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Studies of Some Model Experiments with Simple Cyclopentadienone

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Diels-Alder cycloaddition of hemicyclone (**5**) to fumarylchloride, dimethyl fumarate and fumaronitrite was carried out and thermal decarboxylation of the resulting carboxnyl-bridged adducts (**7**), (**13**) was studied of these only **8** lost carbon monoxide to give the cyclohexa-1,3-diene product. The diene-diester (**9**) was hydrolyzed to the diacid (**10**) but attempts to cycloadd dimethyl acetylenedicarboxylate to **11** failed. During the course of this work a few Diels-Alder reactions of the cyclone (**20**) and (**16**) were also examined.

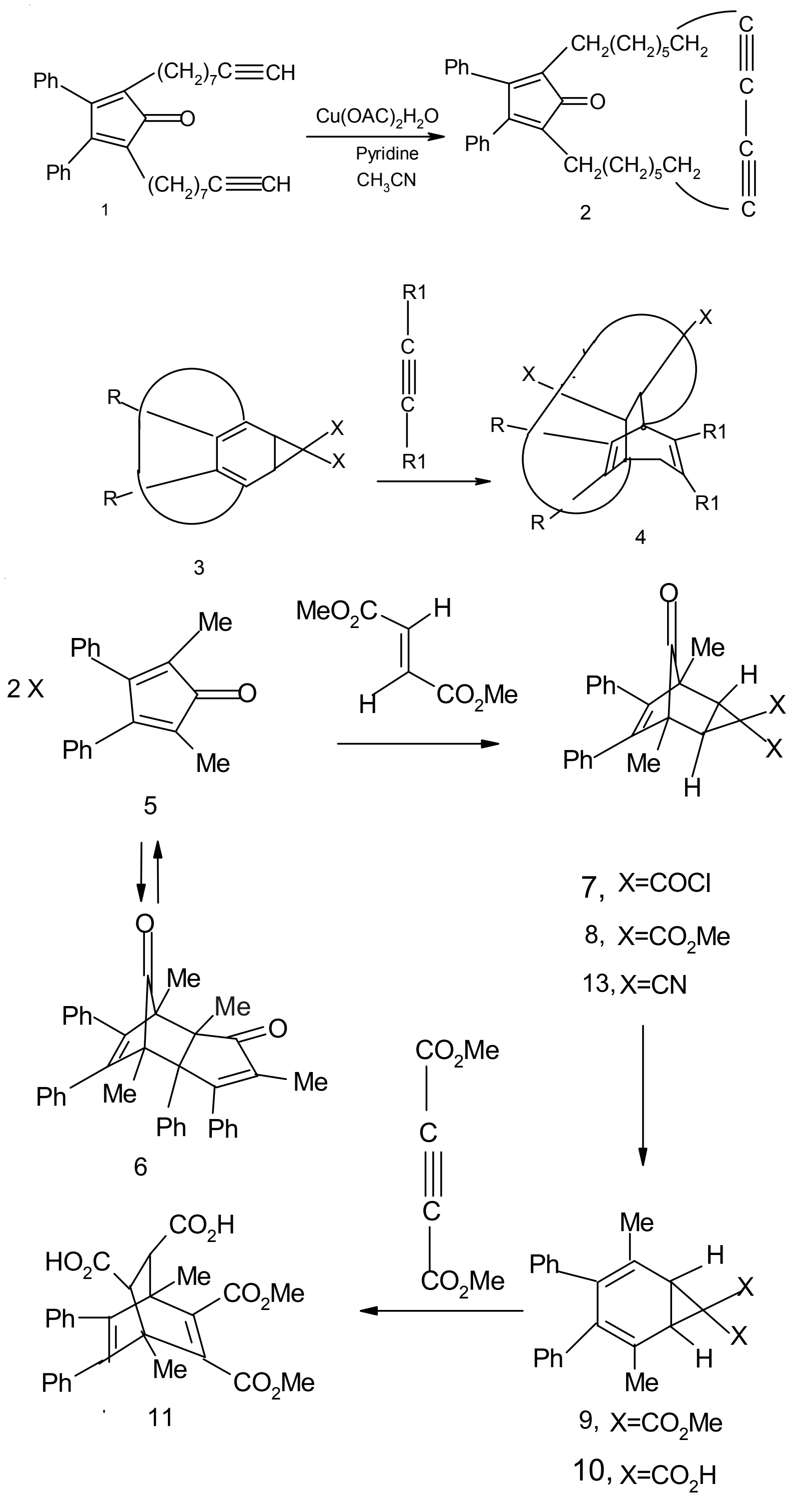
Key Words: Cyclopentadienone, Carbonyl-bridges.

INTRODUCTION

In view of slow and inefficient formation of the cyclone (**1**), in the preparation of macrocyclic pentadienone (**2**) by the cyclization of (**1**) followed by the classical Eglinton-Gal procedure[2], an alternative model Diels-Alder cycloaddition was carried out in the present paper.

RESULTS AND DISCUSSION

In order to obtain the best procedure for the conversion of the cyclone (**2**) into a dicyclic compound of type **3** then into **4**, a number of model experiments were performed using 1,4-dimethyl-2,3-diphenyl cyclopentadienone (hemicyclone) (**5**) produced by thermal dissociation of its Diels-Alder dimer (**6**)[3]. The cycloadditions to hemicyclone (**5**) were carried out with fumaric acid derivatives. Reaction with fumaryl chloride, which is a highly reactive dienophile, was apparently satisfactory, the structure of the crude product being confirmed as **7** by its IR spectrum, which showed absorption at 1785 (bridge CO) and 1763 cm^{-1} (COCl). Thermal decarboxylation of **7**, resulted in extensive decomposition and the product was black. The known[4] reaction of hemicyclone (**5**) with dimethyl fumarate yields the carbonyl-bridged adduct (**8**) which loses carbone monoxide at 200°C with the formation of the diene-diester (**9**) as shown below and so the diene-diester was prepared and then hydrolyzed using aqueous trifluoroacetic acid[5,6] to the diene-diacid (**10**).


Ph
(CH2)7C≡CH
O
Ph
(CH2)7C≡CH
1
Cu(OAC)2H2O
Pyridine
CH3CN
Ph
CH2(CH2)5CH2
O
Ph
CH2(CH2)5CH2
C
C
C
C
2
R
R
X
X
3
R1
C
C
R1
X
X
R
R1
R1
R
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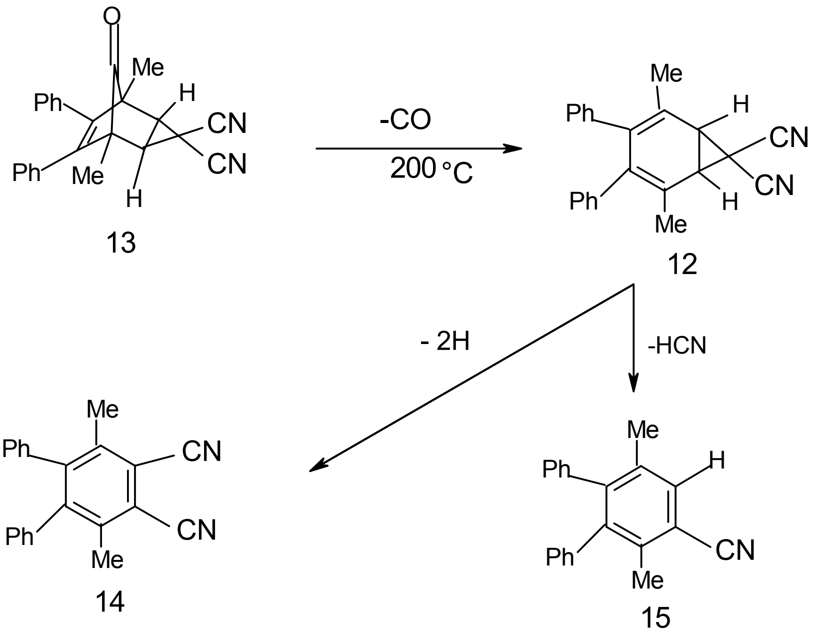
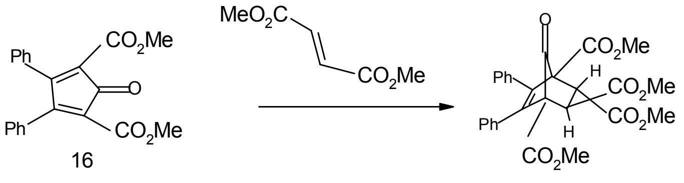
2 X
Ph
Me
O
Ph
Me
5
MeO2C
H
H
CO2Me
O
Me
Ph
H
X
X
Ph
Me
H
7, X=COCl
8, X=CO2Me
13, X=CN
O
Me
Me
O
Ph
Me
Ph
Me
Ph
Ph
6
CO2Me
C
C
CO2Me
Me
Ph
H
X
X
Ph
H
Me
9, X=CO2Me
10, X=CO2H
CO2H
HO2C
Me
CO2Me
Ph
Ph
Me
CO2Me
11

The IR spectrum showed absorption at 1693 cm^{-1} and the NMR spectrum exhibited a multiplet at 7.1-6.75 for aromatic protons, a singlet at 3.64 (H_5 and H_6) and a six protons singlet at 1.84 ppm (two methyl groups). This spectral evidence was thus consistent with the illustrated structure (**10**). Cycloaddition of dimethyl acetylenedicarboxylate to this product would be expected to lead to the bicyclic adduct (**11**), but attempts to effect this reaction were unsuccessful. It may be that the lack of reactivity of the diene-diacid (**10**) is due to steric hindrance by the carboxy groups, the approach of the dienophile to either side of the diene being inhibited. The above steric effect might be much reduced in the diene-dinitrile (**12**). Because of the linearity and smaller bulk of the nitrile group. Accordingly, the carbonyl-bridged dinitrile (**13**) was prepared using fumaronitrile. The structure of (**13**) was confirmed by IR spectrum which showed absorption at 2243 ($C\equiv N$) and 1787 cm^{-1} (CO) and by the spectrum which showed a multiplet at 7.3-6.95 for the ten aromatic protons, an AB quartet (*J* 5.5 Hz) at 3.35 and 3.13 for two protons (H_5 and H_6) and two singlets for the two non equivalent methyl groups at 1.52 and 1.48 ppm. However, on decarbonylation, the resulting diene-dinitrile (**12**) was also with the aromatic mononitrile (**15**), formed by loss of hydrogen cyanide, as shown in the following scheme.



In the course of these model expriments, dimethyl fumarate was also added to the known[7] diester cyclone (**16**) to give the carbonyl-bridged product (**17**). The carbonyl-bridged tetra ester (**17**) was identified by IR spectum which gave absorptions at 1800 (bridge CO) and at 1737 and 1725 sh cm^{-1} (ester CO). The NMR spectrum showed a ten-protons multiplet at 7.3-6.95 for the aromatic protons, four singlet at 3.74; 3.72; 3.67 and 3.59 for the four different methyl groups and an AB quartet at 3.94 and 3.60 ppm (*J* 5 Hz) for the two methine protons. Another attempt to reduce the steric hindrance in the diene-diacid (**10**) was made by trying to eliminate any effect due to the phenyl groups see structure (**18**) by replacing them with a phenanthrene ring-system as in (**19**). The cyclone (**20**) (phenmecyclone) was prepared as its thermally dissociable dimer (**21**) by the known method[8] and was converted into the known[8] dimethyl fumarate adduct (**22**). However, it was found that this carbonyl-bridged compound underwent retro Diels-Alder addition in preference to decarbonylation and the required diene-diester (**23**) could not be obtained.



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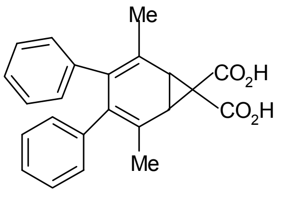

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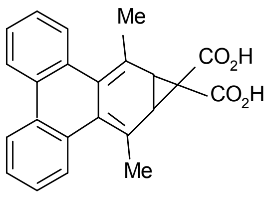

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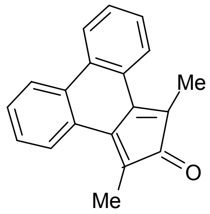
The previously unknown maleic anhydride adduct (**24**) was also prepared[4]. The IR spectrum showed absorption at 1859 and 1774 cm^{-1} (anhydride CO) and at 1780 cm^{-1} (bridge CO). The mass spectrum showed the molecular ion at m/z 356 and the base peak at 285 corresponding to the loss of maleic anhydride from the molecular ion. The NMR spectrum exhibited three separate multepletes for the aromatic protons at 9.0-8.85 (2H and 7.8-7.6) (4H) a two proton singlet at 4.03 (methin protons) and a six-proton singlet at 2.16 ppm (two methyl groups). Decarbonylation of adduct (**24**) could not be effected successfully.

EXPERIMENTAL

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 Kiesel gel



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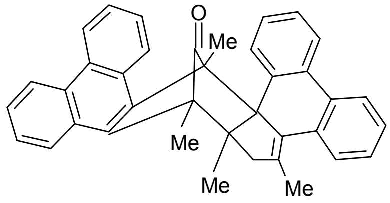

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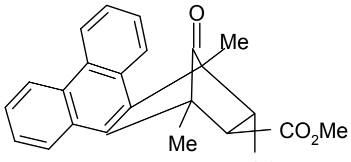

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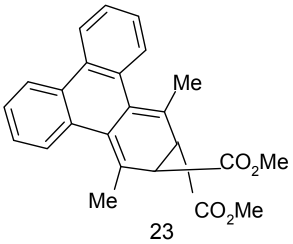

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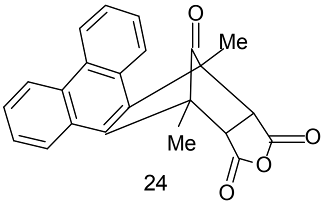

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(60H). (IR) spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra (MS) were recorded on an AET MS9 instrument updated with VGZAB components. (NMR) spectra were recorded on a Jeol GX 270 instrument using (TMS) as the internal standard.

2,5-Dimethyl-3,4-diphenylcyclopentadienone (hemicyclone) Dimer (6): The reaction of benzil with pentan-3-one in the presence of potassium hydroxide (forming the carbinol 4-hydroxy-2,5-dimethyl-3,4-diphenylcyclopenta-2-en-1-one) was carried out as described by Yates *et al.*[9]. The carbinol (21.65 g) was dissolved in dry pyridine (55 mL) and the solution was cooled in ice-water while thionyl chloride (9.30 g; 5.7 mL) was added slowly. On constant stirring, the solution became red and crystals separated. The mixture was left overnight at room-temperature and then acidified with 10 % aqueous hydrochloric acid. The resulting solid was filtered off, washed with water and dried. Recrystallization was carried out by dissolving the solid in hot acetone and adding methanol. Yield 17.1 g, (84°); m.p. 184-186°C (decomp.) (lit.[10] 181-181°C).

Dimethyl-1,4-dimethyl-7-oxo-2,3-diphenylbicyclo-2.2.1-hept-2-ene-*trans*-5,6-dicarboxylate (8): The known[4] carbonyl-bridged *trans*-diester (**8**) was prepared from hemicyclone dimer (**6**) and dimethyl fumarate in refluxing toluene (24 h). Yields 50-61 %; m.p 122-123°C from acetone-light petroleum (b.p. 60-80°C) (lit.[4] 128°C). IR ν_{max} (Nujol) 1780 (bridged CO), 1725 cm^{-1} (ester CO). NMR_H (270 NHz; $CDCl_3$) 7.25-6.8 (10H, m; Ar-H); 3.74 (3H, s; CO_2Me), 3.53 (3H, s; CO_2Me), 3.51 and 3.33 (2H, AB q, *J* 5 Hz; H_5 and H_6), 1.55 (3H, s; Me), 1.21 ppm (3H, s; Me).

Dimethyl-1,4-dimethyl-2,3-diphenylbicyclohexa-1,3-diene-*trans*-5,6-dicarboxylate (9): Decarboxylation of the carbonyl-bridged diester (**8**) in refluxing tetralin for 3.5 h and precipitation of the product with light petroleum (b.p. 30-40°C), gave the known[4] diene-diester (**9**) in almost quantitative yields; m.p 129-130°C from actone-light petroleum (b.p. 60-80°C) (lit.[4] 131°C) IR ν_{max} (Nujol) 1720 cm^{-1} (CO). NMR_H (270 MHz; $CDCl_3$) 7.1-6.7 (10H, m; Ar-H); 3.79 (6H, s; 2 × CO_2Me), 3.64 (2H, s; H_5 and H_6), 1.83 (6H, s; 2 × Me).

1,4-Dimethyl-2,3-diphenylbicyclohexa-1,3-diene-*trans*-5,6-dicarboxylic acid (10): A mixture of the *trans*-dieter (**9**) (3.20 g), actone (15 mL) and 50 % aqueous trifluoroacetic acid (12 mL) was heated under reflux for 23 h and the solution was evaporated under reduced pressure. Several portions of acetone were distilled from the residue (to remove the last traces of trifluoroacetic acid) and recrystallization from acetone-light petroleum (b.p. 60-80°C) then gave *trans*-diacid (**10**) (1.55 g, 52 %); m.p. *ca.* 225°C (decomp.) (rapid heating). Found: C, 75.68; H, 5.95. $C_{22}H_{20}O_4$ (348.4) Calcd. C, 75.84; H, 5.79 %. IR ν_{max} (Nujol) 1693 cm^{-1} (CO). NMR_H 270 MHz; $(CDCl_3)_2CO$ 7.1-6.75 (10H, m; Ar-H); 3.64 (2H, s; H_5) and H_6), 1.84 ppm (6H, s; 2 × Me).

1,4-Dimethyl-7-oxo-2,3-diphenylbicyclo[2.2.1]hept-2-ene-*trans*-5,6-dicarbonitrile (13): The mixture of hemicyclone dimer (**6**) (11.74 g) and fumaronitrile (3.52 g) in toluene (50 mL) was heated under reflux for 24 h. The solvent was removed under reduced pressure and recrystallization of the residue from methanol yielded the carbonyl-bridged dinitrile (**13**) (8.14 g, 53 %); m.p 228.5-230°C. Found: C, 81.84; H, 5.31; N, 8.27. $C_{23}H_{18}N_2O$ (338.4) Calcd. C, 81.63; H, 5.36; N, 8.28 %. IR ν_{max} (Nujol), 2243, (CN), 1787 cm^{-1} (bridged CO). MS m/z 338 (M), 310 (M-CO; base peak). NMR_H (270 MHz $CDCl_3$) 7.3-6.95 (10H, m; Ar-H), 3.35 and 3.13 (2H, AB q; *J* 5.5 Hz; H_5 and H_6), 1.52 (3H, s; Me) 1.48 p.p.m (3H, s; Me).

2,5-Di(methoxycarbonyl)-3,4-diphenylcyclopentadienone (16): The cyclone (**16**) was prepared as described by White[7]; m.p. 164-165°C (lit.[7] 162-164°C).

Tetramethyl-7-oxo-2,3-diphenylbicyclo-2.2.1-hept-2-ene-1,4-*trans*-5,6-tetracarboxylate (17): Reaction of the diester-cyclone (**16**) (1.00 g) with dimethyl fumarate (0.41 g) in reflexing toluene (9 mL) for 19.5 h, followed by cooling of the solution, gave a crystalline solid which was filtered off and recrystallized from dichloromethane-methanol to afford the adduct (**17**) (0.48 g, 34 %); m.p. *ca.* 220°C (decomp.). Found: C, 65.79; H, 4.95 $C_{27}H_{24}O_9$ (492.5) Calcd. C, 65.85; H, 4.91%. NMR_H (270 MHZ; CD_2Cl_2) 7.3-6.95 (10H, m; Ar-H), 3.99 and 3.60 (2H, Abq, *J* 5Hz; H_4 and H_6), 3.74 (3H, s; Me), 3.72 (3H, s; Me), 3.76 (3H, s; Me), 3.59 ppm (3H, s; Me).

1,3-Dimethylcyclopenta-1-phenanthren-2-one (phenmecyclone) dimer (21): This was prepared as described by Jones[8]; m.p. 314-316°C (decomp) lit. 314-316°C (decomp).

Adduct (22) of phenmecyclone (20) and dimethyl fumarate: The known[8] carbonyl-bridged adduct (**22**) was prepared from phenmecyclone dimer (**21**) and dimethyl fumarate in refluxing toluene (25 h). After removal of the solvent under reduced pressure, the residue was chromotographed on silica (Merck 60 H), using light petroleum (b.p. 60-80°C) ethyl acetate (3:1) as eluent, Yield 86 %; m.p. 215-216°C (lit[8]. 214-217°C). IR ν_{max} (Nujol) 1775 (bridged CO), 1721 cm^{-1} (ester CO). NMR_H (270 MHz $CDCl_3$) 8.8-8.7 (2H, m; Ar-H), 7.7-7.55 (4H, m; Ar-H), 3.81 (3H, s; CO_2Me), 3.56 and 3.28 (2H, AB q; *J* 5 Hz; methine protons), 3.33 (3H, s; CO_2Me), 2.26 (3H, s; Me), 1.98 ppm (3H, s; Me).

Adduct (24) of phenmecyclone (20) and meleic anhydride: Reaction of phenmecyclone dimer (**21**) (1.00 g) with maleic anhydride (0.80 g) in refluxing dry benzene (10 mL) for 0.5 h gave the crystalline adduct, which was filtered off, washed with dry light petroleum (b.p. 40-60°C) and recrystallized twice from acetic anhydride. It was finally washed with dry benzene and then light petroleum and dried. Yield 0.92 g (67 %); m.p. 317-319°C. Found: C, 77.39; H, 4.56. $C_{23}H_{16}O_4$ (356.4) Calcd. C, 77.51; H, 4.53 %. IR ν_{max} (Nujol) 1859 and 1774 (anhydride CO), 1780 cm^{-1} (bridge CO). MS m/z 356 (M), 258 (M) (maleic anhydride; base peak). NMR_H 270 MHz; $(CD_3)_2SO$ 9.0-8.85 (2H, m; Ar-H), 8.4-8.25 (2H, m; Ar-H), 7.8-7.6 (4H, m; Ar-H), 4.03 (2H, s; methine protons), 2.16 ppm (6H, s; 2 × Me).

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