Synthesis and Cycloaddition Reactions of Homoadamantano[4,5-*c*]cyclopentadienones. A Facile Route to [4,5]-Fused Homoadamantanobenzene Derivatives[1]

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2′,5′-Disubstituted homoadamantano[4,5-*c*]cyclopentadienones **4a–c** were obtained by base-catalyzed condensations of homoadamantane-4,5-dione with 3-pentanone, 1,3-diphenylacetone, and dimethyl 3-oxoglutarate. Diels–Alder reactions of **4a–c** with acetylenic dienophiles afforded the corresponding homoadamantanobenzene derivatives in moderate to good yields. The reactions of **4a–c** with phenyl vinyl sulfoxide and α-chloroacrylonitrile also gave homoadamantanobenzene derivatives after elimination and decarbonylation. The reaction of **4a** with 1,5-cyclooctadiene afforded the normal Diels–Alder adduct, which was converted to a double Diels–Alder product via decarbonylation followed by an intramolecular [4 + 2] cycloaddition. Reactions of **4a,b** with 4-phenyl-1,2,4-triazoline-3,5-dione gave Diels–Alder adducts, whereas **4c** did not react. Competitive experiments indicated that **4b** was only slightly less reactive than 3,4-dimethyl-2,5-diphenyl- and 2,3,4,5-tetraphenylcyclopentadienones in reactions with dimethyl acetylenedicarboxylate and methyl propiolate.

Benzannulation methodology has received considerable attention over the years because of its synthetic utility.[2] The [4 + 2] cycloaddition is one of the more effective methods, and several kinds of reactive dienes have been developed.[2a–c] The cyclopentadienone system is one of these reactive dienes because its Diels–Alder reactions with acetylenic dienophiles afford arene annulation products via a facile decarbonylation of the initial adducts.[3,4] However, synthetic applications seem to be limited to aromatic-substituted or aromatic-ring-fused cyclopentadienones, possibly because of the thermal instability of unsubstituted or alkyl-substituted cyclopentadienones.[5] We wished to investigate the synthesis of annulated homoadamantane derivatives by cycloaddition reactions of homoadamantane ring-fused cyclopentadienones because the bulky and rigid homoadamantane ring should stabilize the highly reactive dienone system. Benzohomoadamantane[6] has been prepared by transannular cyclization of benzobicyclo[3.3.2]decan-3,7-dione.[7] The Diels–Alder reaction of homoadamantanocyclopentadienones could provide a convenient and efficient route to such ring systems. We here report the synthesis of 2,5-disubstituted homoadamantano[4,5-*c*]cyclopentadienones **4** and their cycloaddition reactions with some dienophiles.

Scheme I

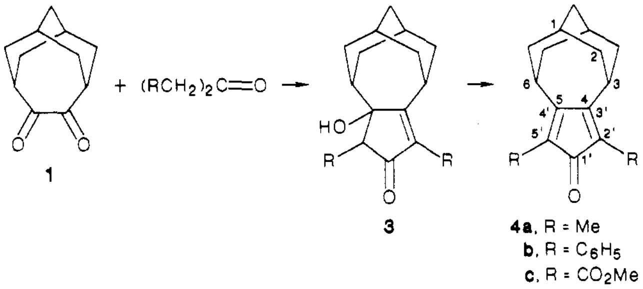

Table I. 2′,5′-Disubstituted Homoadamantano[4,5-*c*]cyclopentadienones[a]

compd	yield, %	mp, °C	^{1}H NMR, δ[b]
4a	50	134–135	1.63 (s, 6 H), 1.2–2.3 (m, 12 H), 3.05 (br s, 2 H)
4b	79	249–250	1.5–2.4 (m, 12 H), 3.3–3.7 (br s, 2 H), 7.1–7.7 (m, 10 H)
4c	50	217–218	1.4–2.4 (m, 12 H), 3.81 (s, 6 H), 3.8–4.2 (m, 2 H)

[a] Satisfactory C,H analytical data (±0.4%) were reported. [b] In $CDCl_3$ at 60 MHz.

Results and Discussion

Synthesis of 2′,5′-Disubstituted Homoadamantano[4,5-*c*]cyclopentadienones. Potassium hydroxide catalyzed condensation of homoadamantane-4,5-dione (**1**)[8] with 3-pentanone (**2a**) in ethanol at room temperature afforded cyclopentenolone **3a** in 80% yield.[9,10] Dehydration of **3a** with thionyl chloride in *n*-hexane afforded 2′,5′-dimethylhomoadamantano[4,5-*c*]cyclopentadienone **4a** in

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(1) Synthesis of Novel Carbo- and Heteropolycycles. 4. For 3; see: Eguchi, S.; Asai, K.; Takeuchi, H.; Sasaki, T. *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) For some recent examples, see (a) Snowden, R. L.; Wüst, M. *Tetrahedron Lett.* **1986**, *27*, 703 and ref 2 cited therein. (b) Narashimhan, N. S.; Gokhale, S. M. *J. Chem. Soc., Chem. Commun.* **1985**, 86. (c) Boger, D. L.; Mullican, M. D. *Tetrahedron Lett.* **1983**, *24*, 4939. (d) Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1672 and ref 4 cited therein. (e) Dieter, R. K.; Lin, Y. J. *Tetrahedron Lett.* **1985**, *26*, 39. (f) Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524. (g) Tius, M. A.; Thurkauf, A. *J. Org. Chem.* **1983**, (h) Boger, D.; Mullican, M. D. *J. Org. Chem.* **1980**, *45*, 5002 and ref 6 cited therein. For application to natural products synthesis, see: Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Products Synthesis Through Pericyclic Reactions*; American Chemical Society: Washington, D. C., 1983; Chapter 5.

(3) For a review, see Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, 261.

(4) For cycloaddition reactivity of some fused-ring cyclopentadienones, see (a) Harano, K.; Yasuda, M.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 4455. For benz[*f*]inden-2-one system, see: (c) Jones, D. W.; Pomfret, A.; Wife, R. L. *J. Chem. Soc., Chem. Commun.* **1980**, 463. (d) Jones, D. W.; McDonald, W. S. *Ibid.* **1980**, 417. (e) For 1-oxoindano[2,3-c]cyclopentadienones, see: Ried, W.; Freitag, D. *Chem. Ber.* **1966**, *99*, 2675. (f) For 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone, see: White, D. M. *J. Org. Chem.* **1974**, *39*, 1951.

(5) (a) For *tert*-butyl substituted cyclopentadienones, see: Garbisch, E. W. Jr.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785. For free cyclopentadienone, see: (b) Gaviña, F.; Costero, A. M.; Gil, P.; Luis, S. V. *ibid.* **1984**, *106*, 2077. (c) Gaviña, F.; Costero, A. M.; Gil, P.; Palazōn, B.; Luis, S. *ibid.* **1981**, *103*, 1797. (d) For bicyclic annulenones, see: Gaviña, F.; Costero, A. M.; Luis, S. *J. Org. Chem.* **1984**, *49*, 4616.

(6) (a) See ref 8 in Doddeck, H.; Klein, H. *Tetrahedron Lett.* **1976**, 1917. (b) 1,4′-Disubstituted benzohomoadamantane derivatives have been prepared recently via this route starting from 4-bromophthalaldehyde by Professor H. Klein (Ruhr University, Bochum, personal communication).

(7) Foehlisch, B.; Dukek, U.; Graessle, I.; Novotny, B.; Schupp, E.; Schwaiger, G.; Widnann, E. *Liebigs Ann. Chem.* **1973**, 1839.

(8) Schlatmann, J. L. M. A.; Korsloot, J. G.; Schut, J. *Tetrahedron* **1970**, *26*, 949.

(9) For the procedure, see: (a) Allen, C. F. H.; Van Allan, J. A. *J. Am. Chem. Soc.* **1950**, *72*, 5165. (b) Johnson, J. r.; Grummitt, O. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 806.

(10) For ring contractions of 1 under basic conditions, see: (a) Liggero, S. H.; Majerski, Z.; Schleyer, P. v. R.; Wolfe, A. P.; Redvanly, C. S.; Wynberg, H.; Boerma, J. A.; Strating, J. *J. Labeled Compd.* **1971**, *7*, 3. (b) Sasaki, T.; Eguchi, S.; Hattori, S. *Synthesis* **1975**, 718.

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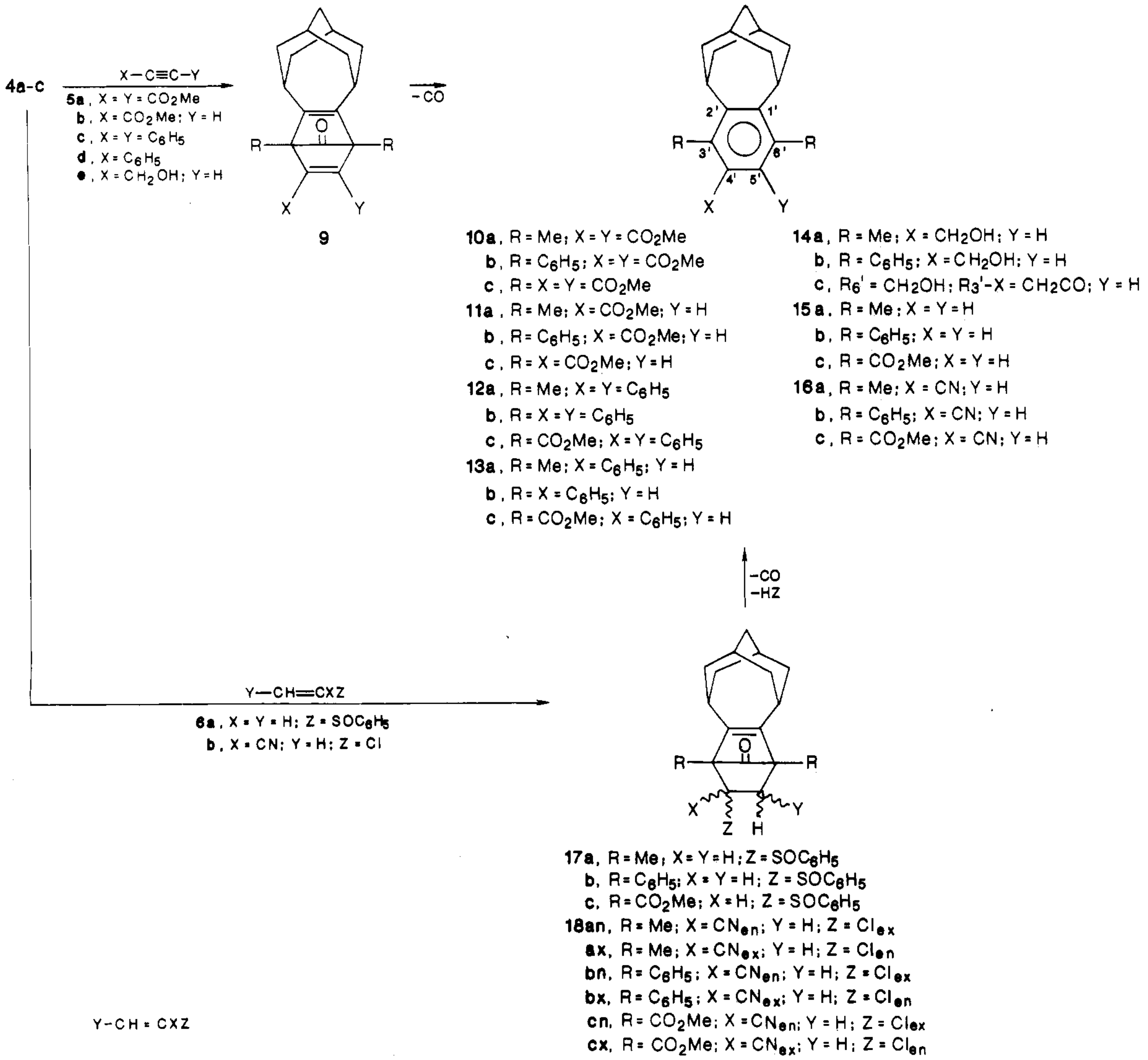
Scheme II



62% yield. Similar base-catalyzed condensations of **1** with 1,3-diphenylacetone (**2b**) and dimethyl 3-oxoglutarate (**2c**) afforded directly the corresponding cyclopentadienones **4b** (79%) and **4c** (50%) (Scheme I). The structures of **4a–c** were confirmed by spectral and analytical data (Table I). The moderate yield of **4c** may be due to its further condensation with **2c** to give the corresponding bicyclo[3.3.0]octane-3,7-dione derivative.[11] The condensation of **1** with acetone afforded only a complex mixture of products that were not characterized.

Compounds **4a–c** were all stable at room temperature.

Diels–Alder Reactions of 4 with Acetylenic Dienophiles. Reaction of **4a** with dimethyl acetylenedicarboxylate (DMAD, **5a**) at 70 °C for 5 h afforded 4′,5′-dimethoxycarbonyl-3′,6′-dimethylhomoadamantano[4,5-*a*]benzene[12] (**10a**) in 94% yield (Scheme II). Similarly, the reaction of **4b** with DMAD at 70 °C for 5 h afforded the corresponding diphenyl derivative **10b** in 93% yield, and the reaction of **4c** with DMAD at 70 °C for 31 h gave the tetramethoxycarbonyl derivative **10c** in 66% yield (Scheme II and Table II). The structures of these products were confirmed by spectral and analytical data (Table III). The results of Diels–Alder reactions of **4a–c** with methyl propiolate (**5b**), diphenylacetylene (**5c**), phenylacetylene (**5d**), and propargyl alcohol (**5e**) afforded the corresponding homoadamantanobenzene derivatives in moderate to good yields (Tables II and III). The reactions of **4a–c** with **5c** required vigorous conditions, and the yields were only moderate. The lower reactivity of **5c** is rationalized by steric hindrance to the approach of the dienophiles, as indicated by molecular models. The reaction of **4c** with propargyl alcohol afforded a lactonized product **14c**.

Diels–Alder Reactions of 4 with Olefinic Dienophiles and Heterodienophiles. The reactions of **4a–c** with phenyl vinyl sulfoxide (**6a**) at 140 °C afforded the corresponding homoadamantanobenzene derivatives **15a–c** in 65, 83, and 44% yields, respectively. The initial adducts **17a–c** were not isolated under our conditions (Table II), although an endo Diels–Alder adduct from 2,5-dimethyl-3,4-diphenylcyclopentadienone and **6a** is known to survive after heating in toluene for 24 h.[13]

The reaction of **4a** with α-chloroacrylonitrile (6b) at 150 °C for 0.5 h produced Diels–Alder adducts **18ax** (32%) and **18an** (56%).[14] Dehydrochlorination and decarbonylation[15]

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[11] Mitschka, R.; Oehldrich, J.; Takahashi, K.; Weiss, U.; Silverton, J. V.; Cook, J. M. *Tetrahedron* **1981**, *37*, 4521 and references cited therein.

[12] The numbering shown in **10–16** was used in this paper for convenience.

[13] Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.

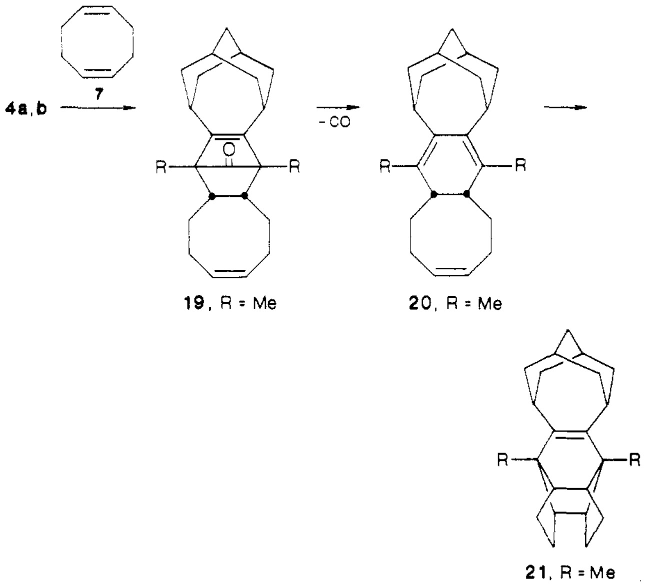
[14] An isomer with an endo CN is designated as **18an**, and an isomer with an exo CN corresponds to **18ax**. The stereochemical assignments should be considered as tentative.

Table II. Diels-Alder Reactions of 4a-c with Some Selected Dienophiles

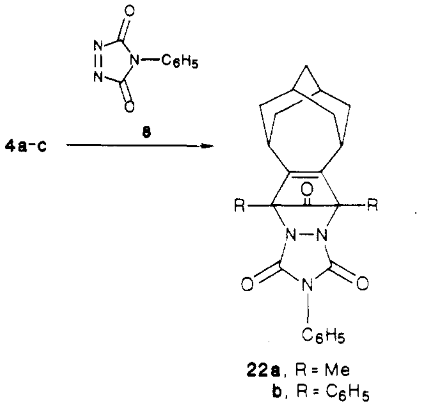
dienone	dienophiles (mol ratio)	solvent	temp, °C	time, h	product	yield, %	mp °C
4a	**5a** (2.3)	benzene	70	5	**10a**	94.1	165-166
4a	**5b** (2.0)	benzene	90	1	**11a**	74.1	99-100
4a	**5c** (1.2)	toluene	180	20	**12a**	60.5	227-229
4a	**5d** (3.0)	benzene	120	12	**13a**	62.8	126-128
4a	**5e** (9.0)	benzene	140	30	**14a**	73.5	117.5-118.5
4a	**6a** (1.7)	toluene	140	48	**15a**	65.0	101-102
4a	**6b** (2.0)	benzene	140	1	**18an**	56.0	121-123
					18ax	31.7	94-96
4a	**7** (15.0)	toluene[a]	140	900	**19**	58.0	127-129[e]
4a	**7** (20.1)	xylene[a,b]	180	156	**19**	20.3	127-129[e]
					21	17.7	125-128[e]
4a	**8** (2.0)	acetone	d	1	**22a**	84.2	165-166
4b	**5a** (2.3)	benzene	70	48	**10b**	93.0	256-258
4b	**5b** (2.0)	benzene	90	24	**11b**	31.0	136-137
4b	**5c** (1.2)	toluene	180	200	**12b**	48.0	>300[f]
4b	**5d** (1.2)	benzene	120	300	**13b**	79.0	84-86[e]
4b	**5e** (10.0)	benzene	140	158	**14b**	79.0	180-182[e]
4b	**6a** (1.7)	toluene	140	480	**15b**	83.0	100-102[e]
4b	**6b** (10.0)	benzene	140	5	**16b**	80.0	167-169
4b	**8** (1.2)	acetone[c]	d	1	**22b**	83.4	216-217
4c	**5a** (2.3)	benzene	70	31	**10c**	66.0	165-166
4c	**5b** (2.0)	benzene	90	24	**11c**	76.0	146-149[e]
4c	**5c** (1.2)	toluene	180	123	**12c**	42.0	246-247
4c	**5d** (1.2)	benzene	120	66	**13c**	50.0	111-113
4c	**5e** (10.0)	benzene	140	38	**14c**	78.0	216-217
4c	**6a** (1.7)	toluene	140	72	**15c**	44.0	78-80
4c	**6b** (10.0)	benzene	140	5	**16c**	61.0	142-143

[a] A small amount of hydroquinone was added. [b] An *o*-, *m*- and *p*-isomeric mixture, bp 138.5-141.5 °C. [c] Tetrahydrofuran was added in 1:1 ratio, v/v. [d] 20-25 °C. [e] From diethyl ether.

Scheme III



Scheme IV



of these adducts proceeded on heating at 230 °C without solvent to yield selectively cyanobenzene derivative **16a** in 76 and 86% yields, respectively (Scheme II). The dehydrochlorination-decarbonylation of the initial adducts **18b,c** from **4b,c** and **6b** occurred readily under the Diels-Alder conditions (140 °C, 5 h) to yield the corresponding diphenyl- (**16b**) and dimethoxycarbonylcyanobenzene (**16c**) derivatives in 83 and 61% yields, respectively (Table II).

In order to examine whether **4** would undergo inter- and intramolecular double Diels-Alder reactions,[4a,16] **4a** was heated with 1,5-cyclooctadiene (**7**) (15-fold excess) in toluene at 140 °C for 900 h, affording a normal Diels-Alder adduct **19** in 58% yield. Because decarbonylation did not occur under these conditions, the reaction was repeated under more vigorous conditions at 180 °C for 156 h, yielding a double Diels-Alder adduct **21** (18%) accompanied by **19** (20%). Thermal decomposition of neat **19** at 230 °C also afforded **21** (22%) accompanied by a little **4a** (3%) (Scheme III). The formation of **21** clearly demonstrates the intramolecular Diels-Alder reaction of a diene **20** produced by decarbonylation of **19**. The structure of **21** was confirmed by its ^{13}C NMR spectrum, which revealed 9 lines (2 s, 3 d, 3 t, and 1 q) (Experimental Section). The reaction of **4b** with **7** under similar conditions did not proceed, presumably because of steric hindrance.

The reactions of **4a,b** with equimolar amounts of the highly reactive heterodienophile 4-phenyl-1,2,4-triazo-

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[16] For examples of carbocycle synthesis by the double Diels-Alder reaction, see: Akhtar, I. A.; Fray, G. I.; Yarrow, J. M. *J. Chem. Soc.* (C) **1968**, 812 and ref 4a.

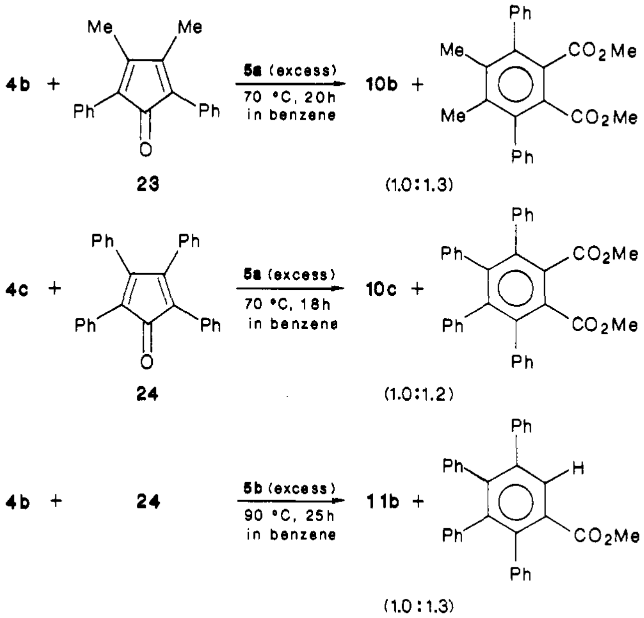
Table III. ^{1}H NMR Data of Diels-Alder Adducts of 4 with Various Dienophiles and Related Derivatives[a]

Compd	Mol Formula[b]	^{1}H NMR,[c] δ
10a	$C_{21}H_{26}O_4$	3.85 (s, 6), 3.47 (br s, 2), 2.25 (s, 6), 2.85–1.55 (m, 12)
11a	$C_{19}H_{24}O_2$	7.30 (s, 1), 3.87 (s, 3), 3.7–3.2 (br s, 2), 2.42 (s, 3), 2.28 (s, 3), 2.25–1.50 (m, 12)
12a	$C_{29}H_{30}$	7.08–6.65 (m, 10), 3.45 (br s, 2), 2.25–1.70 (m, 18)
13a	$C_{23}H_{26}$	7.5–7.2 (m, 5), 6.83 (s, 1), 3.7–3.2 (br s, 2), 2.28 (s, 3), 2.15 (s, 3), 2.35–1.20 (m, 12)
14a	$C_{18}H_{24}O$	6.91 (s, 1), 4.62 (s, 2), 3.40 (br s, 2), 2.27 (s, 6), 2.4–1.4 (m, 13)[d]
15a	$C_{17}H_{22}$	6.81 (s, 2), 3.35 (s, 2), 2.25 (s, 6), 2.2–1.7 (m, 12)
16a	$C_{18}H_{21}N$	7.20 (s, 1), 3.29 (br s, 2), 2.45 (s, 3), 2.25 (s, 3), 2.3–1.4 (m, 12)
18an	$C_{19}H_{22}NOCl$	2.72 (d, J = 13.5, 1), 2.50 (br s, 2), 2.08 (d, J = 13.5, 1), 2.2–1.6 (m, 12)
18ax	$C_{19}H_{22}NOCl$	2.7–2.4 (m, 2), 2.58 (d, J = 13.5, 1), 2.31 (d, J = 13.5, 1), 2.35–1.55 (m, 12), 1.48 (s, 3), 1.26 (s, 3)
10b	$C_{31}H_{30}O_4$	7.55–7.15 (m, 10), 3.40 (s, 6), 3.24–2.98 (m, 2), 2.22–1.50 (m, 12)
11b	$C_{29}H_{28}O_2$	7.48–7.00 (m, 11), 3.38 (s, 3), 3.20–2.95 (m, 2), 2.25–1.55 (m, 12)
12b	$C_{39}H_{34}$	7.05 (s, 10), 6.74 (s, 10), 3.09 (br s, 2), 2.31–1.71 (m, 12)
13b	$C_{33}H_{30}$	7.50–6.71 (m, 16), 3.42–2.98 (br s, 2), 2.30–1.58 (m, 12)
14b	$C_{28}H_{28}O$	7.50–7.26 (m, 11), 4.24 (d, J = 6.8, 2), 3.45–2.90 (m, 2), 2.1–1.6 (m, 13)[d]
15b	$C_{27}H_{26}$	7.62–7.00 (m, 10), 6.84 (s, 2), 3.48–3.06 (br s, 2), 2.30–1.52 (m, 12)
16b	$C_{28}H_{25}N$	7.55–7.00 (m, 11), 3.40–2.97 (br s, 2), 2.29–1.90 (m, 12)
10c	$C_{23}H_{26}O_8$	3.87 (s, 6), 3.82 (s, 6), 3.2–2.9 (br s, 2), 2.25–1.70 (m, 12)
11c	$C_{21}H_{24}O_6$	8.00 (s, 1), 3.92 (s, 3), 3.88 (s, 3), 3.86 (s, 3), 3.7–3.4 (br s, 1), 3.10–2.85 (br s, 1), 2.3–1.5 (m, 12)
12c	$C_{31}H_{30}O_4$	7.04 (s, 10), 3.40 (s, 6), 3.10–2.82 (br s, 2), 2.3–1.7 (m, 12)
13c	$C_{25}H_{26}O_4$	7.4–7.3 (m, 6), 3.87 (s, 3), 3.56 (s, 3), 3.1–2.9 (br s, 2), 2.3–1.7 (m, 12)
14c	$C_{19}H_{20}O_4$	7.25 (s, 1), 5.24 (d, J = 7.5, 1), 5.10 (d, J = 7.5, 1), 5.0–4.7 (br s, 1), 3.93 (s, 3), 3.5–3.7 (br s, 1), 2.3–1.5 (m, 12)
15c	$C_{19}H_{22}O_4$	7.23 (s, 2), 3.82 (s, 6), 3.6–3.3 (br s, 2), 2.3–1.5 (m, 12)
16c	$C_{20}H_{21}NO_4$	7.67 (s, 1), 4.05 (s, 3), 3.92 (s, 3), 3.75–3.42 (br s, 1), 3.18–2.88 (br s, 1), 2.3–1.5 (m, 12)
19	$C_{24}H_{32}O$	5.8–5.5 (m, 2), 2.40–1.45 (m, 24), 1.40 (s, 6)
21	$C_{23}H_{32}$	[e]
22a	$C_{24}H_{25}N_3O_3$	[f]
22b	$C_{34}H_{29}N_3O_3$	[f]

[a] For isolations, yields, and melting points, see Experimental Section and Table II. [b] Satisfactory analytical data (±0.4%; C, H, N) were reported for all new compounds listed in the table. [c] All spectra were measured in $CDCl_3$ at 60 MHz. [d] D_2O exchangeable. [e] See ^{13}C NMR spectral data in Experimental Section. [f] The spectra could not be measured for no solubility in appropriate solvents.

line-3,5-dione (PTAD, **8**)[17] **8** in acetone at 20–25 °C for 1 h afforded the 1:1 adducts **22a,b** in 84 and 83% yields, respectively (Scheme IV). However, the reaction of **4c** with **8** under the same conditions did not proceed, and after a longer reaction time (3 days) only decomposition products were formed. The failure of **4c** to react with PTAD is surprising considering that its reactivity with other acetylenic and olefinic dienophiles is comparable to those of **4a,b** (Table II). This result may reflect a strong dipole–dipole repulsion between the methoxycarbonyl groups of **4c** and the dione moiety of PTAD, prohibiting the approach of the dienophile to the dienone under such mild conditions.

Scheme V



Relative Diene Reactivity of 4b. The diene reactivities of **4b** and other cyclopentadienones were compared by competitive Diels–Alder reactions of **4b**, 3,4-dimethyl-2,5-diphenyl- (**23**),[18] and 2,3,4,5-tetraphenylcyclopentadienones (**24**).[19] An equimolar mixture of **4b** and **23** was heated with 8 equiv of DMAD at 70 °C in benzene for 20 h to afford the corresponding arenes **10b** and **25**[20] (Scheme V). The product ratio was 1:1.3 based on ^{1}H NMR analysis. The combination of **4b** and **24** with **5a** afforded **10b** and **26** in a ratio of 1:1.2, and that of **4b** and **24** with methyl propiolate (**5b**) gave **11b** and **27** in a ratio of 1:1.3. These results as well as the results in Table II clearly demonstrate useful diene reactivity of homoadamantanocyclopentadienones **4a–c**.

In summary, [4 + 2] cycloadditions of homoadamantanocyclopentadienones **4a–c** with acetylenic and some olefinic dienophiles, followed by decarbonylation, constitute an efficient synthetic route to homoadamantanobenzene derivatives. This route is advantageous over the known transannular cyclization of benzobicyclo[3.3.2]decan-3,7-dione[6,7] particularly for the synthesis of derivatives substituted on the benzene ring.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were obtained on a JASCO IRA-1 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-60HL instrument at 60 MHz and a JEOL JNM-60 FT NMR spectrometer at 15.04 MHz. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard, and coupling constants in hertz. Mass spectra were obtained with an ESCO EMD-05B mass spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. Physical data of all new compounds are summarized in Tables I-IV unless otherwise de-

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[17] Cookson, R. C.; Gilani, S. S.; Stevens, I. D. *Tetrahedron Lett.* **1962**, 615.

[18] The dienone **23** was prepared by condensation of 2,3-butanedione with 1,3-diphenylacetone as **4** and had mp 155–157 °C and satisfactory spectral data.

[19] The dienone **24** is commercially available. See also ref 9b.

[20] Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549.

scribed in the Experimental Section.

2′,5′-Dimethyl-4′-hydroxyhomoadamantano[4,5-*c*]cyclopentenone (3a). A mixture of homoadamantanedione **1**[8] (267 mg, 1.50 mmol), 3-pentanone (172 mg, 2.00 mmol), and potassium hydroxide (35 mg) in ethanol (16 mL) was stirred at room temperature for 2 days. After the mixture was concentrated under reduced pressure to about 10 mL, dilution with water afforded a colorless precipitate which was collected by filtration and recrystallized from *n*-hexane to afford **3a** as crystals (297 mg, 80.4%): mp 156–158 °C; IR (KBr) 3460, 2980, 2940, 2850, 1700, 1650, and 1450 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 4.42 (s, 1, D_2O exchangeable), 3.35–3.00 (br s, 1), 2.05–1.15 (m, 14), 1.58 (s, 3), and 0.94 (d, J = 6.8 Hz, 3).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.78; H, 9.55. Found: C, 78.98; H, 9.72.

2′,5′-Dimethylhomoadamantano[4,5-*c*]cyclopentadienone (4a). The cyclopentenolone **3a** (246 mg, 1.00 mmol) was treated with thionyl chloride (2.0 mL, 27.4 mmol) and anhydrous potassium carbonate (1.0 g) in anhydrous benzene (8 mL) and *n*-hexane (6 mL) at room temperature for 1 day. The resulting reddish mixture was diluted with *n*-hexane (50 mL) and washed with water (20 mL × 3) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a reddish yellow solid which was purified on a short silica gel (Fuji-Davison BW-300) column eluting with CH_2Cl_2 to give the dienone **4a** as reddish orange crystals after recrystallization from *n*-pentane (142 mg, 62.3%).

2′,5′-Diphenylhomoadamantano[4,5-*c*]cyclopentadienone (4b). A mixture of **1** (90 mg, 0.51 mmol) and 1,3-diphenylacetone (210 mg, 1.00 mmol) in ethanol (5 mL) containing KOH (20 mg) was stirred at room temperature for 2 days. The resulting dark red solution was evaporated under reduced pressure to give a dark solid which was purified on a silica gel column to give the dienone **4b** as dark red crystals (from CH_2Cl_2–*n*-hexane) (141 mg, 79.2%).

2′,5′-Bis(methoxycarbonyl)homoadamantano[4,5-*c*]-cyclopentadienone (4c). A mixture of **1** (348 mg, 1.95 mmol), dimethyl 3-oxoglutarate (349 mg, 2.00 mmol), anhydrous K_2CO_3, and molecular sieves (3A type, 1.0 g) in ethanol (20 mL) was stirred for 0.5 h. The resulting yellow solution was filtered and evaporated under reduced pressure to give a yellowish residue which was purified on a silica gel column, eluting with CH_2Cl_2 to give the dienone **4c** after recrystallization from CH_2Cl_2–MeOH as orange yellow needles (308 mg, 50.0%). The use of KOH as the base gave 40.5% yield. The longer reaction time decreased the yield of **4c** because of side reactions (see text).

General Procedure for the Diels–Alder Reaction of 4. An appropriate combination of the cyclopentadienones **4a–c** and dienophiles (1.2–15.0 mol equiv) in an appropriate solvent was heated under argon in a sealed tube under the conditions summarized in Table II. The reaction was monitored by disappearance of the characteristic color of the solution. Removal of the solvent under reduced pressure gave a crude product which was purified on a silica gel (Fuji-Davison BW-300) column or by preparative TLC (Merck, Kieselgel 60 F-254, or Wako gel C-200) using CH_2Cl_2–*n*-hexane as the eluent. The products were generally recrystallized from *n*-hexane and/or methanol (Table II).

3′,6′-Dimethyl-4′-cyanohomoadamantano[4,5-*a*]benzene (16a). The Diels–Alder adducts **18an** (12 mg, 0.058 mmol) and **18ax** (5.0 mg, 0.016 mmol) were heated at 230 °C for 10 min under argon. The crude products were taken up in CH_2Cl_2 and purified by perparative TLC (Kieselgel 60 F-254, *n*-hexane) to afford the benzene derivative **16a** as colorless cystals from *n*-hexane (R_f 0.30) (8.0 mg, 83.8%, and 3.0 mg, 75.5%, respectively).

Thermal Decarbonylation of 19. The Diels–Alder adduct **19** (38 mg, 0.11 mmol) was heated under argon for 0.5 h. The residue was taken up in CH_2Cl_2 and purified by preparative TLC (Kieselgel 60 F-254, CH_2Cl_2–*n*-hexane 1:1 v/v) to afford the dienone **4a** (R_f 0.40, 1.0 mg, 3.0%) and the cage compound **21** as a colorless solid (R_f 0.70, 8.0 mg, 22.9%). ^{13}C NMR ($CDCl_3$) δ 143.7 (s, 2 C), 46.8 (d, 4 C), 44.8 (s, 2 C), 36.8 (t, 1 C), 34.8 (t, 4 C), 31.4 (d, 2 C), 29.1 (d, 2 C), 25.1 (t, 4 C), and 22.1 (q, 2 C).

Competitive Diels–Alder Reaction of 4b and 23 with DMAD (5a). A mixture of **4b** (17.6 mg, 0.050 mmol), **23**[18] (13.0 mg, 0.050 mmol), and **5a** (114 mg, 0.80 mmol) in benzene (2 mL) was heated in a sealed tube at 70 °C for 20 h. The solvent and excess **5a** were removed under reduced pressure to give a crude product which was purified by preparative TLC (Kieselgel 60 F-254, CH_2Cl_2) to give a mixture of **10b** and **25**[20] as R_f 0.50 fraction (45 mg). ^{1}H NMR analysis of this mixture using signals at δ 3.41 (s, CO_2*Me* due to **10b**), 3.57 (s, CO_2*Me* due to **25**), 3.24–2.98 (m, bridgehead protons due to **10b**), and 2.08 (s, Me protons due to **25**) determined the ratio of **10b** to **25** as 1.0:1.3.

Competitive Diels–Alder Reaction of 4b and 24 with 5a. A mixture of **4b** (17.6 mg, 0.050 mmol), tetraphenylcyclopentadienone (**24**) (19.2 mg, 0.050 mmol), and **5a** (114 mg, 0.80 mmol) in benzene (2 mL) was heated in a sealed tube under argon at 70 °C for 18 h. Removal of the solvent and excess **5a** under reduced pressure gave a crude product which was purified by preparative TLC (Kieselgel 60 F-254, CH_2Cl_2-*n*-hexane 1:1 v/v) to give a mixture of **10b** and **26**[21] as R_f 0.30 fraction (45 mg). ^{1}H NMR analysis of the mixture using signals at δ 3.51 (s, CO_2*Me* of **26**) and 3.40 (s, CO_2*Me* of **10b**) gave the ratio of **10b** to **26** as 1.0:1.2.

Competitive Diels–Alder Reaction of 4b and 24 with 5b. A mixture of **4b** (17.6 mg, 0.050 mmol), **24** (19.2 mg, 0.050 mmol), and **5b** (67 mg, 0.80 mmol) in benzene (2 mL) was heated in a sealed tube under argon at 90 °C for 25 h. Removal of the solvent and excess **5b** under reduced pressure and preparative TLC (Kieselgel 60 F-254, CH_2Cl_2-*n*-hexane 1:1 v/v) gave a mixture of **11b** and **27**[20] as R_f 0.60 fraction (33 mg). ^{1}H NMR analysis of the mixture by the signals at δ 3.48 (s, CO_2*Me* of **27**) and 3.38 (s, CO_2*Me* of **11b**) determined the ratio of **11b** to **27** as 1.0:1.3.

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Supplementary Material Available: Table IV (IR and MS for compounds **10–16, 18, 19, 21, 22** and UV spectra for compounds **10–16, 18, 19**) (4 pages). Ordering information is given on any current masthead page.

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[21] Kino, K.; Kazuhiko, K.; Kawanishi, M.; Kozima, S.; Hitomi, T. *J. Organomet. Chem.* 1977, *137*, 349.

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