Nonbenzenoid Aromatic Compounds Containing an *anti*-Aromatic Four-membered Ring. Synthesis and Some Properties of 7-Hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (Benzo[3,4]cyclobuta[1,2-*e*]tropolone)

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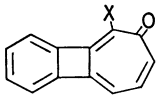
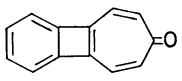
Biphenylene-2,3-quinone reacts with diazomethane in the presence of boron trifluoride etherate to give 7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**5**) and its boron difluoride chelate. The latter is convertible quantitatively into the former. Compound **5** has a reduced troponoid character due to fusion of the benzocyclobutadiene ring. Tautomerism of the tropolone ring in **5** seems to be imposed exclusively to one of the tautomers. Protonation of **5** gives a tropylium ion whose positive charge is partially localized. Bromination, nitration, and azo-coupling of **5** give only 7-substituted products. The reaction of **5** with maleic anhydride gives the Diels-Alder adduct in good yield.

Much information has been obtained on the fused polycyclic aromatic compounds containing both $4n\pi$- and $(4n+2)\pi$-electron ring systems. Of these compounds, tropone and tropolone analogs of biphenylene are of particular interest, since their tropone and tropolone nuclei would have relatively small resonance energy because of perturbation caused by the fused anti-aromatic four-membered ring. The chloro derivative of 6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**1a**) was found to have more bond-alternated tropone nucleus.[1,2] The parent compound (**1b**) further confirmed the above indication.[3] The formation of 7*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-7-one (**2**) was also confirmed by trapping it as the adduct with cyclopentadiene.[7] 5*H*-Cyclobutacyclohepten-5-one (**3**), a lower homolog of **1**, was isolated as the $Fe(CO)_3$ complex.[5]

The first tropolone analog (**4**) of biphenylene was prepared by the ring-enlargement of 1,2-dimethoxybiphenylene with dichlorocarbene, and the tautomerism of **4**, unlike that of monocyclic tropolones,[6] was found to be extremely inclined to one tautomer. We report the synthesis and some reactions of the parent 7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**5**).[7]



(1a) X=Cl
(1b) X=H



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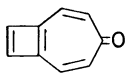

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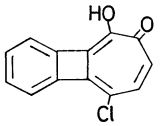
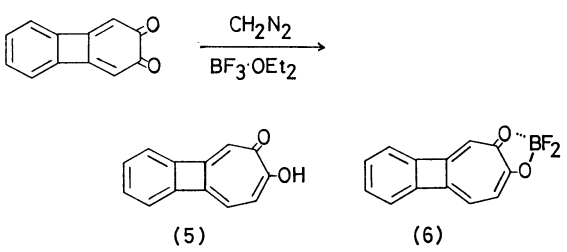


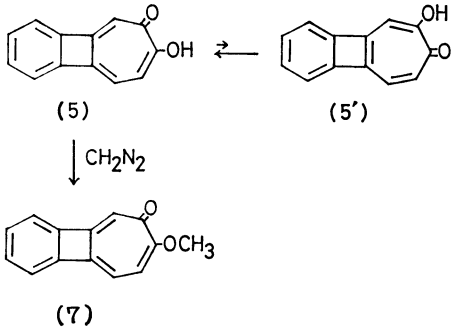
(4)

A convenient route to tropolone derivatives is the ring-enlargement of quinone with diazomethane.[8] Biphenylene-2,3-quinone was treated with diazomethane in the presence of boron trifluoride etherate to give the desired tropolone **5** in 45% yield and its boron difluoride chelate (**6**) in 26% yield. A catalytic amount of boron trifluoride is indispensable for the formation of **5** and **6**. Their spectral data agree with the assigned structure. In the mass spectrum, **5** has the ion peaks at *m/e* 196 (M^+ 100%), 168 (M^+-CO, 62%), and 139 ($M^+-CO-CHO$, 45%), and **6** at *m/e* 244 (M^+, 100%) and 216 (M^+-CO, 51%). The IR spectrum of **5** showed a strong absorption at 1570 cm^{-1} characteristic of tropolones and **6** a broad absorption at 1200—1000 cm^{-1} characteristic of chelate compounds. The ^{1}H-NMR spectrum of **5** ($CDCl_3$, 100 MHz) showed two doublets (J=9.0 Hz) at δ 6.32 (H-9) and 6.64 (H-8), a singlet at δ 6.70 (H-6), a multiplet at δ 7.11 (benzenoid), and a broad singlet at 8.27 (OH). The ^{1}H-NMR spectrum of **6** (DMSO-d_6, 100 MHz) showed a multiplet at δ 7.06 (H-9 and benzenoid), a doublet (J=9.1 Hz) at δ 7.34 (H-8), and a singlet at δ 7.54 (H-5). The chelate **6** was hydrolyzed in acidic aqueous ethanol to **5** quantitatively, which returned to **6** quantitatively on treatment with boron trifluoride etherate.



(5) (6)

The tropolone **5** showed some chemical features characteristic of monocyclic tropolones:[9] it gave red coloration in the chloroform layer with aqueous iron(III) chloride, reacted with aqueous sodium carbonate forming a red precipitate of the sodium salt, but not with aqueous sodium hydrogencarbonate, and dissolved in concentrated sulfuric acid or trifluoroacetic acid forming a red solution of the corresponding proto-



(5) (5′) (7)

Table 1. Vicinal coupling constants of the ^{1}H-NMR of tropolone and its methyl ether

Compound	J_{vic}/Hz		J_{vic}/Hz
	Tropolone	Its methyl ether	
Tropolone	10.9[a]	10.1[a]	0.8
9	9.8[a]	9.3	0.5
5	9.0	9.1	0.1

a) Ref. 11.

nated species (*vide infra*). In contrast to 6-hydroxy-5*H*-benzocyclohepten-5-one (3,4-benzotropolone) (**9**), it gave the methyl ether (**7**) in 59% yield on treatment with ethereal diazomethane for 9 d, no alternate methyl ether of (**5'**) being detected. The structure of **7** was assigned by the following ^{1}H-NMR spectrum: δ 3.78 (s, 3H, methoxyl protons), 6.11 (d, 1H, J=9.1 Hz, H-8), 6.58 (s, 1H, H-5), and 7.13 (m, 4H, aromatic protons). The results suggest that the troponoid character of **5** decreases with fusion of the benzocyclobutadiene ring but the extent of the decrease seems to be smaller than that of tropolone character caused by fusion of benzene in 3,4-benzotropolone (**9**), since **9** gives no methyl ether on treatment with diazomethane.[10]

The potentially expectable tautomerism **5**⇄**5'**, unlike that of monocyclic tropolones, seems to be imposed to one tautomer **5**. The shape of the electronic spectrum of **5** is closely similar to those of the methyl ether **7** and 7-chloro-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**8**),[2] except for the bathochromic shift in the long-wavelength region. This indicates that these compounds have a similar conjugate system. The ^{1}H-NMR spectral coupling constants of the vicinal protons intervening a single bond in the seven-membered ring in **5** and the related compounds are summarized in Table 1. The coupling constant J_{vic}=9.0 Hz of the seven-membered ring in **5** is the same as J_{vic}=9.1 Hz in **7**, and is smaller than the corresponding $J_{vic}(J_{7,8})$=9.8 Hz in 3,4-benzotropolone **9** and J_{vic}= 10.1 Hz in tropolone methyl ether, where the latter two compounds have a nearly planar structure but no tautomerism.[11] Moreover, the difference in the vicinal coupling constant (ΔJ_{vic}=0.1 Hz) between benzocyclobutatropolone **5** and its methyl ether is smaller than not only that (ΔJ_{vic}=0.8 Hz) between monocyclic tropolone and its methyl ether, but also that (ΔJ_{vic}=0.5 Hz) between 3,4-benzotropolone **9** and its methyl ether. This suggests that the seven-membered ring in **5** has larger bond alternation and deviation from planarity than tropolone and benzotropolone. The fact that only one methyl ether **7** was obtained on methylation of **5** might support the exclusive inclination to the one tautomer **5** in the tautomerism **5**⇄**5'**. The ^{13}C-NMR spectrum of **5** has thirteen signals containing only one carbon resonance at 182.3 ppm. The lack of the tautomerism in **5** would be due to the fusion of the benzocyclobutadiene ring. However, it is questionable whether the effect is caused only by the anti-aromaticity of the benzocyclobutadiene ring, since a similar tautomerism con-

Table 2. Difference in ^{1}H-NMR spectral chemical shifts and coupling constants of the ring protons between the neutral and protonated species of troponoids

Compound	$\Delta\delta$				$\Delta J_{8,9}$/Hz
	H_5	H_8	H_9	Aromatic	
5	0.5	0.80	0.50	0.08	0.6
7	0.58	1.19	0.90	0.08	0.6
8	0.44	0.56	0.43	0.08	0.6

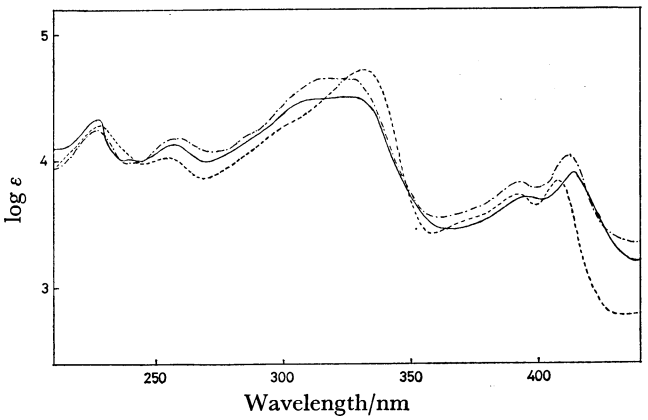
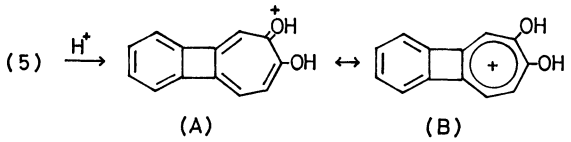


Fig. 1. The electronic spectra of 7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**5**) (——), its derivatives (**7**) (—·—·), and (**8**) (----) in concd sulfuric acid.

siderably inclined to one tautomer was also observed in 1,2-dihydrocyclobuta[*e*]tropolone.[12]

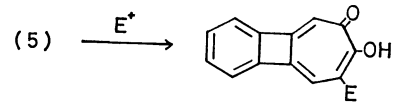
The protonation of monocyclic tropolones affords the corresponding dihydroxytropylium ion, in which the positive charge is delocalized in all the ring carbon atoms. The electronic spectrum of the protonated 7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one **5** is shown in Fig. 1, along with the spectra of the protonated 7-chloro- (**8**) and 7-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**7**). The shape of their spectra is similar. The λ_{max} peaks of these cations are nearly in line with those of benzo[3,4]cyclobuta[1,2]tropylium ion having a partially localized positive charge.[13] The ^{1}H-NMR spectrum of **5** in trifluoroacetic acid showed two doublets (J=9.6 Hz) at δ 6.82 (H_9) and δ 7.44 (H_8) and a multiplet at δ 7.1—7.2 (H_5 and benzenoid). Protonation of **5** resulted in a significant low-field shift ($\Delta\delta_8$=0.80 and $\Delta\delta_9$=0.50 ppm) of the seven-membered ring protons, while the benzenoid protons remained naerly unchanged (Table 2). The low-field shifts ($\Delta\delta_8$ and $\Delta\delta_9$) of the seven-membered ring protons of the protonated **5** is nearly similar to those ($\Delta\delta_8$ and $\Delta\delta_9$) of the protonated **8**, but much smaller than the corresponding shifts ($\Delta\delta_9$=1.12 and $\Delta\delta_8$=0.96 ppm) of the protonated 7*H*-benzocyclohepten-7-one (4,5-benzotropolone). The large low-field shift in **7** seems to be due to protonation on the methoxyl group, because the signal of the methoxyl group shifted to low field by 0.39 ppm on protonation. The difference ($\Delta J_{8,9}$) in the coupling constants between **5** and protonated **5** is similar

to the corresponding values ($\Delta J_{8,9}$) of other 6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one derivatives **7** and **8** (Table 2). The spectral data indicate that the positive charge in the protonated 6*H*-benzocyclobutacyclohepten-6-one system is insufficiently delocalized in the seven-membered ring and considerably localized on the carbonyl oxygen, that is, the protonated **5** is derived more from the canonical form **A** than **B**.



On protonation of **5**, the low-field shift of the benzenoid protons is very small, suggesting no perpheral 12π-conjugation. This is in contrast to the fact that, on protonation of 4,5-benzotropolone, the positive charge delocalized to the benzene ring completing the 10π-electron conjugation, as indicated by the large low-field shift (*ca.* 0.5 ppm). The insufficient positive charge delocalization and the absence of the peripheral conjugation of the protonated **5** might be caused by the requirement that the central four-membered ring of **5** does not take *anti*-aromatic cyclobutadiene structure, while the strained 1,2-dihydrocyclobuta[*e*]tropolone, like monocyclic tropolones, showed a positive charge delocalization on protonation.[12]

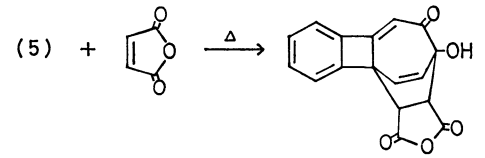
One of the characteristics of tropolonoid compounds is that they react with various electrophilic reagents to afford the substitution products. The tropolone **5** underwent the following electrophilic substitutions, reacting with bromine to give 8-bromo-7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**10**) in 47% yield. Similarly, **5** underwent nitration and azo-coupling reactions to give 8-nitro (**11**) and 8-tolylazo derivatives (**12**), in 30 and 89% yields, respectively.



(10) E=Br
(11) E=NO_2
(12) E=$N_2C_6H_4CH_3$-p

The results indicate that **5** has a character similar to that of monocyclic tropolones. Its extremely inclined tautomerism is suggested also by the fact that **5** undergoes electrophilic substitution only at the 8-position excluding 5-position. This is in line with the behavior of 6-hydroxy-7*H*-benzocyclohepten-7-one (4,5-benzotropolone) which has no tautomerism and is attacked by electrophiles only at the 5-position.[13,14] However, the chemical behavior of **5** differs somewhat from that of 6-hydroxy-5*H*-benzocyclohepten-5-one **9** which is attacked by electrophiles at 7-position as well as 9-position,[10,15,16] undergoing also ring contraction.[17]

Tropolone **5** reacted with maleic anhydride to give 1:1 Diels-Alder adduct (**13**) in a good yield. The structure of **13** was assigned mainly by its ^{1}H-NMR spectrum: two aliphatic doublets (δ 3.61 and 3.85, J=9.0 Hz), two olefinic doublets (δ 6.22 and 6.62, J=9.0 Hz) and an olefinic singlet (δ 6.16). The Diels-Alder adduct (**13**) was obtained by refluxing both



(13)

in xylene and in benzene, no isomerization of the adduct being observed.[18] Monocyclic tropolones undergo no Diels-Alder reaction in refluxing benzene[19] but they do in refluxing xylene with maleic anhydride.[20] Thus, **5** seems to have considerable bond localization, becoming susceptive of the cyclo-addition owing to the fusion of benzocyclobutadiene. Tropolone **5** and its methyl ether were subjected to Diels-Alder reaction with 1,3-diphenylisobenzofuran and condensation with guanidine, respectively, no definite product being obtained.

Experimental

Reaction of Biphenylene-2,3-quinone with Diazomethane in the Presence of Boron Trifluoride. Boron trifluoride etherate (0.9 ml of 47% solution, 3 mmol) was added to a solution of biphenylene-2,3-quinone (455 mg, 2.5 mmol) in dichloromethane (20 ml) on an ice–water bath under an atmosphere of nitrogen. A yellow precipitate appeared. After 10 min, to the mixture was added a solution of diazomethane in ether (45 ml) prepared from *N*-nitroso-*N*-methylurea (2.06 g, 20 mmol) and alkali. The mixture turned to a red-violet solution. After being stirred for 30 min, the solution was poured into water. The mixture was extracted with dichloromethane. The extract was washed with water and dried over anhydrous sodium sulfate. After evaporation, the residue was chromatographed on silica gel to give the following products in turn. Boron difluoride chelate (**6**) of 7-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (156 mg, 25.6%), red-violet needles (from acetonitrile), mp 237.2—237.9 °C. Found: C, 63.75; H, 2.76%. Calcd for $C_{13}H_7O_2BF_2$: C, 63.99, H, 2.89%. IR(KBr): 1524, 1409, 1310, 1150—1040, 849, and 748 cm^{-1}. NMR (DMSO-d_6, 100 MHz): δ 7.34 (d, 1H, J=9.1 Hz, H_8), 7.45 (s, 1H, H_5), 7.06—7.27 (m, 5H, aromatic and H_9). MS(75 eV): *m/e* 244 (M^+, 100%) and 216 (M^+-CO, 51%). UV (CH_3CN): 231 (log ε 4.33), 262 (4.32), 308 (4.74), 393 (3.85), and 416 nm (4.00). 7-Hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**5**), 219 mg (44.7%), yellow needles (from ethanol), mp 166—167 °C. Found: C, 79.53; H, 4.22%. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11%. IR (KBr): 3250, 1580, 1450, 1430, 1241, 1206, 903, 757, and 680 cm^{-1}. NMR($CDCl_3$, 100 MHz): δ 6.32 (d, J=9.0 Hz, H_9), 6.64 (d, 1H, J=9.0 Hz, H_8), 6.70 (s, 1H, H_5), 7.11 (m, 4H, aromatic), and 8.27 (s, 1H, OH). NMR (CF_3COOH): δ 6.82 (d, 1H, J=9.5 Hz), 6.82—7.19 (m, 5H), and 7.44 (d, 1H, J=9.5 Hz). ^{13}C-NMR($CDCl_3$): 113.7, 117.9, 118.4, 119.0, 120.7, 130.0, 132.4, 146.6, 147.1, 149.9, 157.3, 160.8, and 182.3 ppm. MS (75 eV): *m/e* 196 (M^+, 100%), 168 (M^+-CO, 28%), and 139 ($M^+-CO-CHO$, 45%). UV(EtOH): 228 (log ε 4.09), 249 (4.13), 290 (4.52), 372 (3.77), 390 (3.83), and 422 nm (3.71). UV(H_2SO_4): 227 (log ε 4.34), 257 (4.14), 308sh (4.48), 325 (4.51), 394 (3.70), and 413.5 nm (3.90). At last, the

unreacted starting material (7 mg, 1.5% recovery) was eluted out.

Hydrolysis of the Chelate **6**. A mixture of the chelate **6** (50 mg, 0.21 mmol), hydrochloric acid (2 mol dm^{-3}, 3 ml), water (1 ml) and acetone (15 ml) was refluxed for 2 h. The mixture was poured into water. The aqueous mixture was extracted with dichloromethane. The extract was washed with water and dried over anhydrous sodium sulfate. After evaporation, the residue was sublimed under reduced pressure (≈125 °C/2 mmHg). Tropolone **5** (38 mg, 92%) was obtained.

Reaction of Tropolone **5** *with Boron Trifluoride Etherate.* Boron trifluoride etherate (47% solution, 0.03 ml, 0.1 mmol) was added to a mixture of tropolone **5** (20 mg, 0.1 mmol) in anhydrous ether (10 ml). The mixture was stirred for 1 h and the solvent evaporated. The residue was chromatographed on silica gel with elution of dichloromethane. Chelate **6** (24 mg, 96%) was obtained.

Tropolone Methyl Ether **7**. Tropolone **5** (49 mg, 0.25 mmol) was dissolved in a solution of diazomethane, prepared from *N*-nitroso-*N*-methylurea (0.93 g, 0.9 mmol) and alkali, in ether (20 ml). The solution was kept in refrigerator for 9 d. After evaporation, the residue was chromatographed on silica gel with elution of dichloromethane. Tropolone methyl ether **7** (yellow needles, mp 191—193 °C) (30 mg, 59%) was obtained, the starting material (17 mg, 35%) being recovered. Found: C, 80.16; H, 5.05%. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79%. IR(KBr): 1608, 1541, 1330, 1234, 1078, 1010, 842, and 764 cm^{-1}. NMR($CDCl_3$): δ 3.79 (s, 3H, methyl), 6.13 (d, 1H, J=9.4 Hz, H_9), 6.31 (d, 1H, J=9.4 Hz, H_8), 6.60 (s, 1H, H_5), and 7.13 (m, 4H, aromatic). NMR(CF_3COOH): δ 4.18 (s, 3H, methyl), 7.03 (d, 1H, J=10.0 Hz, H_9), 7.18 (s, 1H, H_5), 7.48 (d, 1H, J=10.0 Hz, H_8), and 7.23 (s, 4H, aromatic). UV (EtOH): 227 (log ε 4.12), 244 (4.15), 288 (4.63), 320 (3.79), 361 (3.98), and 376 nm (3.95). UV(H_2SO_4): 227 (log ε 4.25), 258 (4.18), 315 (4.65), 328 (4.64), 393 (3.82), and 412 nm (4.03).

*8-Bromo-7-hydroxy-6H-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (***10***)*. To a solution of **5** (0.1 g, 0.5 mmol) in acetic acid (5 ml) was added a solution of bromine (90 mg, 0.56 mmol) in acetic acid (1 ml) over a period of 5 min. After being stirred for 30 min, the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane. The solution was washed with water and dried over anhydrous sodium sulfate. After evaporation, the crystalline residue was recrystallized from ethanol to give the title compound (67 mg, 47%) as yellow-orange needles, mp 166—168 °C. Found: C, 57.23; H, 2.37%. Calcd for $C_{13}H_7O_2Br$: C, 56.76; H, 2.56%. IR(KBr): 3300, 1580, 1340, and 1230 cm^{-1}. NMR($CDCl_3$): δ 6.61 (s, 1H, H_9), 6.70 (s, 1H, H_5), 7.13 (m, 4H, aromatic), and 8.88 (broad s, 1H, OH). UV(EtOH): 234 (log ε 4.13), 291 (4.54), 370 sh, 388 (3.75), and 425 sh nm.

*8-Nitro-7-hydroxy-6H-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (***11***)*. To a solution of **5** (0.1 g, 0.5 mmol) in acetic acid (5 ml) was added a solution of concentrated nitric acid (60—62%, 64 mg, 6 mmol) in acetic acid (0.1 ml) at 0 °C over a period of 5 min. After being stirred for 30 min, the solution was diluted with water (40 ml). The resulting yellow crystals were collected by filtration and washed with water. After drying, the crystals were recrystallized from ethanol to give pure title compound **11** (36 mg, 29%), yellow-orange needles, mp 174—175 °C. Found: C, 64.38; H, 2.72; N, 5.48%. Calcd for $C_{13}H_7O_4N$: C, 64.73; H, 2.92; N, 5.81%. IR(KBr): 3200, 1600, 1580, 1530, 1320, and 1220 cm^{-1}. NMR($CDCl_3$): δ 6.55 (s, 1H, H_9), 6.76 (s, 1H, H_5), and 7.27 (m, 4H, aromatic). UV (EtOH): 233 (log ε 4.28), 254 (4.25), 305 (4.49), 382 (4.12), and 537 nm (3.63).

*8-Tolylazo-7-hydroxy-6H-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (***12***)*. To a solution of **5** (0.1 g, 5 mmol) and sodium acetate (3 g) in water (4 ml) and acetic acid (24 ml) was added a solution of the diazonium salt, prepared from *p*-toluidine (70 mg, 0.56 mmol), hydrochloric acid (2 mol dm^{-3}, 0.5 ml) and sodium nitrite (43 mg, 0.62 mmol), at 0—2 °C over a period of 15 min. After being stirred for 20 min, the solution was kept in a refrigerator overnight. The solvent was then evaporated. The dark violet residue was diluted with water. The aqueous solution was controlled at pH 3 and the resulting crystals (0.142 g, 88%) were collected by filtration. Recrystallization from acetonitrile gave the pure title compound **12** as blue-violet needles (mp 213—214 °C). Found: C, 76.37; H, 4.39; N, 8.89%. Calcd for $C_{20}H_{14}O_2N_2$: C, 76.42; H, 4.49; N, 8.91%. IR (KBr): 3300, 1630, 1480, and 1300 cm^{-1}. NMR($CDCl_3$): δ 2.38 (s, 3H, CH_3), 6.53 (s, 1H, H_9), 6.70 (s, 1H, H_5), and 7.30 (m, 8H, aromatic). UV(EtOH): 252 (log ε 4.55), 340 (4.67), and 564 nm (4.32).

Diels-Alder Reaction of **5**. A solution of **5** (0.1 g, 0.5 mmol) and maleic anhydride (0.15 g, 1.5 mmol) in anhydrous xylene (2.5 ml) was refluxed for 5.5 h. The solvent was evaporated. The resulting pale yellow residue was recrystallized from benzene–dichloromethane to give the adduct **13** (0.103 g, 68.8%) as colorless prisms (mp 194—196 °C). Found: C, 69.50; H, 3.41%. Calcd for $C_{17}H_{10}O_5$: C, 69.39; H, 3.43%. IR(KBr): 1855, 1760, and 1650 cm^{-1}. NMR ($CDCl_3$): δ 3.61 (d, 1H, J=9.0 Hz, methine), 3.85 (d, 1H, J=9.0 Hz, methine), 5.2 (broad s, 1H, OH), 6.16 (s, 1H, H_5), 6.22 (d, 1H, J=9.0 Hz, H_8), 6.62 (d, 1H, J=9.0 Hz, H_9), and 7.3—7.9 (m, 4H, aromatic). UV(EtOH): 223 sh, 287 (log ε 4.21), and 310 nm (4.15).

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