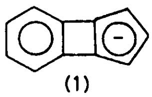
Nonbenzenoid Aromatic Compounds containing a Fused Four-membered Ring. Formation and Properties of Benzo[3,4]cyclobuta[1,2]cyclohepten-6-one Derivatives [1]

By **Masaru Sato, Seiji Ebine,* and Josuke Tsunetsugu,** Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

The ring-enlargement reaction of 1-methoxybiphenylene with dichlorocarbene gives 5-chlorobenzo[3,4]cyclobuta[1,2]cyclohepten-6-one (6) as well as fluorenone derivatives (7) and (8), although in low yields. Similar reactions of 2-methoxybiphenylene and its derivatives give the corresponding benzocyclobutacycloheptenones (11), (12), (14), (15), (17), and (18). The spectral data of the benzocyclobutacycloheptenones suggest that the four-membered ring assumes a tetramethylenecyclobutane (or dimethylenecyclobutene) form, excluding a potential cyclobutadiene form, and the seven-membered ring resembles the tropone ring of benzocycloheptenone.

CONSIDERABLE interest has recently been focused on the properties of fused polycyclic compounds containing both $4n\pi$- and $(4n + 2)\pi$-electron ring systems. Biphenylene,[2] a representative of this type of compound, is stable despite the presence of a $4n\pi$-electron system. The stability appears to be due to the fact that the four-membered ring is in a tetramethylenecyclobutane form, rather than a cyclobutadiene form, as shown by *X*-ray analysis.[3] However, a contribution of a cyclobutadiene form to biphenylene is suggested by a paramagnetic ring-current effect towards the benzenoid protons in the ^{1}H n.m.r. spectrum [4] and the ring junction carbon atoms in the ^{13}C n.m.r. spectrum.[5] Replacement of one of the benzene rings in biphenylene with a heteroaromatic ring produces analogues such as thianorbiphenylene,[6] monoazabiphenylene,[7] and 5,10-diazabenzo[*a*]biphenylene,[8] which have been shown to retain properties similar to those of the parent biphenylene. Biphenylene analogues in which one of the benzene rings is replaced with a nonbenzenoid aromatic ring, such as norbiphenylene anion (1),[9] homobiphenylene cation (2),[10] benzo[*a*]benzo[3,4]cyclobuta[1,2-*d*]cycloheptene cation (3),[11] and dibenzo[*a,c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-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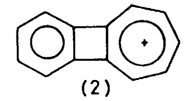
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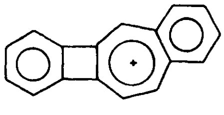
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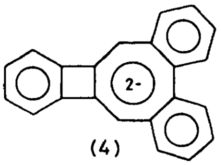
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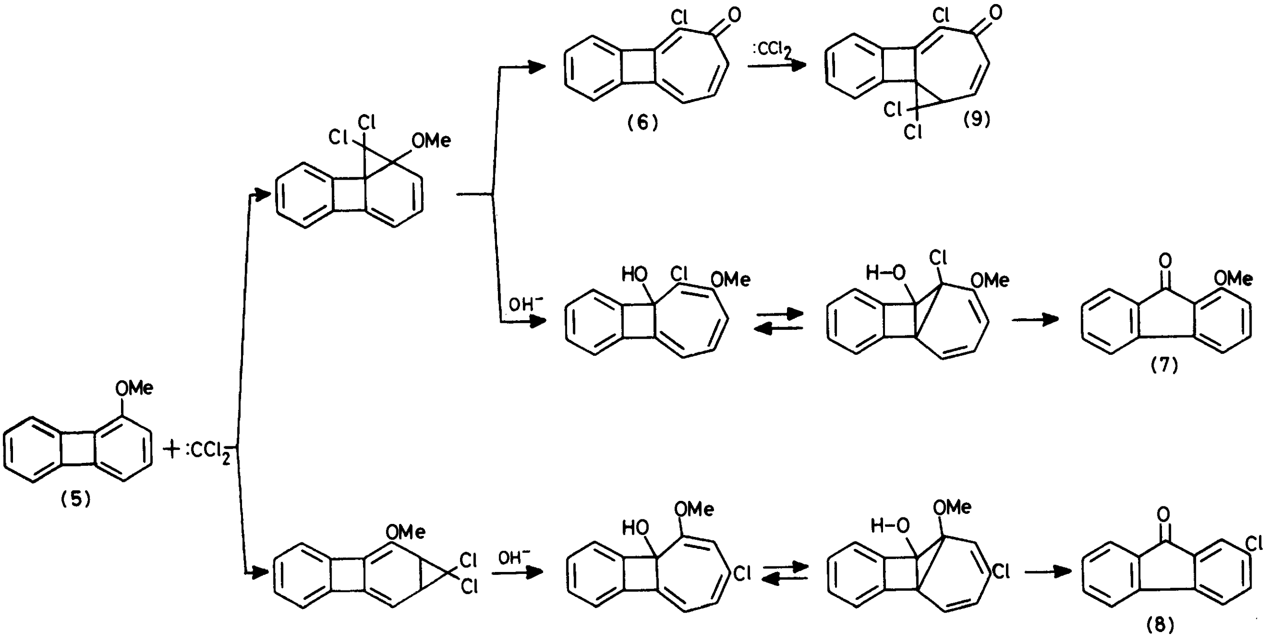
octene dianion (4),[12] have been described. We now report the synthesis of benzo[3,4]cyclobuta[1,2]cyclohepten-6-one derivatives, in which one of the benzene rings of biphenylene is replaced by a neutral non-benzenoid aromatic tropone ring, and discuss the effect of benzocyclobutadiene annelation on the tropone nucleus in these compounds.



Scheme 1

Benzo[3,4]cyclobuta[1,2]cyclohepten-6-one derivatives were prepared in one step by ring enlargement of methoxybiphenylenes with dichlorocarbene. The reaction of 1-methoxybiphenylene with dichlorocarbene, generated by the action of alkali on chloroform in the presence of trimethylhexadecylammonium chloride,[13] afforded 5-chlorobenzo[3,4]cyclobuta[1,2]cyclohepten-6-one (6) in 1.7% yield along with 55—65% of the starting biphenylene. The mass spectrum of (6) showed a parent peak at m/e 214 (22%) and a base peak at 186, due to loss of CO, typical of troponoids.[14] The electronic spectrum showed a characteristic strong absorption at 294 nm (log ε 4.55). The ^{1}H n.m.r. spectrum showed signals at δ 7.1—7.5 (4 H, m, benzenoid), 6.72 (1 H, dd, $J_{7,8}$ 12.6, $J_{8,9}$ 6.9 Hz, H-8), 6.51 (1 H, dd, $J_{7,9}$ 1.4 Hz, H-7), and 6.31 (1 H, dd, H-9). The i.r. spectrum showed a tropone-like carbonyl absorption at 1 603 cm^{-1}. Two other products, 1-methoxyfluorenone (7) [15] (0.8%) and 2-chlorofluorenone (8) [16] (1.3%), were identical (mixed m.p. and i.r. spectrum) with authentic samples.

Use of a longer reaction time gave an additional product, tentatively identified as the chlorobenzocyclobutacycloheptenone–dichlorocarbene adduct (9). The mass spectrum showed peaks at m/e 296 (M^+, 0.1%), 261 ($M^+ - \text{Cl}$, 19%), and 233 ($M^+ - \text{Cl} - \text{CO}$, 100%). The i.r. spectrum showed strong absorptions at 1 643 and 1 612 cm^{-1}. The n.m.r. spectrum showed a doublet (J 6.4 Hz) in the aliphatic region (δ 3.08) assigned to H-9, and a doublet (J 13.0 Hz) and a double doublet (J 13.0 and 6.4 Hz) in the olefinic region (δ 6.33 and 6.66), assigned to H-7 and -8, respectively.

The reaction of 2-methoxybiphenylene with dichlorocarbene under similar conditions gave 7-chlorobenzo[3,4]cyclobuta[1,2]cyclohepten-6-one (11) (3.4%) and its 9-chloro-isomer (12) (1.2%). The mass, i.r., and u.v. spectra of (11) and (12) were very similar to those of the 5-chloro-isomer (6). The n.m.r. spectrum of (11) exhibited a singlet at δ 6.59 assignable to H-5, and two doublets at δ 6.18 and 7.35 with a small coupling constant (J 9.0 Hz) assignable to H-9 and -8, respectively. A large low-field shift of the H-8 signal is probably due to the combined electron-attracting effect of the carbonyl and chloro-substituents.* The n.m.r. spectrum of (12), on the other hand, showed a doublet (J 1.8 Hz) at δ 6.41, assigned to H-5, coupled with H-7. A large coupling constant (J 13.0 Hz) between H-8 [δ 6.63 (d)] and H-7 [δ 6.43 (dd)] was in agreement with structure (12).

Similarly, the reaction of 2,6-dimethoxybiphenylene (13) with dichlorocarbene provided 2-methoxy-7-chloro- (14) (3.2%) and 2-methoxy-9-chloro-benzo[3,4]cyclo-

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* The H-7 signal of 6-chloro-9-methoxybenzocyclohepten-5-one appears at δ 7.58 in a similar manner; see ref. 17.

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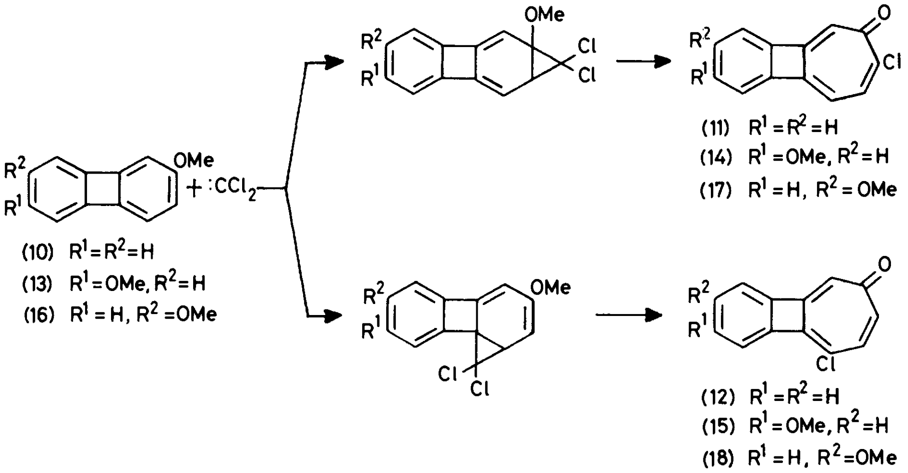
buta[1,2]cyclohepten-6-one (15) (2.0%). The reaction of 2,7-dimethoxybiphenylene (16) with dichlorocarbene gave 3-methoxy-7-chloro- (17) (3.9%) and 3-methoxy-9-chloro-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (18) (2.5%).

These methoxybiphenylene–dichlorocarbene additions can be considered to proceed in the following manner. Addition of dichlorocarbene to 1-methoxybiphenylene (5) occurs at the 1,8b-bond to give 5-chlorobenzo[3,4]-cyclobuta[1,2]cyclohepten-6-one (6) and 1-methoxy-fluorenone (7), and at the 2,3-bond to give 2-chloro-fluorenone (8) (Scheme 1). Hydroxide ion should play an important part in the formation of the fluorenone derivatives. This is supported by the fact that the reaction of (5) with Seyferth's reagent as a source of dichlorocarbene gave (6) (1.5%) as the sole isolated product, no fluorenone derivative being detected. The observed orientation of dichlorocarbene addition to methoxybiphenylene is explicable as follows. The double-bond character of biphenylene is shown to be highest at the 2,3-bond and next highest at the 1,8b-bond, by HMO calculation [18] and by the reaction of biphenylene with ethyl diazoacetate.[19] It can, therefore, be presumed that the 2,3-bonds of (5) and (10) are highly reactive and that the 1,8b-bond of (5) and the 4,4a-bond of (10) are also reactive because of activation by the methoxy-groups. Thus the addition takes place at the 1,8b- and 2,3-bonds of (5) and at the 2,3- and 4,4a-bonds of (10). The same orientation was observed with other 2-methoxybiphenylenes (13) and (16). In the dichloro-carbene–methoxybiphenylene additions described here, no product was isolated which would result from addition of dichlorocarbene at the 1,2- and 3,4-bonds. This indicates that the benzene rings of biphenylene are largely fixed in one of two canonical formulae, as illustrated in the Schemes. A similar trend has been observed in dichlorocarbene–methoxynaphthalene additions.[17]



SCHEME 2

The electronic spectrum of the 7-chloro-isomer (11) is shown in the Figure, along with those of 2-chloro-tropone [20] and 6-chlorobenzocyclohepten-7-one.[21] The spectra of the 5- (6) and 9-chloro-isomers (12) were very similar to that of (11) (Table 1). The shapes of the spectra of the benzocyclobutacycloheptenones seem to resemble that of benzocyclohepten-7-one, although the absorptions of the former show a considerable bathochromic shift particularly in the long-wave region as compared with the latter, suggesting that troponoid characteristics remain to a considerable extent in the benzocyclobutacycloheptenones.

The lower frequency i.r. absorption (1 603 cm^{-1}) of the 5- (6) and 7-chloro isomers (11) in the region of 1 550—1 630 cm^{-1} (Table 2), presumably assignable to carbonyl stretching,[22] is at higher frequency than that of 2-chlorotropone (1 590 cm^{-1}),[20] but is the same as that of 6-chlorobenzocyclohepten-7-one (1 605 cm^{-1}).[21] A pair of weak absorptions in the region 1 640—1 710 cm^{-1} suggests a slight contribution from a dimethylene-cyclobutene form.[23]

The benzenoid protons of 5- (6), 7- (11), and 9-chloro-benzo[3,4]cyclobuta[1,2]cyclohepten-6-one (12), as well as those of the parent compound,[24] resonate in the normal region (δ 7.1—7.5; Table 3), in contrast with the fact that the corresponding protons of biphenylene,[4] monoazabiphenylene,[7] and thianorbiphenylene [6] resonate at δ 6.6—6.9. It has been suggested that the central four-membered ring in the latter compounds sustains a paramagnetic ring current, resulting in a high-field shift of the benzenoid protons. The absence of a high-field

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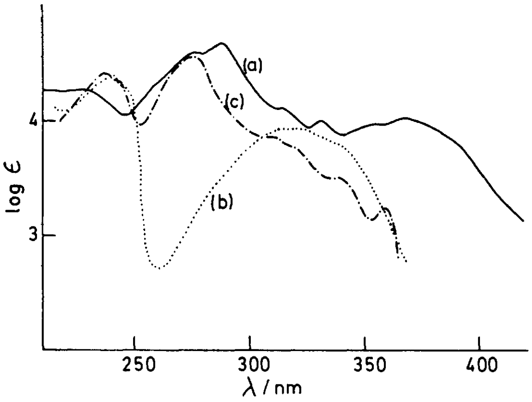
shift of the benzenoid protons in compounds (6), (11), and (12), therefore, suggests that the 4b,9a-bond in the seven-membered ring has little π-bond character and that the central four-membered ring is in a dimethylenecyclobutene or tetramethylenecyclobutane form, excluding a potential cyclobutadiene form. The n.m.r. chemical shifts of the seven-membered ring protons of compounds (6), (11), and (12) (δ 6.18—6.72), except for H-8 of (11), appear at higher field than those of tropone (δ 7.0).[25] The coupling constant difference for compound (6) ($J_{7,8} - J_{8,9} = 5.7$ Hz) is considerably larger than the corresponding values for tropone ($J_{2,3} - J_{3,4} = 3.7$ Hz) and 2-chlorotropone ($J_{6,7} - J_{5,6} = 4.1$ Hz).[26] These two facts indicate an increased bond alternation in the seven-membered ring of the benzocyclobutacycloheptenones, as compared with monocyclic tropones. The coupling constants between H-8 and H-9 in (6) (6.9 Hz) and (11) (9.0 Hz) were smaller than the corresponding values for 2-chlorotropone ($J_{5,6}$ 8.3, $J_{3,4}$ 9.5 Hz),[26] respectively, suggesting that the planarity of 2-chlorotropone [27] is significantly reduced in the seven-membered ring in benzocyclobutacycloheptenones.

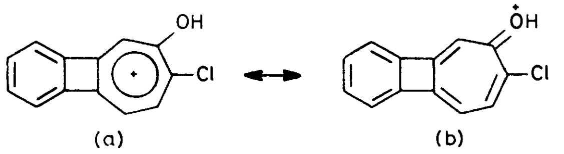


Electronic spectra of (a) 7-chlorobenzo[3,4]cyclobuta[1,2]cyclohepten-6-one, (b) 2-chlorotropone, and (c) 6-chlorobenzocyclohepten-7-one (in ethanol)

The 7-chlorobenzocyclobutacycloheptenone (11) dissolved in sulphuric acid showed an electronic spectrum closely similar to that of homobiphenylene cation (2),[10] indicating the formation of 7-chloro-6-hydroxyhomobiphenylene cation (19). The n.m.r. low-field shift (Δδ 0.5 p.p.m.) of the seven-membered ring protons on dissolving (11) in trifluoroacetic acid is considerably smaller than that (Δδ 1.1—2.0 p.p.m.) of tropone itself. The chemical shifts of the seven-membered ring protons in the cation (19) carrying a hydroxy-group are higher than those for the parent cation (2),[10] whereas those of tropylium and hydroxytropylium ions are almost identical.[26] The reason may be that contributions to the structure of the cation (19) from the protonated cycloheptatrienone structure (19b) where the positive charge is localized on the hydroxy-group, rather than the tropylium structure (19a), are significant.

The basicity of 7-chlorobenzo[3,4]cyclobuta[1,2]cyclohepten-6-one (11) was determined by examining the u.v. spectrum as a function of H_0 of the solvent (aqueous sulphuric acid). Although (11) did not behave as an ideal Hammett base, a rough titration curve was obtained with a mid-point (half protonation) at $H_0(\mathrm{p}K_\mathrm{R})$ -3.6. This can be compared with the $\mathrm{p}K_\mathrm{R}$ value (-3.5) for 6-chlorobenzocyclohepten-7-one, indicating that the basicity of (11) is closely similar to that of benzocycloheptenone derivatives, and intermediate between those of tropone (-1.02) [28] and dibenzocycloheptenone (-5.25).[29] An analogous trend has been observed in the benzocycloheptene cation series: benzocycloheptene cation ($\mathrm{p}K_\mathrm{R}^+$ $+1.7$),[30] benzo[*a*]benzo[3,4]cyclobuta[1,2-*d*]cycloheptene cation (3) (-1.3),[11] dibenzocycloheptene cation (-1.9).[30]

Finally, 2-methoxy- (10) and 2,6- (13) and 2,7-dimethoxy-biphenylenes (16) were prepared according to the method of Campbell and Rees.[31] The oxidation of 1-amino-5-methoxybenzotriazole with lead tetra-acetate gave a mixture of (13) and (16) in 79% yield, which was separated by chromatography on alumina. The oxidation of a mixture of 1-aminobenzotriazole and 1-amino-5-methoxybenzotriazole gave biphenylene (57%), (6) (33%), and a mixture of (13) and (16) (24%).



(19)

EXPERIMENTAL

Materials.—1- [32] and 2-Methoxybiphenylenes [32] were prepared according to the literature. 2,6- [33] and 2,7-Dimethoxybiphenylenes [34] were prepared from 2-nitro-4-methoxyaniline by the method of Campbell and Rees.[31] The intermediates and products are described below.

Diethyl mesoxalate 2-nitro-4-methoxyphenylhydrazone (72% yield), yellow needles, had m.p. 132—133° (from ethanol) (Found: C, 49.75; H, 5.0; N, 12.45. $C_{14}H_{17}N_2O_7$ requires C, 49.55; H, 5.05; N, 12.4%), $\nu_{max.}$ (KBr) 3 420, 2 920, 1 720, 1 580, 860, and 805 cm^{-1}, δ ($CDCl_3$) 1.40 (6 H, dt, 2 × CH_3), 3.90 (3 H, s, OCH_3), 4.42 (4 H, dq, 2 × CH_2), 7.34 (1 H, dd, H-5, *J* 2.5 and 9 Hz), 7.71 (1 H, d, H-3, *J* 2.5 Hz), and 8.17 (1 H, d, H-7, *J* 7 Hz).

Diethyl (*5-methoxybenzotriazol-*1*-yl*)*iminomalonate* (82.3%

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yield), dark-red prisms, had m.p. 82—83° (from ethanol) (Found: C, 52.5; H, 4.9; N, 17.75. $C_{14}H_{16}N_4O_5$ requires C, 52.5; H, 5.05; N, 17.5%), $\nu_{max.}$ (KBr) 1 737, 1 255, and 1 024 cm^{-1}, δ ($CDCl_3$) 1.42 (6 H, dt, 2 × CH_3), 3.93 (3 H, s, OCH_3), 4.53 (4 H, dq, 2 × CH_2), 7.22 (1 H, dd, H-6), 7.41br (1 H, s, H-4), and 7.79 (1 H, d, H-7, *J* 7 Hz).

1-*Amino*-5-*methoxybenzotriazole* (85% yield), plates, had m.p. 135—136° (from ethanol) (Found: C, 51.25; H, 4.6; N, 34.25. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.15%), $\nu_{max.}$ (KBr) 3 300, 3 230, 1 415, 1 283, 830, and 801 cm^{-1}, δ ($CDCl_3$) 3.89 (3 H, s, OCH_3), 5.34br (2 H. s, NH_2), 7.17 (1 H, m, H-6), 7.27 (1 H, d, H-4, *J* 1.3 Hz), and 7.56 (1 H, dd, H-7, *J* 1.3 and 9 Hz).

Oxidation of 1-amino-5-methoxybenzotriazole with lead tetra-acetate, by the procedure of Campbell and Rees,[31] gave a mixture of two biphenylenes (79% yield), which was separated by alumina column chromatography into 2,6-[33] and 2,7-dimethoxybiphenylenes.[34]

TABLE 1

Electronic spectra of benzo[3,4]cyclobuta[1,2]cyclohepten-6-ones (in ethanol)

Compound		$\lambda_{max.}$/nm (log ε)
5-Cl	(6)	282.5sh (4.14), 294 (4.67), 325sh (3.87), 345 (3.70)
7-Cl	(11)	225 (4.28), 278sh (4.61), 287.9 (4.69), 313.4 (4.12), 331.3 (3.99), 365.2 (4.02)
9-Cl	(12)	218 (4.23), 289.3 (4.55), 328 (3.79), 360 (3.79)
7-Cl-2-MeO	(14)	232 (4.38), 305.6 (4.75), 338 (4.11), 378.8 (3.95), 399.2 (3.92)
9-Cl-2-MeO	(15)	226 (4.32), 308 (4.55), 312 (4.54), 375 (3.69), 395 (3.61)
7-Cl-3-MeO	(17)	229.7 (4.19), 278.7 (4.45), 298 (4.40), 340 (3.93), 379 (4.12), 395 (4.11)
9-Cl-3-MeO	(18)	228 (4.30), 281sh (4.40), 298 (4.45), 337 (3.80), 373 (4.06), 389 (4.03)

2-Methoxybiphenylene[32] was also obtained on oxidation of a mixture of 1-aminobenzotriazole and 1-amino-5-methoxybenzotriazole with lead tetra-acetate. Thus, 1-aminobenzotriazole (8.66 g) and 1-amino-5-methoxybenzotriazole (4.33 g) gave a mixture of biphenylene (2.84 g), 2-methoxybiphenylene (1.62 g), and dimethoxybiphenylenes (0.66 g).

Standard Procedure for Methoxybiphenylene–Dichlorocarbene Addition.—The methoxybiphenylene (8 mmol), chloroform (2 ml, 2.4 mmol), aqueous 50% sodium hydroxide (4 ml), and hexadecyltrimethylammonium chloride (25 mg) were placed in a 30 ml Erlenmeyer flask equipped with a potassium hydroxide tube, and stirred at about 20 °C for 2 h. [Dichloromethane (2 ml) was added to the mixture as a diluent if the methoxybiphenylene was insufficiently soluble in 2 ml of chloroform.] The mixture was then diluted with water and extracted with dichloromethane. The extract was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and evaporated and the residue was chromatographed on silica gel (elution with benzene–ether). Each fraction separated was purified by further chromatography or sublimation.

5-*Chlorobenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*one* (6), 1-*Methoxyfluorenone* (7), *and* 2-*Chlorofluorenone* (8).—1-Methoxybiphenylene was subjected to the reaction with dichlorocarbene. After the standard work-up, chromatography of the reaction mixture, followed by re-chromatography and sublimation, gave three products, besides the starting material (0.93 g, 64%). The first product, yellow crystals, m.p. 123° (22 mg, 1.3%), was identified as 2-chlorofluorenone by comparison (mixed m.p. and i.r. spectra) with an authentic sample.[16] The second product, pale yellow needles (30 mg, 1.7%), was 5-*chlorobenzo*[3,4]-*cyclobuta*[1,2]*cyclohepten*-6-*one* (6), m.p. 178—179° (from ethanol) (Found: C, 72.6; H, 3.15. $C_{13}H_7ClO$ requires C, 72.75; H, 3.3%); for spectra see Tables 1—3. The third product was identified as 1-methoxyfluorenone (13 mg, 0.8%) (yellow needles, m.p. 142.5°) by comparison (mixed m.p. and i.r. spectra) with an authentic sample.[15]

When the reaction was run for 4—5 h, an additional product, crystals, m.p. 155—156.5°, was isolated and tentatively assigned the structure (9) of the dichlorocarbene *adduct* from the following spectral data: $\nu_{max.}$ (KBr) 1 687w, 1 643s, 1 612m, 1 210, 930, and 756s cm^{-1}, δ ($CDCl_3$) 3.08 (1 H, d, *J* 6.4 Hz), 6.33 (1 H, d, *J* 13.0 Hz), 6.66 (1 H, dd, *J* 6.4 and 13.0 Hz), and 7.2—7.6 (4 H, m) (Found: C, 56.7; H, 2.25. $C_{14}H_7Cl_3O$ requires C, 56.5; H, 2.35%).

7- (11) *and* 9-*Chlorobenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*ones* (12).—2-Methoxybiphenylene–dichlorocarbene addition was carried out by the standard procedure. Re-chromatography and sublimation of the reaction mixture gave two products, as well as starting material (1.02 g, 70%). One product (58 mg, 3.4%) was recrystallized from hexane–benzene to give 7-*chlorobenzo*[3,4]*cyclobuta*[1,2]-*cyclohepten*-6-*one* (11) as yellow needles, m.p. 157—158° (Found: C, 73.0; H, 3.1. $C_{13}H_7ClO$ requires C, 72.75; H, 3.3%). The other product, orange crystals (21 mg, 1.2%), was recrystallized from benzene–hexane to give 9-*chlorobenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*one* (12), m.p. 147.5—148° (Found: C, 72.5; H, 3.25%). For spectra see Tables 1—3. The electronic spectrum of (11) in sulphuric acid showed $\lambda_{max.}$ 228 (log ε 4.29), 255.4 (4.03), 332 (4.72), 392 (3.73), 408 (3.84), and 495 nm (2.95). Its n.m.r. spectrum in trifluoroacetic acid showed δ 6.61 (1 H, d, $J_{8,9}$ 9.5 Hz, H-9), 7.03br (1 H, s, H-5), 7.91 (1 H, d, H-8), and 7.1—7.4 (4 H, m, aromatic).

TABLE 2

I.r. spectra of benzo[3,4]cyclobuta[1,2]cyclohepten-6-ones (KBr discs)

Compound		$\nu_{max.}$/cm^{-1}
5-Cl	(6)	1 689, 1 643, 1 613, 1 603
7-Cl	(11)	1 690, 1 643, 1 603
7-Cl-2-MeO	(14)	1 693, 1 642, 1 596, 1 580
7-Cl-3-MeO	(17)	1 699, 1 641, 1 606, 1 592
9-Cl	(12)	1 695, 1 650, 1 600, 1 583
9-Cl-2-MeO	(15)	1 702, 1 643, 1 585, 1 578
9-Cl-3-MeO	(18)	1 702, 1 640, 1 585, 1 570

7- (14) *and* 9-*Chloro*-2-*methoxybenzo*[3,4]*cyclobuta*[1,2]-*cyclohepten*-6-*one* (15).—2,6-Dimethoxybiphenylene–dichlorocarbene addition was carried out by the standard procedure. Re-chromatography and sublimation gave two products, as well as starting material (0.81 g, 47%). One product, yellow crystals (62 mg, 3.2%), was recrystallized from ethanol to give 7-*chloro*-2-*methoxybenzo*[3,4]*cyclobuta*-[1,2]*cyclohepten*-6-*one* (14) as yellow needles, m.p. 162—163° (Found: C, 69.0; H, 3.55. $C_{14}H_9ClO_2$ requires C, 68.7; H, 3.7%). The other (40 mg, 2.0%) was recrystallized from cyclohexane–benzene to give 9-*chloro*-2-*methoxybenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*one* (15) as yellow crystals, m.p. 166—167° (Found: C, 68.6; H, 3.55%). For spectra see Tables 1—3.

TABLE 3

N.m.r. data of benzo[3,4]cyclobuta[1,2]cyclohepten-6-ones (60 MHz; $CDCl_3$)

Compound		δ					J/Hz
		Benzenoid	H-5	H-7	H-8	H-9	
5-Cl [a]	(6)	7.18—7.58 (4 H, m)		6.51	6.72	6.31	$J_{7,8}$ 12.6, $J_{8,9}$ 6.9, $J_{7,9}$ 1.4
7-Cl	(11)	7.16—7.33 (4 H, m)	6.59		7.35	6.18	$J_{8,9}$ 9.0
7-Cl-2-MeO	(14)	6.64—6.89 (2 H, m), 7.17 (1 H, d, J 8.2 Hz)	6.43		7.30	6.10	$J_{8,9}$ 9.0
7-Cl-3-MeO	(17)	6.66—6.92 (2 H, m), 7.07 (1 H, d, J 8.3 Hz)	6.51		7.29	5.98	$J_{8,9}$ 8.9
9-Cl	(12)	7.1—7.5 (4 H, m)	6.41	6.43	6.63		$J_{7,8}$ 13.0, $J_{5,7}$ 1.8
9-Cl-2-MeO	(15)	6.69—7.0 (2 H, m), 7.27 (1 H, d, J 8.0 Hz)	6.29	6.25	6.61		$J_{7,8}$ 14.0, $J_{5,7}$ 1.9
9-Cl-3-MeO	(19)	6.71—6.95 (2 H, m), 7.28 (1 H, d, J 9.0 Hz)	6.37	6.20	6.61		$J_{7,8}$ 13.0, $J_{5,7}$ 1.9
Unsubst. [b]		7.2	6.46	6.38	6.61	6.27	$J_{7,8}$ 12.0, $J_{8,9}$ 7.6 $J_{5,9}$ 1.0, $J_{7,9}$ 0.9

[a] Taken at 100 MHz. [b] Data from ref. 24.

7- (17) *and* 9-*Chloro*-3-*methoxybenzo*[3,4]*cyclobuta*[1,2]-*cyclohepten*-6-*one* (18).—2,7-Dimethoxybiphenylene (16) was subjected to addition with dichlorocarbene by the standard procedure. Re-chromatography and sublimation gave starting material (0.97 g, 58%) and two products. One product, orange crystals (77 mg, 3.9%) was recrystallized from cyclohexane–benzene to give 7-*chloro*-3-*methoxybenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*one* (17) as orange needles, m.p. 167—167.5° (Found: C, 68.85; H, 3.5. $C_{14}H_9ClO_2$ requires C, 68.7; H, 3.7%). The other (48 mg, 2.5%) was recrystallized from benzene–cyclohexane to give 9-*chloro*-3-*methoxybenzo*[3,4]*cyclobuta*[1,2]*cyclohepten*-6-*one* (18) as yellow needles, m.p. 188.5—189.5° (Found: C, 68.65; H, 3.7%). For spectra see Tables 1—3.

Basicity of the Benzocyclobutacycloheptenone (11).—This was determined by measuring the u.v. spectrum of (11) in aqueous sulphuric acid. The pK_R value was determined by the method of Davis and Geissman.[35] The difference [ε (332 nm) — ε (277 nm)] was plotted over ten points of an H_0 range of -9.25 to -2.33. A rough titration curve was obtained, whose midpoint, corresponding to 50% protonation, was at p$K_R = H_0 = -3.6$.

The basicity of 6-chlorobenzocyclohepten-7-one was determined in a similar manner (pK_R -3.5).

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[35] C. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3507.