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Generation and [4+2] cycloaddition of 1,6-methano[10]-annulene-3,4-quinodimethane: a novel synthesis of dimethyl 1,6-methanobenzo[3,4-*a*][10]annulene-13,14-dicarboxylate†

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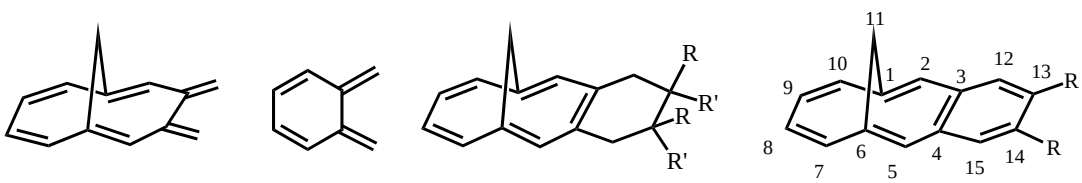
Abstract—A new quinodimethane, 1,6-methano[10]annulene-3,4-quinodimethane (**1**), was generated and trapped by the Diels–Alder reactions with various dienophiles to provide 1,6-methano[10]annelenes **3** fused with a six-membered ring at the 3,4-positions, one of which was derived to a benzene ring analogue **4**. © 2001 Published by Elsevier Science Ltd.

The reactive *o*-quinodimethane and its derivatives bearing a *cis*-diene moiety have been widely investigated from the theoretical and synthetic viewpoints, especially for the preparation of ring-fused systems.[1a,1b] While considerable literature on the chemistry of 1,6-methano[10]annulenes has been accumulated,[2] bridged annulene-*o*-quinodimethane compounds have remained virtually unknown so far because of lack of proper synthetic methods. We report here the first generation of 1,6-methano[10]annulene-3,4-quinodimethane (**1**) as an unstable intermediate, the formation of which was revealed by trapping experiments of the Diels–Alder reactions with various dienophiles, providing a practical preparation of the six-membered ring-fused [10]annulenes **3**, one of which was derived to a benzene ring-fused bridged [10]annulene **4** (Fig. 1).

In our synthetic strategy, diethyl 1,6-methano[10]annulene-3,4-dicarboxylate (**10**) first synthesized by Vogel and co-workers[3] was chosen as a potential key compound for the synthesis of the titled compound. Since there were some disadvantages in their method for large-scale preparation such as selective introduction of a double bond and the many tedious steps involved, an alternative method was developed, as shown in Scheme 1. The Wittig reaction of 1,6-diformylcycloheptatriene (**5**) with 5 equiv. of ethyl (triphenylphosphoranylidene)acetate in benzene at reflux for 6 h gave diester **6** in 98% yield. Then the reaction of **6** with one equiv. of bromine in the presence of an excess amount of triethylamine at 0°C for 2 h gave **8** in 94% yield, in which the bromination to one of the α,β-unsaturated double bonds to give **7** and succes-



1 **2** **3** **4**

Figure 1.

Keywords: *ortho* quinodimethane; 1,6-methano[10]annulene-3,4-quinodimethane; Diels–Alder reaction.

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† Dedicated to Professor Dr. R. C. Neidelein on the occasion of his 65th birthday.

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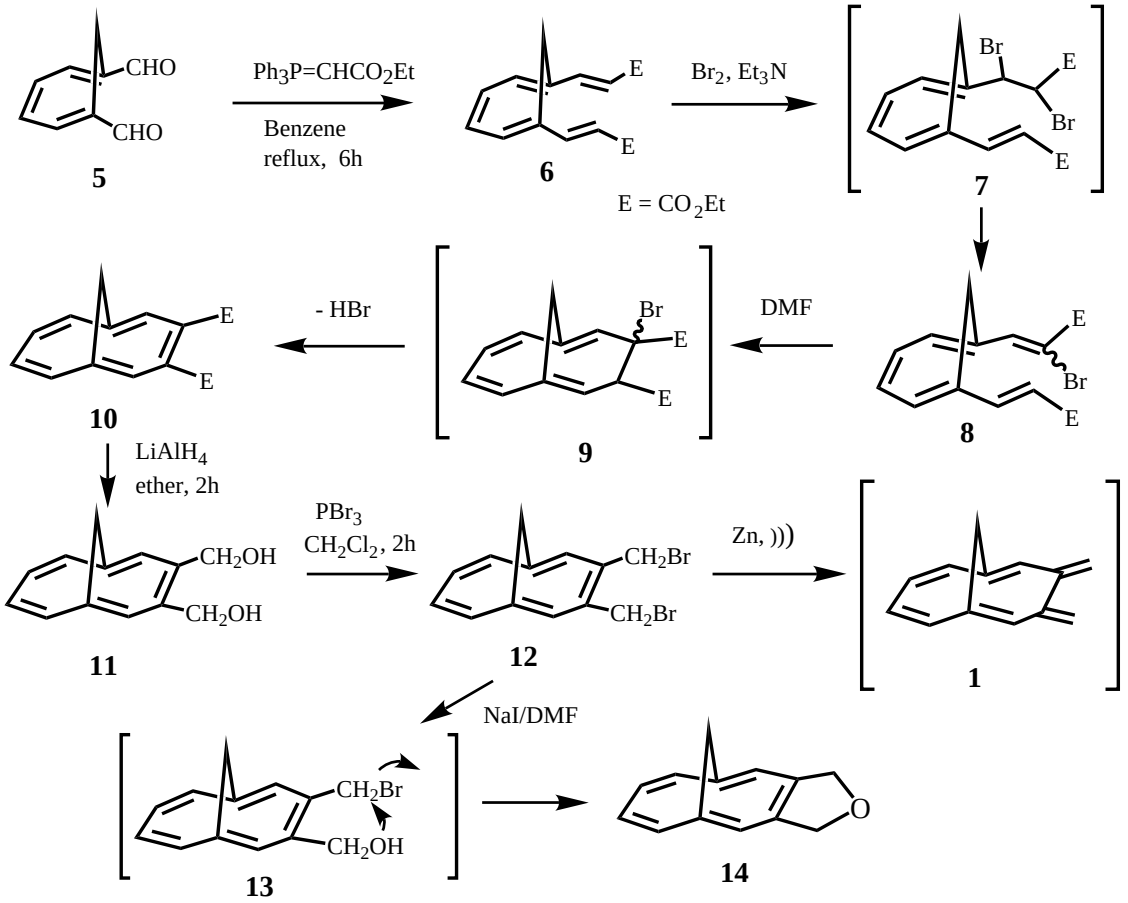
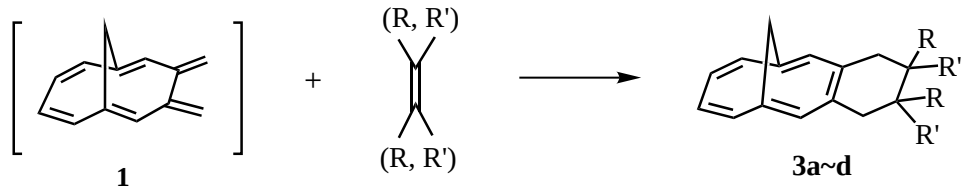


Scheme 1.

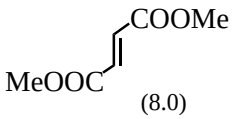
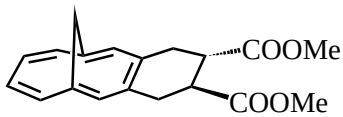
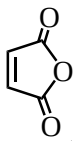
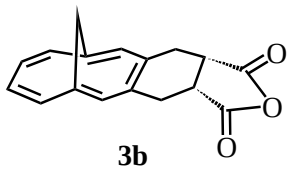
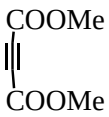
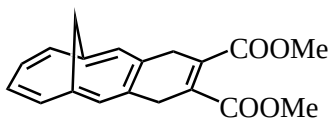
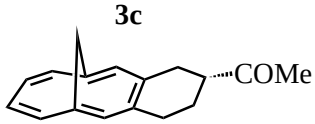
sive dehydrobromination proceed in one-pot. And then, by following Vogel's method, the treatment of **8** in DMF at 150°C for 30 min gave **10** in 87% yield.

The reduction of diesters **10** with $LiAlH_4$ in dry ether gave diol **11** as colorless needles in over 90% yield. Treatment of **11** with PBr_3 in dichloromethane under ice cooling gave dibromide **12** as yellow needles in 75% yield. The debromination of **12** was examined by two methods. First, treatment of **12** by using zinc powder under the irradiation of ultrasound at 20°C for 6 h only gave an unidentified complex mixture. Secondly, the reaction of **12** by using NaI in DMF at 80°C for 3 h gave 2,5-dihydrofuran fused [10]annulene **14** in 87% yield. The formation of **14** may be explained as follows. First, one bromine on the methylene carbon was substituted by water originated from a crystal of NaI to form **13**, and then the oxygen on the hydroxyl group attacks another methylene carbon to give **14**. Several efforts for the isolation and direct detection of **1** by ^{1}H NMR spectroscopic measurements at −50°C immediately after the reaction were unsuccessful because of its instability. The reaction was then conducted in the presence of a little excess equivalent of various dienophiles such as dimethyl fumalate, maleic anhydride, dimethyl acetylenedicarboxylate, and methylvinylketone by the supersonic method with zinc mentioned above to give the corresponding cycloadducts **3a**–**d**, respectively. The results are shown in Table 1, manifesting the generation of **1** in which the *cis*-diene moiety easily reacted with an excess amount of dienophiles to form six-membered ring-fused bridged [10]annulenes in proper yields. The spectral data of **3a** and **3b**, respectively, showed a sole product, which are plausibly *end* adducts, because the dienophiles could approach **4** from the less hindered *endo* side. Furthermore, treatment of adduct **3c** with Pd–C in diphenyl ether at 200°C for 1 h gave a new entry of 1,6-methanobenzo[3,4-*a*][10]annulene **4** in 86% yield. The ^{1}H NMR chemical shifts of the bridge protons were observed at δ 1.10 and −0.31 ppm (acetone-d_6) showing a somewhat greater ring current of **4** than that of the 2,3-fused isomer (δ 1.38 and −0.06 ppm).[4] Interestingly, the ^{1}H NMR spectrum of **4**[5] completely changed on standing it in an acetone-d_6 solution for 2 days. From the resulted solution, **15** was isolated quantitatively and characterized. The peroxidation of **4** may occur with singlet oxygen generated by triplet oxygen and **4** [λ_{max} (MeOH) = 351 nm ($\log \varepsilon = 3.70$)] which worked as a sensitizer, because it does not proceed in the dark. The oxidation of **3c** with 3.5 equiv. of DDQ in benzene at reflux for 2 h gave adduct **16** [mp >280°C] in 45% yield. In this reaction, **3c** was dehydrogenated first to give **4**, to which DDQ was then added at the 2,5-positions.

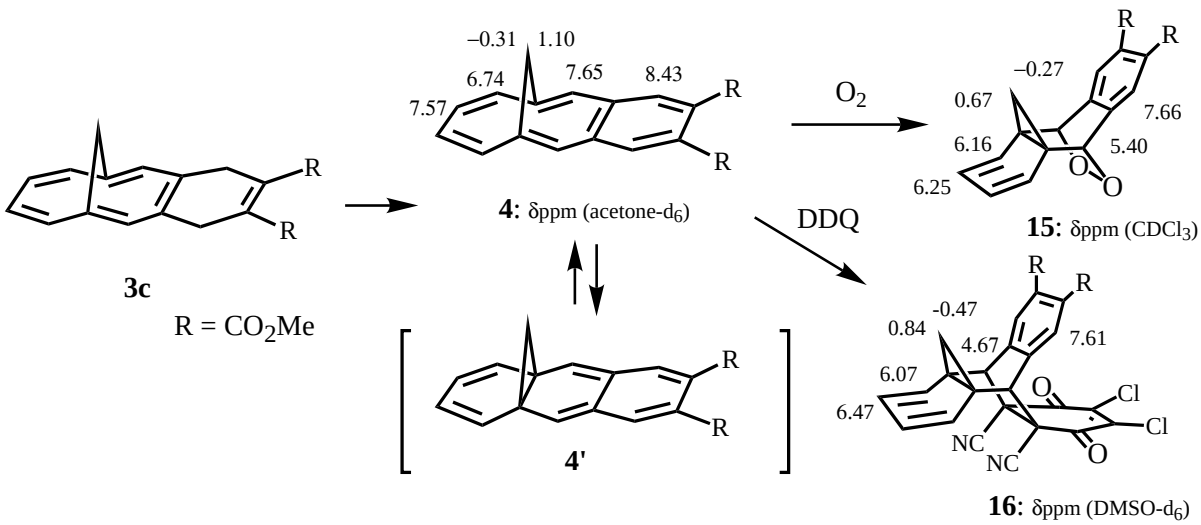
Table 1. The Diels–Alder reactions of **1** with dienophiles



1 **3a~d**

Entry	Dienophile (equiv)	Product	Yield (%)	Physical properties: IR (C=O) & ^{1}HNMR (bridged methylene protons)
1	 (8.0)	 **3a**	59	Yellow oil, ν=1728(CO) δppm= –0.29, –0.49.
2	 (3.5)	 **3b**	56	Colorless needles, ν=1771(CO) δppm= –0.36, –0.49.
3	 (10.0)	 **3c**	70	Pale yellow oil, ν=1732(CO) δppm= –0.15, –0.44.
4	 (10.0)	 **3d**	54	Pale yellow oil, ν=1713(CO) δppm= –0.20, –0.44.

The stereochemistry of *anti*-adducts **15** and **16** were tentatively assigned, as depicted in Scheme 2.[3] This high reactivity of the 2,5-positions of **4** was due to either the unstable array of double bonds containing the *exo*-dimethylene cycloheptadiene moiety of **4** or the quinodimethane moiety of **4′**, as shown in Scheme 2.



Scheme 2.

Acknowledgements

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5. Physical properties of **12** and **4**.
   Compound **12**: Pale yellow needles, mp 104–106°C, IR (KBr) 3008w, 2958m, 1444m, 1212s, 1203s, 1152m, 922w, 811m, 712s, 592s cm^{-1}; ^1H NMR ($CDCl_3$–TMS) δ 7.47 (s, 2H), 7.37 (m, 2H), 7.23 (m, 2H), 5.00 (d, $J=10.5$ Hz, 2H), 4.83 (d, $J=10.5$ Hz, 2H), −0.11 (d, $J=8.8$ Hz, 1H), −0.17 (d, $J=8.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$–TMS) δ 133.7, 132.0, 129.1, 126.8, 112.9, 35.0, 34.9; MS m/z 330, 328, 326 (M^+, 2.4, 4.9, 2.6%), 249 (45), 247 (46), 167 (100), 152 (62); anal. found: C, 47.68; H, 3.64%. Calcd for $C_{13}H_{12}Br_2$: C, 47.60; H, 3.69%.
   Compound **4**: Pale yellow oil, IR (film) 3008w, 1732s, 1488m, 12776s, 1234s, 1128m, 1048m cm^{-1}; ^1H NMR (acetone-d_6–TMS) δ 8.43 (s, 2H), 7.57 (m, 2H), 7.65 (s, 2H), 6.74 (m, 2H), 3.99 (s, 6H), 1.10 (d, $J=9.6$ Hz, 1H), −0.31 (d, $J=9.6$ Hz, 1H); ^{13}C NMR (acetone-d_6–TMS) δ 168.8, 136.3, 133.8, 133.6, 129.0, 128.4, 127.1, 125.6, 52.8, 32.5; MS m/z 308 (M^+, 49%), 178 (100); HRMS observed, 308.1071; calcd for $C_{19}H_{16}O_4$: 308.1048.