806.

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