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THE EFFECT OF Ag$^{\oplus}$ ON SOME DIELS-ALDER CYCLOADDITION PRODUCTS OF 1,2,5,6-TETRAMETHYL-3,4-DIMETHYLENETRICYCLO[3.1.0.0^{2,6}]HEXANE

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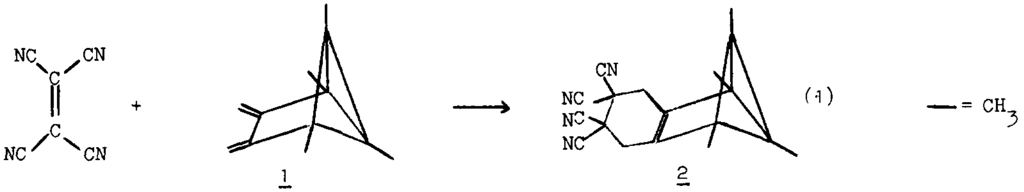
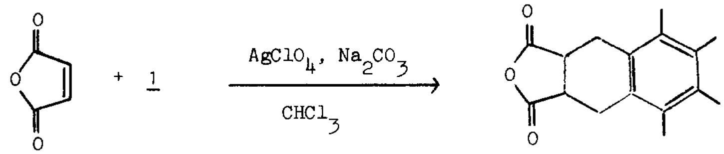
In continuing our investigations of the reactivity of highly strained molecules[1,2] we started a study of the behaviour of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane 1[3] in cycloaddition reactions. Of special interest is the interaction of the bicyclobutane and diene moiety in the molecule and the chemical reactivity as a result of that interaction.



In chloroform solution 1 reacts with tetracyanoethylene and the normal Diels-Alder adduct 2 is obtained in quantitative yield.[3] (reaction (1)).

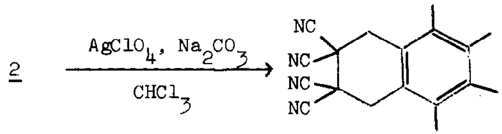
In contrast 1 reacts rapidly with maleic anhydride but the main products are not a result of normal Diels-Alder cycloaddition.[4] However 1 (3.10^{-3} mol) does react smoothly at room temperature with maleic anhydride (6.10^{-3} mol) in chloroform or methylene chloride solution (20 ml) in the presence of silver perchlorate (4.10^{-4} mol) and suspended sodium carbonate (4.10^{-3} mol)[5] to form 3 in an almost quantitative yield (reaction (2)).



3

(2)

Structure assignment of 3 (m.p. 261.6-262.2) rest on the following data: correct elemental analysis, mass spectrum: parent peak at m/e = 258, base peak at m/e = 184, PMR ($CDCl_3$) δ = 3.53 (m, 4H), δ = 2.65 (m, 2H), δ = 2.22 (broad s, 12H) ppm, IR (nujol) C=O vibrations at 1830, 1757 cm^{-1} and the U.V. spectrum ($CHCl_3$) λ_{max} 273 nm, log ϵ = 2.5. Under the same reaction conditions compound 2 is converted quantitatively to 4[6] (reaction (3)): PMR ($CDCl_3$) δ = 3.71 (s, 4H) δ = 2.28 (s, 6H) δ = 2.22 (s, 6H) ppm, mass spectrum: parent peak at m/e = 288, base peak at m/e = 160, U.V. spectrum ($CHCl_3$) λ_{max}= 274 nm, log ϵ = 2.6.

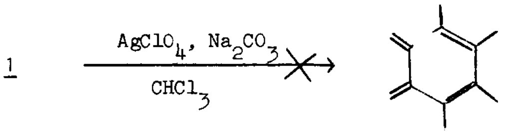


4

(3)

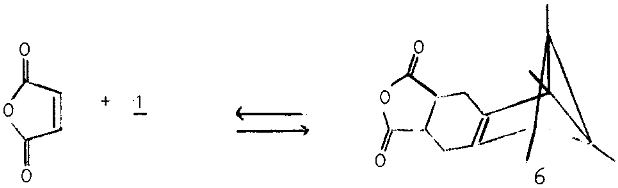
The $Ag^{\oplus}$ catalysed valence isomerisation of bicyclobutanes is well known.[7] However the use of sodium carbonate needs some consideration here. When 1 was treated with silver perchlorate in chloroform solution it reacted within a few minutes to give products which have not yet been identified. When the same reaction was performed in the presence of maleic anhydride compound 3 was formed in only 30% yield and the other products formed from 1 were similar (according to PMR) to those formed in the absence of maleic anhydride. In contrast when 1 (1 equivalent) was treated with maleic anhydride (0.5 equivalent) and silver perchlorate in the presence of sodium carbonate compound 3 was isolated in 85% and the excess of 1 was recovered unchanged in 87% yield. This might indicate that the activity of $Ag^{\oplus}$ is reduced by sodium carbonate or alternatively an acid catalysed reaction of 1 is prevented.[8]

Although o-xylylenes are known to be reactive in Diels-Alder cycloadditions[9], we conclude from the above mentioned observations that the o-xylylene derivative 5 (reaction (4)) is probably not an intermediate in reaction (2) under the conditions used.



5 (4)

An explanation might be that a normal Diels-Alder addition takes place here (reaction (5)) but that the equilibrium (5) lies on the side of the reactants.



6 (5)

The action of $Ag^{\oplus}$ then leads irreversibly to 3.

How can we account for the equilibrium in reaction (5)? It is obvious that the Diels-Alder cycloaddition is generally an energetically favourable process. However additional factors are operating here. Strain is increased in 6 compared to 1 as a result of double bond formation between carbon atoms C_3 and C_4. In addition to that the difference in stability of the molecules might be attributed to differences in orbital interaction between the bicyclobutane ringsystem and unsaturated bridge as was recently reported for similar systems.[10]

References and notes:

1. H. Hogeveen and H.C. Volger, Chem. Commun. 1967, 1133.
2. H. Hogeveen and J. Thio, Tetrahedron Lett. 1972, 3463.
3. H. Hogeveen and P.W. Kwant, ibid. 1973, 3747.
4. Reaction of 1 with maleic anhydride gives a complex reaction mixture which is under investigation. When the crude reaction mixture was treated with silver perchlorate in the presence of sodium carbonate a small amount of 3 (about 4%) could be isolated.
   Reaction of 1 with maleic anhydride in the presence of sodium carbonate gives the same complex mixture as in the absence of sodium carbonate.

5. In all described experiments the reaction conditions and concentrations were similar unless stated otherwise.
6. The same compound was obtained when 2 was pyrolysed: H. Hogeveen and P.W. Kwant, submitted for publication.
7. I. Murata, K. Nakasuji and H. Kume, Tetrahedron Lett. 1973, 3405 and references cited therein.
8. Similar observations were reported for transition metal (complex) promoted rearrangements of bicyclobutanes in methanol solution.
   a) L.A. Paquette, S.E. Wilson, G. Zon, J.A. Schwartz, J.Amer.Chem.Soc. 94, 9222 (1972).
   b) P.G. Gassman and R.R. Reitz ibid. 95, 3057 (1973).
9. a) N.L. Bauld, F.R. Farr and Chiu-Shan Chang, Tetrahedron Lett. 1972, 2443 and references cited therein.
   b) J.F.W. McOmie and D.H. Perry, Synthesis 1973, 416.
10. W.L. Jorgensen and W.T. Borden, J.Amer.Chem.Soc. 95, 6649 (1973).