Reaction of 1,2-Dimethoxybiphenylene with Dichlorocarbene. Chemical Detection of the Bond Fixation in Biphenylene Derivatives

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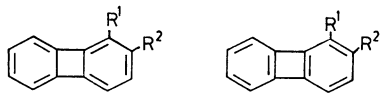
1,2-Dimethoxybiphenylene reacted with dichlorocarbene to give three chloro(methoxy)-6*H*-benzo[3,4]-cyclobuta[1,2]cyclohepten-6-one derivatives, two chloro(methoxy)fluorenones and two dimethoxyfluorenones. The reaction with dibromocarbene gave similar products. The formation of these products serves as unequivocal chemical evidence for bond fixation of 1,2-dimethoxybiphenylene. The chloro(methoxy)-6*H*-benzo[3,4]cyclobuta-[1,2]cyclohepten-6-one was led to 9-chloro-5-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one, the first tropolone analogue of biphenylene. This compound was shown to exist in only one of the two possible tautomers in contrast with general monocyclic tropolones.

Delocalization of π-electrons in benzene nucleus of aromatic compounds can be perturbed by some demands of an electronic environment or the incorporation of steric strain. The former is demonstrated in such molecules as naphthalene, phenanthrene, and other condensed-ring aromatic compounds, where some bond fixation in one benzene ring results from the fusion with the other benzene rings. The latter is illustrated in benzocyclobutene derivatives. Biphenylene provides the special case of double bond fixation in which both electronic and steric factors are participated: biphenylene prefers one canonical structure (**1a**) over the others, especially the structure (**1b**) carrying an anti-aromatic cyclobutadiene ring. Such a partial bond fixation of biphenylene was proved by electron diffraction[1] and X-ray analysis,[2] and suggested from the proton-proton coupling constant of the aromatic ring[3] and some chemical reactions.[4] It is also well-known that the carbene addition may be valuable as a chemical probe for the detection of bond fixation in aromatic molecules.[5] The carbene addition to naphthalenes, for example, takes place at C_1–C_2 and C_3–C_4 double bond but does not at C_2–C_3 double bond,[6] and methoxycarbonylcarbene reacts with biphenylene preferentially at the C_2–C_3 double bond.[7] In connection with our work on chemistry of small ring-annelated non-benzenoid aromatics, we are investigating the reaction of dichlorocarbene with methoxybiphenylenes, because the reaction can provide a convenient synthetic route to the troponoid analogues of biphenylene. The addition of dichlorocarbene to 1- (**2**) and 2-methoxybiphenylenes

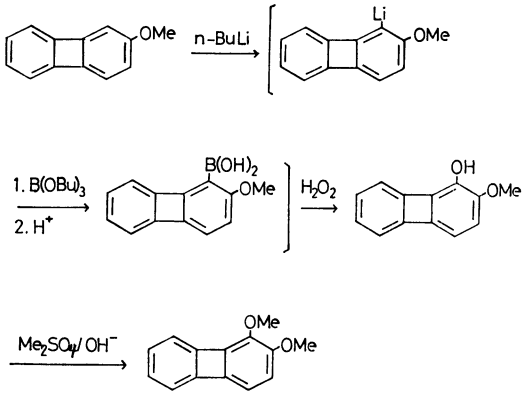


(1) $R^1=R^2=H$ (2) $R^1=OMe$, $R^2=H$ (3) $R^1=H$, $R^2=OMe$
(4) $R^1=R^2=OMe$

(**3**) takes place at C_2–C_3 and C_1–C_{8b}, or C_2–C_3 and C_4–C_{4a} double bonds, respectively, as previously reported.[8] We now wish to report the details about the addition of dihalocarbene to 1,2-dimethoxybiphenylene (**4**).[9]

Results and Discussion

2-Methoxybiphenylene (**3**)[10] was metalated with butyllithium and the lithio intermediate was allowed to react with tributyl borate, and the resulting 1-biphenylenylboronic acid was subsequently oxidized with hydrogen peroxide to give 1-hydroxy-2-methoxybiphenylene. This fact is parallel to the predominant α-metalation of biphenylene.[11] 1-Hydroxy-2-methoxybiphenylene was treated with dimethyl sulfate and alkali to afford 1,2-dimethoxybiphenylene (**4**) is a nearly quantitative yield.



1,2-Dimethoxybiphenylene (**4**) reacted with dichlorocarbene, generated from chloroform (3 equiv.) and 33% aqueous sodium hydroxide in the presence of catalytic amount of hexadecyltrimethylammonium chloride,[12] to give three chloro(methoxy)-6*H*-benzo[3,4]cyclobuta-[1,2]cyclohepten-6-ones (**8a**, **9a**, and **10a**), two chloro-(methoxy)fluorenones (**11a** and **12a**), and two dimethoxyfluorenones (**13** and **14**), along with the recovered starting material (70.0%). The yields, IR, NMR, and electronic spectra of these compounds are summarized in Table 1. Similarly, the reaction of **4** with dibromocarbene generated by the Dehmlow's method[13] gave two bromo(methoxy)-6*H*-benzo[3,4]cyclobuta[1,2]-cyclohepten-6-ones (**9b**) and (**10b**), two bromo-(methoxy)fluorenones (**11b**) and (**12b**), and 3,4-dimethoxyfluorenone (**14**). The yields, IR, ^{1}H-NMR, and electronic spectra of those products are summarized

Table 1. Spectral data for the products from the reaction of **4** with dichlorocarbene

Compound	Yield (%)	IR (cm^{-1})	^{1}H-NMR (ppm, Hz)	UV (nm, log ε)
8a	1.3	1613	3.80(s, 3H), 6.29(s, 2H), 7.0—7.5 (m, 4H)	298(4.73), 364(3.95), 379(3.87)
9a	0.6	1608	4.07(s, 3H), 6.20(d, 1H, J=9.0), 7.05—7.45 (m,4H), 7.42(d, 1H, J=9.0)	306(4.52), 336(4.06), 365(3.37)
10a	5.6	1602	4.08(s, 3H),6.37(d, 1H, J=13.2), 6.71(d, 1H, J=13.2), 7.12—7.4(m, 4H)	288(4.12), 312(4.54), 345(3.68), 387(3.92)
11a	4.7	1705	4.30(s, 3H), 7.18(d, 1H, J=7.8), 7.25—7.75(m, 5H)	264(4.85), 300(3.56), 328(3.50), 405(3.18)
12a	0.8	1706	3.95(s, 3H), 6.83(d, 1H, J=9.5), 7.56(d, 1H, J=9.5),7.25—7.8(m, 3H), 8.2(m, 1H)	254(4.72), 302(3.34), 370(3.65)
13[a]	0.9	1710	3.89(s, 3H), 4.12(s, 3H), 6.94(d, 1H, J=8.2), 7.19(d, 1H, J=8.2) 7.2—7.75(m, 4H)	
14[a]	1.9	1702	3.92(s, 3H), 3.96(s, 3H), 6.75 (d, 1H, J=8.3), 7.05—8.0 (m, H), 7.44(d, 1H, J=8.3)	

a) See Ref. 14.

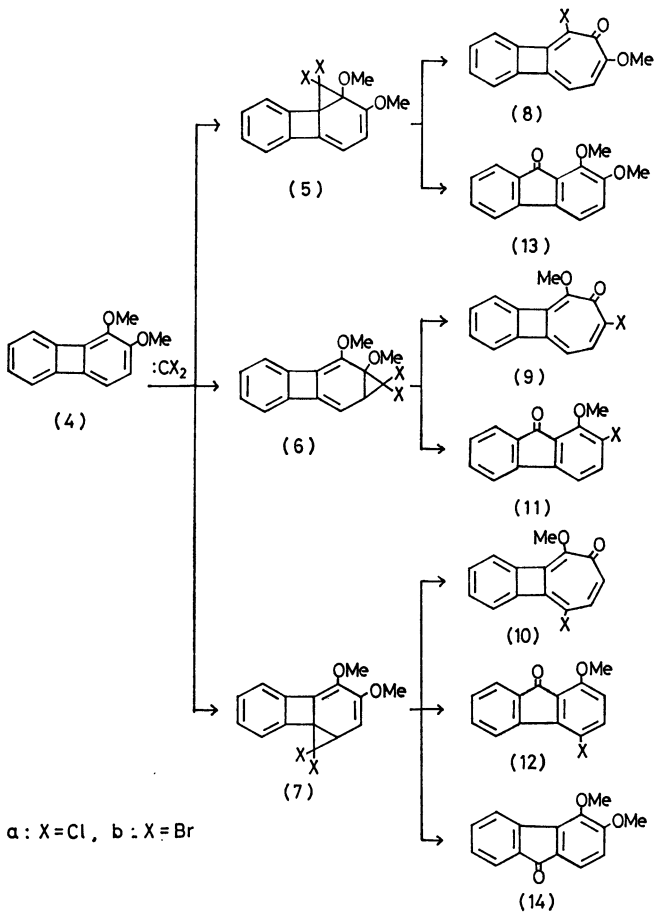
Table 2. Spectral data for the products from the reaction of **4** with dibromocarbene

Compound	Yield (%)	IR (cm^{-1})	^{1}H-NMR (ppm, Hz)	UV (nm, log ε)
9b	0.4	1605	4.08(s,3H), 6.13(d, 1H, J=8.5), 7.10—7.33(m, 4H), 7.77(d, 1H, J=8.5)	284(4.39), 306(4.59), 337(4.22)
10b	6.2	1602	4.06(s, 3H), 6.28(d, 1H, J=13.2), 6.79(d, 1H, J=13.2), 7.17—7.37 (m, 4H)	273(4.28), 314(4.60)
11b	4.1	1708	4.15(s, 3H), 7.14(d, 1H, J=7.4), 7.18—7.82(m, 5H)	264(4.79), 295(3.44), 332(3.29), 407(3.04)
12b	1.2	1705	3.98(s, 3H), 6.75(d, 1H, J=8.8), 7.54(d, 1H, J=8.8), 7.19—7.82 (m, 3H), 8.28—8.49(m, 1H)	255(4.65), 302(3.22), 314(3.22), 376(3.53)
14[a]	5.0			

a) See Ref. 14.

in Table 2. Chloro(methoxy)-6*H*-benzo[3,4]cyclobuta-[1,2]cyclohepten-6-one derivatives (**8a**, **9a**, and **10a**) had the molecular ion at *m/e* 244, and the corresponding bromo derivatives **9b** and **10b** had the molecular ion at *m/e* 290 in their mass spectra. These tropone derivatives showed the strong absorption near 1600 cm^{-1} in their IR spectra. Their electronic spectra were closely similar to each other and moreover to those of other 6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one derivatives reported previously.[8] In the NMR spectra, **10a** showed two olefinic doublets (AB type) at δ 6.37 and 6.71 ppm (J=13.2 Hz), and similarly **9a** at δ 6.20 and 7.42 ppm (J=9.0 Hz). The large coupling constant in the former and the small one in the latter mean the intervention of a double bond and a single bond, respectively, between the vicinal protons. Hence **10a** and **9a** can be assigned to 9- and 7-chloro-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-ones, respectively. The two olefinic protons in **8a** appeared accidentally as a singlet at δ 6.29 ppm but on addition of the shift reagent (Eu-fod) the singlet separated into two doublets (J=9.0 Hz), whereby **8a** is assigned to 5-chloro-7-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one. The NMR spectra of **10b** and **9b** showed two doublets at δ 6.28 and 6.79 (J=13.2 Hz), and 6.13 and 7.77 (J=8.5 Hz), respectively. Therefore, in a similar manner, **10b** and **9b** were assigned to 9-bromo- and 7-bromo-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-ones, respectively. Two dimethoxyfluorenones (**13** and **14**), and two chloro(methoxy)-fluorenones (**11a** and **12a**) were identified as 1,2- and 3,4-dimethoxyfluorenones,[14] and 2- and 4-chloro-1-methoxyfluorenones, respectively, by the mixed mp and IR spectral coincidence with the authentci samples. The latter two authentic compounds were prepared by another route: 1-methoxyfluorenones[15] was chlorinated with sulfuryl chloride in the presence of azobis-(isobutyronitrile) to give 2- and 4-chloro-1-methoxyfluorenones in 23 and 57% yields, respectively. 2-Bromo- (**11b**) and 4-bromo-1-methoxyfluorenones (**12b**) were assigned by the close similarity of their IR, UV, and ^{1}H-NMR spectra to those of **11a** and **12a**, respectively.

The formation of these products seems to be elucidated best as proceeding through the reaction path shown in Scheme 1. Dichlorocarbene added to **4a** giving the intermediate adducts **5**, **6**, and **7**. The adduct **7** converted spontaneously to **10** and, on the other hand, was attacked by a hydroxide ion at C_{4a} and C_{8b} to give **12** and **14**, respectively. The path to fluorenone derivatives is similar to that in the reaction between 1-methoxybiphenylene and dichlorocarbene.[8] Similarly, the adduct **5** afforded **8** and **13**, and the adduct **6** did **9** and **11**. Thus, the addition of dichlorocarbene must have taken place at the fixed C_{8b}–C_1, C_2–C_3, and C_4–C_{4a} double bonds of the canonical structure **4a** of 1,2-dimethoxybiphenylene, although dibromocarbene cannot add to the corresponding C_{8b}–C_1 double bond. No adduct from another canonical structure **4b** was obtained. This is the first example in the reaction of

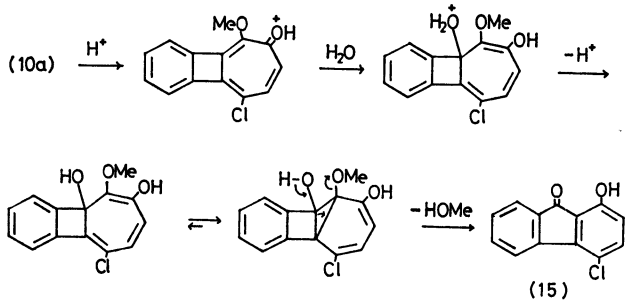


Scheme 1.

biphenylene series where all the possible products resulting from one of the Kekule's canonical structures are obtained, and this observation serves as unequivocal chemical evidence for the bond fixation of biphenylene system.

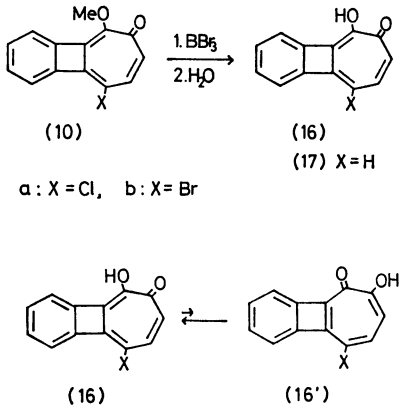
The addition of dichlorocarbene to C_{8b}–C_1, C_2–C_3, and C_4–C_{4a} double bonds of **4a** gave 2.2, 5.3, and 8.3% yields of the products, respectively, while the addition of dibromocarbene to the corresponding double bonds did in 0, 4.4, and 12.4% yields, respectively. In the reaction of **4** with dihalocarbene, the addition of the carbene to C_4–C_{4a} double bond was most favorable. The observation may be explained by the absence of steric hindrance in the approach of the carbene and by the best stabilization of the intermediate **7** in term of both conjugated methoxyl groups compared with others **5** and **6**. The predominant addition of dihalocarbene to C_4–C_{4a} double bond is also observed in the dichlorocarbene-addition to 2-methoxybiphenylene[8] but is in contrast with the exclusive addition of ethyl diazoacetate to the C_2–C_3 double bond of biphenylene itself.[7] In the latter, the addition of the carbene may be controlled by the electron-deficiency of C_{8b}–C_1 double bond induced with rehybridization of the junction carbon (C_{8b}).[16] The similar conjugative effect of methoxyl group was observed in the addition of dichlorocarbene to methoxynaphthalenes.[17,18] The less addition of dichlorocarbene to the C_{8b}–C_1 double bond than to the C_4–C_{4a} double bond seems to be in part due to the steric hindrance of the methoxyl group. Dibromocarbene added in the best yield to C_4–C_{4a} double bond and did not add to the most crowded double bond (C_{8b}–C_1). Therefore, the difference in yields between dichloro- and dibromocarbene addition to 1,2-dimethoxybiphenylene is probably due to the bulkiness of dibromocarbene compared with dichlorocarbene.

Attempted hydrolysis of the tropolone methyl ether **10a** with concentrated hydrochloric acid in boiling ethanol led to the hydroxyfluorenone derivative **15**. This facile rearrangement may be due to the release of the central four-membered ring strain, according to Scheme 2.



Scheme 2.

The tropolone methyl ether **10a** was treated with boron tribromide in dichloromethane at −65 °C and subsequently hydrolyzed to give 9-chloro-5-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**16a**), that is, the tropolone analogue of biphenylene in 93% yield. Similarly, bromo derivative **10b** was hydrolyzed to 9-bromo-5-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]-cyclohepten-6-one (**16b**) in 55% yield. Attempts to debrominate **10b** with tributyltin hydride[19] or zinc-copper couple in aqueous THF[20] in order to develope the route to the parent 5-hydroxy-6*H*-benzo[3,4]-cyclobuta[1,2]cyclohepten-6-one (benzo[3,4]cyclobuta-[1,2-*c*]tropolone) (**17**) were not successful. Catalytic hydrogenation of **16b** to **17** was also tried in vain.



The tautomerism **16**⇄**16'**, like monocyclic tropolones, is potentially expected. The equilibrium, however, proved to be imposed predominantly or exclusively to the tautomer **16** by the following facts. The electronic spectrum of **16a** is closely similar to that of the methyl

ether **10a**. The NMR coupling constant $J_{7,8}=13.3$ Hz of **16a** is nearly the same as that of the corresponding protons of **10a** ($J=13.2$ Hz). If the rapid equilibrium **16**⇄**16′** exsists, the coupling constant $J_{7,8}$ in **16** should be reduced to the corresponding value ($J_{6,7}=10.9$ Hz) of tropolone.[21] If the tautomer **16′** exists, the high-field shift of the benzenoid protons would be expected due to the paramagnetic ring current of the central four-membered ring, but actually this was not observed in **16a**. The absence of the contribution of **16′** is probably due to the instability of anti-aromatic cyclobutadiene structure in the central four-membered ring. The tropolone derivative **16a** gave a red coloration in chloroform layer with aqueous iron(III) chloride, like monocyclic tropolones. The tropolone **16a** could not be extracted with aqueous sodium hydrogen carbonate but reacted with aqueous sodium carbonate to give a red precipitate from which **16a** was recovered by neutralization with hydrochloric acid (2 mol dm^{-3}). The acidic property of **16a** is also shown by the fact that **16a** reacted with diazomethane to give the methyl ether **10a**, an alternate tautomeric methyl ether of **16a′** not being detected after careful search of the reaction mixture.

Experimental

1-Hydroxy-2-methoxybiphenylene. To a solution of 2-methoxybiphenylene (9.10 g, 0.05 mol) in dry ether (100 ml) was added the solution of butyllithium prepared from lithium (1.29 g, 0.186 mol) and butyl bromide (10.3 g, 0.075 mol) in dry ether (10 ml) under nitrogen. After the mixture was stirred for 1 h at room temperature, it was refluxed for 20 h. The resulting mixture was dropwise added to a solution of tributyl borate (19.1 g, 0.083 mol) in dry ether (60 ml) at −78 °C under nitrogen. After the addition had been completed, the cooling bath was removed and the mixture was stirred for 1 h at room temperature. To the mixture was added 10% HCl (25 ml). The ethereal layer was separated and the aqueous layer was extracted with ether. The ethereal solution combined was washed with water and then transfered to a 2-necked round-bottomed flask equipped with a reflux condenser. To the ethereal solution was added 30% hydrogen peroxide (22 ml) dropwise at such a rate that mild reflux was maintained. After the addition had been completed, the mixture was stirred for 0.5 h. The ethereal layer was separated and the aqueous layer was extracted with ether. The ethereal solution combined was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave yellow crystals, the silica gel chromatography of which gave the recovered starting material (0.81 g, 8.9%) and 1-hydroxy-2-methoxybiphenylene (yellow needles, mp 94—95 °C) (6.03 g, 60.9%). Found: C, 78.83; H, 5.27%. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09%. IR(KBr): 3380, 1498, 1438, 1138, and 739 cm^{-1}. NMR ($CDCl_3$): δ 3.77 (s, 3H), 5.6 (broad s, 1H), 6.08 (d, 1H, $J=7.6$ Hz), 6.25 (d, 1H, $J=7.6$ Hz), 6.42—6.83 (m, 4H). MS (75 eV): *m/e* 198 (M^+, 100%), 183 (M^+-CH_3, 75.5%), and 155 (M^+-CH_3-CO, 58%).

1,2-Dimethoxybiphenylene (4): To a solution of 1-hydroxy-2-methoxybiphenylene (5.94 g, 0.03 mol) and dimethyl sulfate (60.5 ml, 0.64 mol) in methanol (33 ml) was slowly added a solution of sodium hydroxide (54.9 g) in water (65 ml) under stirring at such a rate as the temperature of the solution was kept at 20—30 °C. After the addition had been completed, the mixture was warmed at 60 °C for 1 h. To the mixture was added water (465 ml). The crystals precipitated were collected by filtration and recrystallized from ethanol to give white-yellow leaflets (5.97 g, 94%), mp 132.5—133.5 °C. Found: C, 79.14; H, 5.74%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%. IR (KBr): 1488, 1407, 1292, 1240, 1228, 802, and 736 cm^{-1}. NMR($CDCl_3$): δ 3.77 (s, 3H), 3.98 (s, 3H), 6.13 (d, 1H, $J=7.5$ Hz), 6.88 (d, 1H, $J=7.5$ Hz), and 6.5—6.83 (m, 4H). MS(75 eV): *m/e* 212 (M^+ 100%), 197 (M^+-CH_3, 70%), and 169 (M^+-CH_3-CO, 59%).

Reaction of 1,2-Dimethoxybiphenylene (4) with Dichlorocarbene. A mixture of 1,2-dimethoxybiphenylene (**4**) (1.70 g, 8 mmol), chloroform (2 ml, 24 mmol), dichloromethane (5 ml), 33% aqueous sodium hydroxide (4 ml), and hexadecyltrimethylammonium chloride (25 mg) was stirred for 3 h at room temperature. The resulting red mixture was diluted with water and extracted with dichloromethane. The extract was washed twice with saturated aqueous sodium chloride and dried over sodium sulfate. After the solvent had been evaporated, the red-orange crystalline residue was chromatographed on silica gel with elution of benzene–ether. The following compounds were in turn eluted and purified with thin-layer chromatography and recrystallization. Their spectral data were summarized in Table 1. 2-Chloro-1-methoxyfluorenone (**11a**)(90 mg, 4.7%), yellow needles, mp 122—122.5 °C. Found: C, 68.84; H, 3.71%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. 1,2-Dimethoxybiphenylene (**4**) (recovery 70.0%). 3,4-Dimethoxyfluorenone (**14**) (36 mg, 1.9%), mp 142.5 °C, yellow rods (lit,[14] 145.5 °C). 4-Chloro-1-methoxyfluorenone (**12a**) (16 mg, 0.8%), fine yellow needles, mp 152—152.5 °C. Found: C, 68.68; H, 3.74%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. 1,2-Dimethoxyfluorenone (**13**) (17 mg, 0.9%), orange-yellow plates, mp 113—114 °C (lit,[14] 113 °C). 7-Chloro-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**9a**) (12 mg, 0.6%), fine yellow needles, mp 142—143 °C. Found: C, 68.68; H, 3.89%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. 9-Chloro-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]-cyclohepten-6-one (**10a**) (110 mg, 5.6%), yellow needles, mp 135—136 °C. Found: C, 68.60; H, 3.79%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. 5-Chloro-7-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**8a**) (26 mg, 1.3%), yellow crystals, mp 150—151 °C. Found: C, 68.76; H, 3.76%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%.

Reaction of 1,2-Dimethoxybiphenylene (4) with Dibromocarbene. To a mixture of 1,2-dimethoxybiphenylene (**4**) (1.70 g 8 mmol), dichloromethane (3 ml), 33% aqueous sodium hydroxide (9 g), and hexadecyltrimethylammonium chloride (30 mg) was dropwise added bromoform (3.5 ml, 40 mmol) for a period of 15 min on an ice–water bath. After the mixture was stirred for 30 min, the ice–water bath was removed. The mixture was further stirred for 1.5 h at room temperature. The resulting mixture was treated in the same work-up as that in the reaction of **4** with dichlorocarbene described above. The following products were isolated: 2-Bromo-1-methoxyfluorenone (**11b**) (95 mg, 4.1%), yellow needles, mp 72.8—73.8 °C. Found: C, 58.33; H, 3.10%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%. 1,2-Dimethoxybiphenylene (**4**) (1.07 g, 70% recovery). 3,4-Dimethoxyfluorenone (**14**) (96 mg, 5.0%), yellow needles, mp 139.7—140.2 °C (lit,[14] 145.5 °C). Found: C, 74.74; H, 5.05%. Calcd for $C_{15}H_{12}O_2$: C, 74.79; H, 5.03%. 4-Bromo-1-methoxyfluorenone (**12b**) (27 mg, 1.2%), yellow needles, mp 134.8—135.8 °C. Found: C, 58.16; H, 3.15%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%. 7-Bromo-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**9b**) (9 mg, 0.4%), yellow nee-

dles, mp 147—148 °C. Found: C, 58.00; H, 3.06%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%. 9-Bromo-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**10b**) (143 mg, 6.2%), yellow needles, mp 144.3—144.8 °C. Found: C, 58.17; H, 3.45%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%. The spectral data were summarized in Table 2.

2- *(**11a**) and 4-Chloro-1-methoxyfluorenones (**12a**).* A solution of 1-methoxyfluorenone[16] (210 mg, 1 mmol), sulfuryl chloride (160 mg, 1.2 mmol), and azobis(isobutyronitrile) (small amount) in dichlormethane (10 ml) was stirred for 1.5 h. After the solvent was evaporated up, the residue was chromatographed on silica gel with elution of benzene–ether. The first elute gave pale yellow crystals (mp 191—192 °C, 11 mg). The second elute gave 2-chloro-1-methoxyfluorenone (56 mg, 23%) as yellow needles (mp 120—121 °C). Found: C, 68.73; H, 3.61%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. The third fraction was 4-chloro-1-methoxyfluorenone (136 mg, 57%), as yellow needles, mp 152.5—153 °C. Found: C, 68.27; H, 3.67%. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%.

*4-Chloro-1-hydroxyfluorenone (**15**).* *A*: To a solution of 4-chloro-1-methoxyfluorenone (**10a**) (65 mg) in dichloromethane was added boron tribromide (0.12 ml) at −65 °C under nitrogen. The red-brown solution was stirred for 45 min at the same temperature. The solution was warmed up to room temperature and 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 sublimed under reduced pressure (110 °C/10 mmHg) to give a yellow crystalline product (55 mg, 90%), which was recrystallized from hexane, mp 158.5—159.5 °C. Found: C, 67.67; H, 2.99%. Calcd for $C_{13}H_7ClO_2$: C, 67.70; H, 3.06. UV (EtOH): 254 (log ε 4.76), 299 (3.35), 382 (3.61) nm. IR (KBr): 3387, 1699, 1614, 1297, 1183, and 741 cm^{-1}. NMR ($CDCl_3$): δ 6.74 (d, 1H, J=9.0 Hz), 7.29 (d, 1H, J=8.9 Hz), 7.3—7.8 (m, 3H), 8.13 (m, 1H), and 8.64 (broad s, 1H).

B: A mixture of 9-chloro-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**10a**) (37 mg), concd HCl (2 ml), and ethanol (5 ml) was refluxed for 4 h. The solution was poured into water, and the resulting mixture was extracted with ether. The ethereal extract was washed with water and dried over anhydrous sodium sulfate. After evaporation, the residue was chromatographed on silica gel to give, along with the starting material (16 mg, 45%), 4-chloro-1-hydroxyfluorenone (**15**) (18 mg, 52%), yellow needles, mp 158—159 °C. Admixed mp 158—159 °C.

*9-Chloro-5-hydroxy-6H-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**16a**).* To a solution of 9-chloro-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**10a**) (105 mg, 0.43 mmol) in dichloromethane (15 ml) was added boron tribromide (0.2 ml) at −65 °C under nitrogen. After being stirred for 30 min at the same temperature, the solution was warmed gradually to room temperature and poured into water. The mixture was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate. After the solution had been evaporated up, the residue was sublimed at about 140 °C/2 mmHg to give yellow crystals (92 mg, 93% yield), which were recrystallized from ethanol to give bright-yellow needles, mp 207—208 °C. Found: C, 67.87; H, 2.98%. Calcd for $C_{13}H_9ClO_2$: C, 67.70; H, 3.06%. UV (EtOH): 278 (log ε 4.27), 312 (4.64), 348 (3.86), 386sh (3.40), and 419 (3.10) nm. IR (KBr): 3250, 1602, 1569, 1373, 1215, 833, and 729 cm^{-1}. NMR (DMSO-d_6): δ 6.49 (d, 1H, J=13.3 Hz), 7.02 (d, 1H, J=13.3 Hz), 7.2—7.45 (broad s, 4H), and 10.3 (1H). MS (60 eV): *m/e* 230 (M^+, 63%) and 202 (M^+−CO, 100%).

*9-Bromo-5-hydroxy-6H-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**16b**).* To a solution of 9-bromo-5-methoxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**10b**) (118 mg, 0.41 mmol) in dichloromethane (15 ml) was added boron tribromide (0.4 ml) at −65 °C under nitrogen. After the solution had been stirred for 30 min at the same temperature and then poured into water. The mixture was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and then evaporated up. The residue was sublimated under reduced pressure. The crystals obtained were recrystallized from ethanol to give yellow needles, mp 199—200 °C. Found: C, 56.61; H, 2.37%. Calcd for $C_{13}H_7BrO_2$: C, 56.76; H, 2.56%. UV (EtOH): 213 (log ε 4.47), 280 (4.27), 313 (4.63), 347 (4.01), and 392 (3.42) nm. IR (KBr): 3260, 1595, 1570, 1375, 1220, and 750 cm^{-1}. NMR ($CDCl_3$): δ 6.49 (d, 1H, J=13.5 Hz), 7.04 (d, 1H, J=13.5 Hz), and 7.20—7.42 (m, 4H).

*Reaction of (**16a**) with Diazomethane.* To a solution of diazomethane in ether (20 ml) prepared from *N*-nitrosomethylurea (103 mg, 1 mmol) was added 9-chloro-5-hydroxy-6*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (**16a**) (40 mg, 0.17 mmol) on an ice-water bath. The solution was stirred for 6 h. The solution was extracted with aqueous sodium carbonate. The ethereal layer was dried over anhydrous sodium sulfate, and then evaporated up. The residue was chromatographed on silica gel with elution of dichloromethane to give the methyl ether **10a** as yellow crystals (38 mg, 90%). The aqueous layer was acidified with HCl (2 mol dm^{-3}) and then extracted with ether. From the ethereal extract the starting material was recovered (3 mg, 7%).

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