PREPARATION OF TETRACYANO DOUBLE BRIDGED MALEIC ANHYDRIDE ADDUCT AS INITIAL TARGET TO CATENA COMPOUNDS

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ABSTRACT

The tetracyano double bridged maleic anhydride was prepared from a mixture of the diene anhydride (3), and tetracyanoethylene in tetrahydrofuran which give the white powdery adduct (8) in good yield, via the diels-Alder reaction, and some new experiment models were carried out in order to complete a new approach for the synthesis of catena compounds.
***Key Words** : Tetracyano-double Bridged, Maleic anhydride, Catena.*

INTRODUCTION

Catenanes are compounds containing interlocking monocyclic rings, the rings being held together mechanically rather than chemically. They derive their name from Latin (catena = chain), the general structure of a catenane of two or more `links' resembling a chain.We can divide the approaches to the synthesis of catena – compounds[1] into the following categories:-

{a} Statistical methods. If a long- chain compounds is cylised in the presence of a large- ring compound, the is a small probability that some of the molecular chains will be treated through rings at the moment of ring-closure. For example, cyclisation of a long chain diester in the presence of a macrocyclic hydrocarbon was claimed by Wassermann[2] to give a very small yield of a catenane.

{B} Directed methods. In a directed synthesis the two components are held together by one or more auxiliary linkages, so that a chain is held within a ring for the crucial cyclisation. Cleavage of the auxiliary linkage then gives a catenane. this principle was used for the first time by Schill and Lüttringhus,[3] in our research work**,** the directed method is considered for the preparation of catena compounds via Diels- Alder cycloaddition reactions as carried out in pervious papers.[4,5]

EXPIREMENTAL

Unless otherwise stated, the following conditions apply. Thin layer chromatography (TLC), using silica plates, was the tool for following up the reaction mixture during and after each process, the plates being examined under UV light at 254 or 336 nm. Column chromatography was carried out on either silica gel (60-120 mesh) or merk kieselgel (60H). (IR) spectra were recorded on a Parkin-Elmer 1420 spectrophotometer. Mass spectra (MS) were recorded on an AET MS9 instrument updated with VGZAB components. (NMR) spectra were recorded on a jeol GX 270 instrument using (TMS) as the internal standard.

1,4-Dimethyl-7-oxo-2,3-diphenylbicyclo-2.2.1-hept-2-ene-cis-5,6-dicarboxylic   acid anhydride (2): Reaction of hemi cyclone dimer (1) with maleic anhydride in refluxing dry benzene (1 hr) gave the known[6] adduct (2), which was faltered off and washed well with dry light petroleum (b,p, 40~60°C). Yield 96~99%, m.p. 191~192°C (decomp.) (lit.[6] 191°C). IRν_{max} (Nujol) 1860, 1835 sh, and 1772 (anhydride CO), 1789 cm^{-1} (bridge CO). NMR$_H$ 270 MHz; $(CD_3)_2CO$ 7,3~7,0 (10H, m; Ar-H), 3,94 (2H, s; H$_5$ and H$_6$), 1,53 ppm (6H, s; 2xMe).

1,4-Dimethyl-2,3-diphenylbicyclohexa-1,3-diene-cis-endo-5,6-dicarboxylic   acid anhydride (3): Decarboxylation of the carbonyl-bridged anhydride (2) in refluxing tetralin for 1~2 hr (monitored by TLC), followed by precipitation of the product with light petroleum (b.p 40~60°C), gave the known[6] diene-anhydride (3). Yields 72~74%; m.p. 157~160°C (lit.[6] 158°C). IRν_{max} (Nujol) 1855 and 1768 cm^{-1} (anhydride CO). NMR$_H$ (270 MHz; (CD)$_3$CO 7,3~6,9 (10H, m; Ar-H); 4,36 (2H, s; H$_5$ and H$_6$), 1,78 ppm (6H, s; 2xMe).

1,4-Dimethyl-7,7,8,8-tetracyano-2,3-diphenylbicyclo-   2.2.3-   hept-ene-cis-endo-5,6-dicarboxylic Acid Anhydride (8): A mixture of the diene-anhydride (3) (1.00g) and tetracyanoethylene (0.40g) in tetrahydrofuran (25ml) was stirred at 25°C for about 18 days; even after this time, examination of the solution by TLC showed that the reaction was still incomplete. The solvent was removed under reduced pressure, and the yellow-brown crystalline residue was washed with dry benzene several times. Recrystallisation was attempted from acetone-light petroleum (b.p.60-80°C°) and then Acetone-ether, but was not satisfactory. Yellow impurities were removed by washing with boiling ether, and the white powdery adduct (8) was dried (0.69g, 50%); m.p.284~285°C. Found :C, 73.20; H, 4.11; N, 11.98. C$_{28}$H$_{18}$N$_4$O$_3$ (458.5) requires C, 73.35, H,3.96; N, 12.22%. IRν_{max} (Nujol) 1863 and 1780 cm^{-1} (anhydride CO).MS m/z 458 (M; base peak).NMR$_H$ 270 MHz; (CD3)$_2$CO 7.3~7.2 (8H, m; Ar-H), 6.8~6.75 (2H, m; Ar-H), 4.18 (2H, s; H$_5$ and H$_6$), 1.87 ppm (6H, s; 2 ×Me).

RESULTS AND DISCUSSION

An attempts were made to utilize the diene-anhydride (3) obtained from the decarbonylation of the carbonyl-bridged anhydride (2) as described by Allen and Van Allen[6]. It was found that the diene-anhydride (3) was very susceptible to dehydrogenation, and was partially converted into the aromatic anhydride (5) even on attempted recrystallisation. Which was the attempted preparation to the adduct (6) by reaction of the diene-anhydride (2) with dimethyl actylenedicarboxylate. Had this been successfully accomplished, the anhydride-bridge of (6) would have been hydrolysed to this cis- groups would have been sought. However, reaction of the diene-anhydride (3) with dimethyl acetylenedicarboxylate even under very mild conditions (e.g. in refluxing acetone) was found to produce the aromatic diester (7) and the dianhydride (4). Evidently the required adduct (6) was formed but rapidly fragmented by retro <u>Diels</u>-Alder reaction to give the a(7) and maleic anhydride, the latter then added to the diene-anhydride (3) to give the anhydride (4)[6]. Since there had been continuous worry about the purity of the diene-anhydride (3), and its very facile dehydrogenation, a final experiment was carried out at room-temperature with tetracyanoethylene, which is known to be a very reactive dienophile. It was hoped that the reaction would go in high yield, and give reassurance that cycloadditions could be performed on the impure diene-anhydride (3) with out difficulty. The reaction, however, was found to be very slow (still incomplete after 18 days). The product was characterized as (8) by the IR spectrum, which showed the molecular ion at m/z 458 (base peak) and the NMR spectrum, which exhibited a multiplet for the ten aromatic protons at 7.32~7.2, a singlet for H$_5$ and H$_6$. At 4.18 and a singlet at 1.87 ppm for the six protons of the two equivalent methyl   groups.
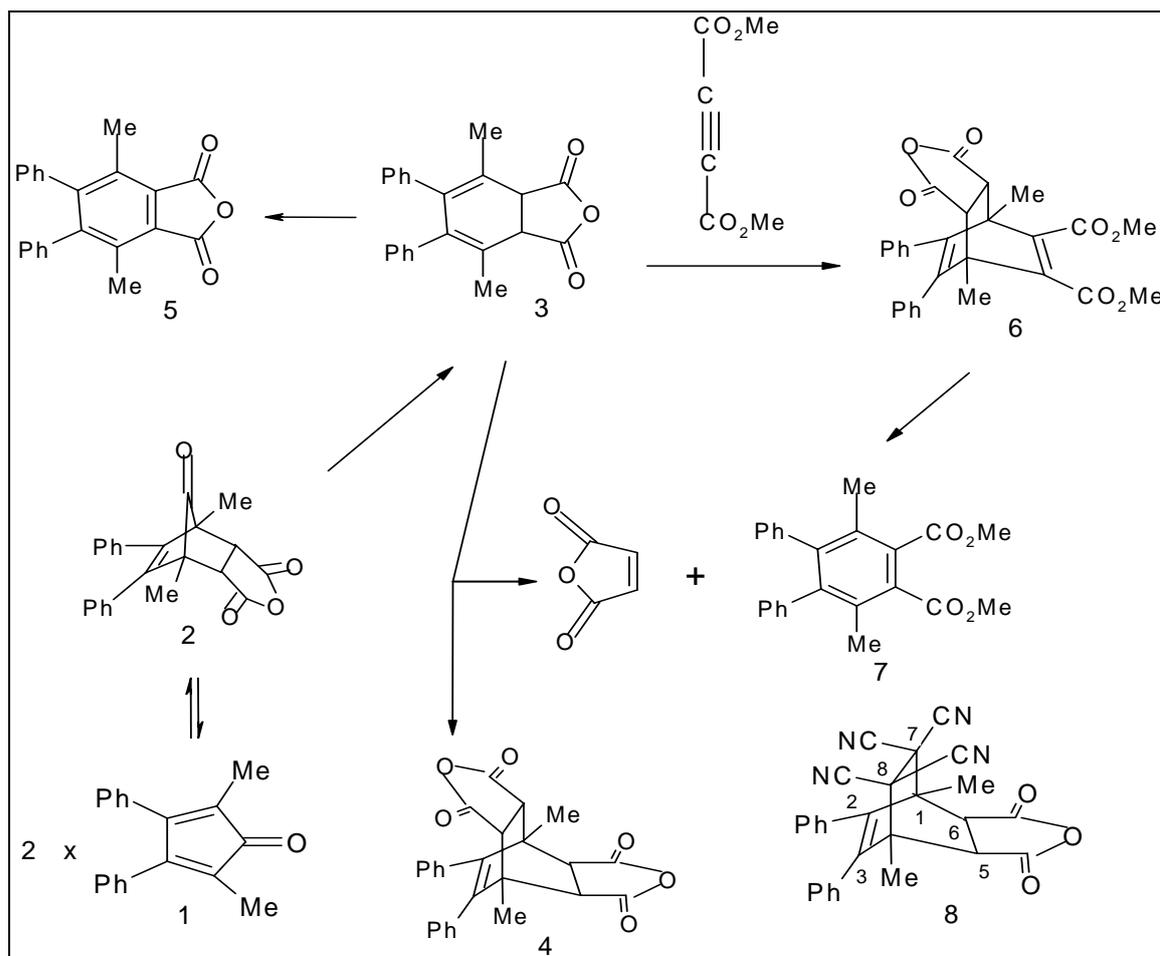
In view of the results of these model reactions, it is clear that a completely new approach will be necessary for the successful use of the Diels-Alder cycloaddition and its retrogression in the synthesis of catena coumpounds.[3,7]

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