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# Cycloaddition of Bis-cyclohexa-2,4dienones: Synthesis of Novel Carbocycles

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### CYCLOADDITION OF BIS-CYCLOHEXA-2,4-DIENONES: SYNTHESIS OF NOVEL CARBOCYCLES

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#### **GRAPHICAL ABSTRACT**



**Abstract** Syntheses of novel carbocycles (4) and (5) based on cycloaddition of bis-cyclohexa-2,4-dienone (3) and cyclopentadiene is reported. An improved method for the preparation of tetramethyl bisphenol-F(2), a precursor of bis-cyclohexa-2,4-dienone (3), is also presented.

**Keywords** Bis(3,5-dimethyl-3-acetoxy-4-oxocyclohexa-1,5-dienyl)methane; bis(3,5-dimethyl-4-hydroxyphenyl)methane; cycloaddition

#### INTRODUCTION

Phenolic compounds, both from natural and synthetic origins, constitute an important family of antioxidants.<sup>[1]</sup> Bisphenols can be broadly classified as two phenolic units connected to each other by a methylene or similar group. Bisphenols find numerous applications in industries such as food packaging, molding, casting, coating, encapsulating, and adhesives.<sup>[2,3]</sup> Interestingly, they have also been employed in the design of supramolecular hosts.<sup>[4]</sup> Literature records a number of methods for their synthesis from phenols, using a variety of catalysts such as mineral acids,<sup>[5]</sup> mesoporous silica,<sup>[6]</sup> solid acid catalysts,<sup>[7]</sup> zeolites,<sup>[3,8]</sup> nonzeolite molecular sieves,<sup>[9]</sup> acid pretreated montmorillonite clays,<sup>[10]</sup> cation-exchange resins,<sup>[11,12]</sup> and bases.<sup>[13]</sup>

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There are several reports of oxidation of phenols to corresponding cyclohexa-2, 4-dienones and subsequent cycloaddition reactions.<sup>[14–16]</sup> The adducts from such cycloadditions have been exploited for the development of new routes toward synthesis of natural products possessing interesting biological profiles.<sup>[17,18]</sup>

Our interest in this area prompted us to explore cycloaddition of biscyclohexadienone of type (3) with cyclopentadiene to access novel molecular architectures such as that in adduct 4, which is hitherto unknown in the literature. Our efforts to prepare carbocycle 4, from 3 are described here.

We reported previously a preparation of tetramethyl bisphenol-F (2) from 2,6-dimethyl phenol (1) by heating it under reflux in the presence NaOH.<sup>[13]</sup> We now report an improvised procedure for an expedient preparation of 2 using aqueous HCl (36%). The oxidation of bisphenol 2 to corresponding bis-cyclohexadienone 3 was not known in the literature prior to our own report<sup>[13]</sup> and to the best of our knowledge there has been no report on the cycloaddition of biscyclohexadienones. We also found during this study that the oxidative acetylation of tetramethyl bisphenol 2 to biscyclohexadienone 3 using lead tetra-acetate may be accomplished in toluene instead of benzene.<sup>[13]</sup>

Cyclohexadienones are reactive intermediates that easily undergo dimerization.<sup>[15]</sup> In a similar manner, bis-cyclohexadienone **3**, containing two cyclohexadienone moieties, could also be expected to undergo intramolecular cycloaddition with either  $\alpha,\beta$ - or  $\gamma,\delta$ -double bonds to give two different products **6** and **7** (Fig. 1).

In principle the reaction of cyclopentadiene and bis-cyclohexadienone 3 could give rise to 11 major isomers (6–14) (Fig. 1) (4 and 5 in Scheme 2), in addition to their corresponding stereoisomers.

Structures 8 and 9 may result from cycloaddition of cyclopentadiene as  $4\pi$  and 3 as  $2\pi$  partner. Similarly 8 and 9 could undergo subsequent intramolecular cycloaddition to generate 10 and 11 respectively. On the other hand, the two cyclohexadienone units in 3 could also participate independently in cycloaddition with cyclopentadiene to form 12 and 13 involving participation of  $\alpha,\beta$ - or  $\gamma,\delta$ -double bonds. While 4 and 5 could be formed from cycloaddition of 3 behaving as a  $4\pi$  component and cyclopentadiene as  $2\pi$  component with addition of respectively one and two molecules of cyclopentadiene, the structure 5 could also give rise to 14 via intramolecular cycloaddition of the remaining cyclohexadienone unit with the double bond in the cyclopentene ring.

Thus the reaction of bis-cyclohexadienone **3** and cyclopentadiene could in principle give rise to a number of products. However, we obtained only adducts **4** and **5** from the reaction. The adduct **4** was also obtained alternatively by heating **5** with cyclopentadiene in toluene at  $90 \,^{\circ}$ C for 28 h.

The structures of **4** and **5** were readily discernible through their spectral and analytical data. The <sup>1</sup>H NMR spectrum of adduct **5** exhibited singlets at  $\delta$  1.30, 1.53, 1.73, and 1.98 for protons on methyl groups and singlet at  $\delta$  2.07 for protons on acetate methyl groups. It also showed a doublet at  $\delta$  2.00, a multiplet at  $\delta$  2.51, and a doublet of doublet at  $\delta$  3.66 for protons on the methine group, along with two multiplets at  $\delta$  2.76 and 2.91 and a singlet at  $\delta$  3.02 for protons on methylene groups in addition to singlets at  $\delta$  5.26, 5.49, and 6.52, a multiplet at  $\delta$  5.72, and a doublet of doublet at  $\delta$  5.89 for olefinic protons. Its <sup>13</sup>C NMR spectrum displayed signals at  $\delta$  15.38, 15.80, 20.04, 20.06, 22.74, and 24.26 for six methyl carbons and



Figure 1. Structures of possible products resulting from cycloaddition of cyclopentadiene and bis-cyclohexadienone 3.

signals at  $\delta$  35.27, 38.39, and 43.32 for three methine carbons with  $\delta$  48.92 and 51.90 for two methylene carbons,  $\delta$  53.96 for a quaternary carbon, and  $\delta$  78.19 and 80.75 for two carbons attached with the acetate group. Similarly, signals at  $\delta$  127.71, 128.55, 129.96, 133.68, 134.18, 136.56, 139.7, and 142.75 for eight olefinic carbons in addition to characteristic signals at  $\delta$  169.34, 170.28, 198.61, and 206.85 for acetate and ketonic carbonyl carbons were also observed. The structure of **5** was further proved by its single-crystal x-ray analysis (Fig. 2), which clearly displayed the *endo* stereochemistry of the adduct with a free cyclohexadienone unit.

Because the structure of adduct **4** is highly symmetrical, its <sup>1</sup>H, <sup>13</sup>C, 2D <sup>1</sup>H <sup>1</sup>H correlation spectroscopic (COSY), <sup>1</sup>H <sup>13</sup>C heteronuclear single-quantum coherence (HSQC) NMR spectra showed only half the number of signals of total protons





and carbons. Thus the <sup>1</sup>H NMR spectrum of **4** exhibited singlets at  $\delta$  1.29, 1.51, and 2.05 for protons on methyl groups and a doublet at  $\delta$  1.98, a multiplet at  $\delta$  2.52, and a doublet of doublet at  $\delta$  3.64 for protons on methine groups, along with multiplets at  $\delta$  2.72 and 2.88 and a singlet at  $\delta$  3.16 for protons of methylene groups. It also showed a singlet at  $\delta$  5.35, a doublet of doublet at  $\delta$  5.51, and a multiplet  $\delta$  5.69 for olefinic protons. The <sup>13</sup>C NMR spectrum was also consistent with proposed structure, which exhibited resonances at  $\delta$  15.96, 20.56, and 22.76 for methyl carbons and signals at  $\delta$ 



Figure 2. ORTEP representation of carbocycle (5). (Figure is provided in color online.)





35.34, 38.36, and 52.29 for three methine carbons with  $\delta$  43.61 and 53.76 for two methylene carbons. It also displayed resonances at  $\delta$  51.39 and 88.68 for a quaternary carbon and a carbon attached with acetate group respectively. Similarly it should signals



Figure 4. <sup>1</sup>H <sup>13</sup>C HSQC NMR of bis-adduct (4).

at 126.68, 128.69, 134.59, and 141.27 for olefinic carbons and characteristic signals at  $\delta$  170.27 and 206.70 for acetate and ketonic carbonyl carbons. The structure deduced from <sup>1</sup>H and <sup>13</sup>C NMR was further proved by 2D <sup>1</sup>H <sup>1</sup>H COSY and <sup>1</sup>H <sup>13</sup>C HSQC NMR.

In <sup>1</sup>H <sup>1</sup>H COSY NMR spectrum of adduct 4 exhibited signals at  $\delta$  1.29, 1.51, and 2.05, having no corresponding off-diagonal peaks to represent the three methyl groups. Other diagonal peaks at  $\delta$  1.98, 2.52, and 3.64 having one, four, and two corresponding off-diagonal peaks represent three protons of methine groups. It also exhibited diagonal peaks at  $\delta$  2.72 and 2.88 with three corresponding off-diagonal peaks for each for the two protons of methylene group of the cyclopentadiene moiety. The diagonal peak at  $\delta$  3.16 having no off-diagonal peak represents the central methylene group. The diagonal peak at  $\delta$  5.35 has no corresponding off-diagonal peak and diagonal peaks at  $\delta$  5.51 and 5.69 have two and three corresponding off-diagonal peaks and display three olefinic protons.

The <sup>1</sup>H  $^{13}$ C HSQC NMR spectrum displayed cross peaks for proton and carbon at  $\delta$  (1.29, 15.96), (1.51, 20.56), and (2.05, 22.76) for three methyl groups and  $\delta$  (1.98, 35.34), (2.52, 38.36), and (3.64, 52.29) for three methine groups with  $\delta$  (2.72, 53.76) and (2.88, 53.76) for methylene group of cyclopentene ring. It also showed resonance at  $\delta$  (3.16, 43.61) for the central methylene group along with characteristic resonance at  $\delta$  (5.35, 126.68), (5.51, 128.69), and (5.69, 134.59) for olefinics. The quaternary carbon, carbon attached to acetate group, acetate carbonyl, and keto carbon did not display any signals because they have no protons on corresponding carbon atoms.

#### **EXPERIMENTAL**

Infrared (IR) spectra were recorded on a Perkin-Elmer PC-16 Fourier transform (FT) IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker-400 FT NMR spectrometer using CDCl<sub>3</sub> as solvent containing tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a Shimadzu QP-5050 mass spectrometer. 2,6-Dimethyl phenol and dicyclopentadiene were purchased from Sigma Aldrich. Freshly cracked cyclopentadiene was used. Hydrochloric acid (36% w/v) was purchased from Merck. All other solvents were purchased from Merck and distilled prior to use.

Column chromatography was performed using Acme's silica gel (60–120 mesh) and the elution was done using light petroleum and ethyl acetate mixtures. Thin-layer chromatography (TLC) was performed using Acme's silica gel, and spots were visualized in iodine vapor. The yields (%) are reported based the recovery of the starting material after column chromatography.

#### **Tetramethyl Bisphenol-F (2)**

Hydrochloric acid (10 ml, 36% w/v) was added dropwise over a period of 15 min to a stirred solution of 2,6-dimethyl phenol (1) (10 g, 0.082 mol) and formaldehyde (15 ml, 37% w/v, 0.185 mol) in light petroleum (60:80) (40 ml) at room temperature (~27 °C) and was further stirred for 5 h. The reaction mixture was diluted 10 times its volume with water and was further stirred for 15 min. The solid thus obtained was filtered on a Buchner funnel, washed thoroughly with water, and dried at 85–90 °C under vacuum to give a solid, which was chromatographed on a column of silica gel. Elution of the column with light petroleum/ethyl acetate (90:10) afforded bisphenol **2** as a white crystalline solid (10.5 g, 93%). Its identity was confirmed by comparison of its mp, IR, and <sup>1</sup>H and <sup>13</sup>C NMR with the reported data.<sup>[13]</sup>

#### Biscyclohexadienone (3) in Toluene (Vide Supra)

Lead tetra-acetate (2.66 g, 0.006 mol) was added to a solution of tetramethyl bisphenol-F (**2**) (0.5 g, 0.002 mol) in dry toluene (30 ml) in portions with continuous stirring over a period of 15 min. The reaction mixture was stirred at room temperature ( $\sim$ 27 °C) for 1 h, after which it was diluted with ethyl acetate (150 ml) and stirred further for 15 min. Removal of the residue by filtration and concentration of the filtrate under reduced pressure furnished a pale yellow liquid, which was chromatographed over a column of silica gel. Elution of the column with light petroleum and ethyl acetate (95:5) gave **3** as a light yellow crystalline solid (45%). Comparison of its mp, IR, and <sup>1</sup>H and <sup>13</sup>C NMR with the reported data proved its identity.<sup>[13]</sup>

#### Adducts 4 and 5

A solution of bis-cyclohexadienone (3) (4.0 g, 0.010 mol) in dry toluene (40 ml) was heated to 90 °C in an oil bath while circulating cooled water (10–15 °C) and freshly cracked cyclopentadiene (23 ml) was added to it in portions (1 ml every 2 h). The reaction was continued for 46 h, after which it was allowed to cool to room temperature ( $\sim 27 \,^{\circ}$ C). The solvent was removed under reduced pressure to furnish a thick yellow liquid, which was chromatographed over a column of silica gel. Elution of the column with light petroleum/ethyl acetate (90:10) afforded the bis-adduct (4) as a white solid (0.5 g, 21%), mp 240 °C. IR (KBr) 3040, 1739, 1732, 1637, 1440, 1367, and 1234 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 1.29 (s, 6H, 2CH<sub>3</sub>), 1.51 (s, 6H,  $2CH_3$ , 1.98 (d, 2H, J = 4.8 Hz methine), 2.05 (s, 6H, COOCH<sub>3</sub>), 2.52 (m, 2H, methine), 2.72 (m, 2H, methylene), 2.88 (m, 2H, methylene), 3.16 (s, 2H, methylene), 3.64 (dd, 2H, J = 6.0 Hz, 2.0 Hz, methine), 5.35 (s, 2H), 5.51 (dd, 2H, J = 5.6 Hz, 2.4 Hz),5.69 (m, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>): 15.96, 20.56, 22.76 (3C methyl), 35.34, 38.36, 52.29 (3C methine), 43.61, 53.76 (2C, methylene), 51.86 (1C quaternary carbon), 80.86 (1C attached with acetate), 126.68, 128.89, 134.59, 141.27 (4C, olefinic) 170.27 (C=O, OCOCH<sub>3</sub>) 206.65 (C=O, ketone). HRMS (EI): m/z calculated for C<sub>31</sub>H<sub>36</sub>O<sub>6</sub>: 504.61; found 504.250 (M<sup>+</sup>). Analysis calculated for C<sub>31</sub>H<sub>36</sub>O<sub>6</sub> (504): C, 73.80; H, 7.14%. Found: C, 73.86; H, 7.34%.

Further elution of the column with light petroleum/ethyl acetate (85:15) afforded the monoadduct **5** as a white crystalline solid (1.5 g, 51%), mp 178 °C, IR (KBr): 3040, 1739, 1732, 1685, 1447, 1377, and  $1260 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 1.30 (s, 3H, CH<sub>3</sub>), 1.53 (s, 3H, CH<sub>3</sub>), 1.73 (s, 3H, CH<sub>3</sub>), 1.98 (s, 3H, CH<sub>3</sub>), 2.00 (d, 1H, J = 3.6 Hz, methine), 2.07 (s, 6H, acetate methyl), 2.51 (m, 1H, methine), 2.76 (m, 1H, methylene), 2.91 (m, 1H, methylene), 3.02 (s, 2H, methylene), 3.66 (dd, 1H, J = 4.4 Hz, 2.0 Hz, methine), 5.26 (s, 1H, olefinic), 5.49 (s, 1H, olefinic), 5.72 (m, 1H), 5.89 (dd, 1H, J = 6.0 Hz, 2.4 Hz, olefinic proton of cyclopentene ring), 6.52 (s, 1H, olefinic). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 15.38, 15.80, 20.04, 20.06 (4C methyl), 22.74, 24.26 (2C acetate methyl), 35.27, 38.39, 43.32 (3C, methine), 48.92 (1C

quaternary carbon), 51.90, 53.96 (2C, methylene) 78.28, 80.75 (2C, attached with acetate), 127.71, 128.55, 129.96, 133.68, 134.18, 136.56, 139.7, 142.75 (8C, olefinic), 169.34, 170.28 (2C, C=O OCOCH<sub>3</sub>), 198.61, 206.85 (2C, C=O ketone). HRMS (EI): m/z calculated for C<sub>26</sub>H<sub>30</sub>O<sub>6</sub> 438.51; found 438.20 (M<sup>+</sup>). Analysis calculated for C<sub>26</sub>H<sub>30</sub>O<sub>6</sub>(438): C, 71.23; H, 6.84%. Found: C, 71.61; H, 7.02%. ORTEP diagram of single crystal analysis is shown in Fig. 2.

#### Conversion of 5 into 4

A solution of the adduct 5 (2 g, 0.004 mol) in dry toluene (20 ml) was heated to 90 °C in an oil bath while circulating cooled water (10–15 °C), and freshly cracked cyclopentadiene (14 ml) was added to it in portions (1 ml every 2 h). The reaction was continued for 28 h, after which it was allowed to cool to room temperature. The solvent was removed under reduced pressure to give a thick yellow liquid, which was chromatographed over silica elution with light petroleum/ethyl acetate (90:10) to afford adduct 4 (0.5 g, 37%), mp 240 °C. Its identity was confirmed by completely matched mp, IR, and <sup>1</sup>H and <sup>13</sup>C NMR data with compound 4 mentioned previously.

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