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The Oxidation of Biphenylene and Its Derivatives with $Mn(OAc)_3$ and $Pb(OAc)_4$

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The reaction of biphenylene with $Pb(OAc)_4$ gave 2-substituted biphenylenes and 2,3-biphenylenedione. The reaction of 2-methylbiphenylene and 2,3-dimethylbiphenylene with $Mn(OAc)_3$ yielded products in which the methyl substituent had been oxidized. The reaction of 2-methoxybiphenylene with $Pb(OAc)_4$ gave 2-acetoxy-3-methoxybiphenylene and *r*-2,*c*-3-diacetoxy-2-methoxy-2,3-dihydrobiphenylene, which is the first example of a 2,3-dihydrobiphenylene. The reactions of 2-carboxy-, 2-methoxycarbonyl- and 2,7-dibromobiphenylene with $Mn(OAc)_3$ and (in part) with $Pb(OAc)_4$ yielded nuclear acetoxymethylated products. The conversion of *r*-2,*c*-3-diacetoxy-2-methoxy-2,3-dihydrobiphenylene into 5,10-diacetoxy-7(8*H*)-benzocyclooctenone was observed.

A previous study on the oxidation of biphenylene (**1**) with $Mn(OAc)_3$ resulted in the formation of a propellane, 7-oxa-10,11-benzotricyclo[4.3.2.$0^{1,6}$]undeca-2,4,10-triene-8-one.[1)] This led us to investigate the reactions of mono- and disubstituted biphenylenes in the hope of obtaining further evidence on the anomalous reactivity of biphenylene towards $Mn(OAc)_3$. The reaction of biphenylene with $Pb(OAc)_4$ was also studied, since this reagent should show a similar reactivity under certain reaction conditions,[2)] although one of the authors has already reported that the reaction of biphenylene (**1**) with $Pd(OAc)_4$, followed by hydrolysis gave 2-hydroxybiphenylene.[3)]

Results

When biphenylene (**1**) was oxidized with $Pb(OAc)_4$ in a 1:2 molar ratio, it gave 2-acetoxybiphenylene (**2**) and 2,3-biphenylenedione (**3**) (Table 1, Entry 2). When the molar ratio of the oxidant to substrate was increased, the yields were not very much affected, but a third product, 2-formylbiphenylene (**4**), was obtained (Entries 3 and 4). 2-Acetoxymethylbiphenylene (**5**) was detected by its CH_2 and CH_3 peaks in the ^{1}H-NMR spectrum of the crude product.

When 2-methylbiphenylene[4)] (**7**) was oxidized with $Mn(OAc)_3$ and with $Pb(OAc)_4$, the products were found to be **4** and **5**. When acetic anhydride was added to the reaction mixture of $Mn(OAc)_3$, **5** was the major product, while the yield of **4** decreased, and compounds **6**, **8a**, and **8b** were isolated. The structures of **8a** and **8b** were determined by comparison with the corresponding authentic samples (see Experimental). The results are summarized in Table 2. It was shown that the recovery of **7** was much less than that of **1** in the oxidation with $Pb(OAc)_4$.

When the reaction of 2-methoxybiphenylene[5)] (**11**) with $Mn(OAc)_3$ was examined in molar ratios of 1:2 and 1 : 4 in acetic acid at room temperature, it gave a complex mixture which could not be separated. The reaction of **11** with $Pb(OAc)_4$, in a molar ratio of 1:1 under similar reaction conditions gave two com-

TABLE 1. OXIDATION OF BIPHENYLENE (**1**) WITH $Pb(OAc)_4$ IN ACETIC ACID

Entry	Molar ratio of substrate :oxidant	Time / min	Temp / °C	Recovered substrate (%)	Product(yield/%)[a)] **2**	**3**	**4**
1	1 : 2	180	100	42	7	2	
2	1 : 2	20	Reflux	39	12	1	
3	1 : 3	20	Reflux	29	13	2	2
4	1 : 4	20	Reflux	25	10	3	1

a) Yields are based on the amount of the substrate used.

TABLE 2. OXIDATION OF 2-METHYLBIPHENYLENE (**7**) WITH $Pb(OAc)_4$ AND $Mn(OAc)_3$ IN ACETIC ACID AT THE REFLUX TEMPERATURE

Entry	Oxidant	Molar ratio	Time / min	Recovered substrate (%)	Product(yield/%)[a)] **4**[b)]	**5**[b)]	**6**	**8a**	**8b**
1	$Pb(OAc)_4$	1 : 2	20	11	21	15			
2	$Mn(OAc)_3$	1 : 4	35		27	21			
3	$Mn(OAc)_3$	1 : 4[c)]	8	2	4	35	1	2	2

a) Yields are based on the amount of the substrate used. b) Yields were estimated from their ^{1}H-NMR spectra. c) Acetic anhydride (10 ml) was added.

pounds; **12** (5%) and **13** (9%). Spectroscopic properties of **13** indicate that the structure of **13** could be either 2,3-diacetoxy-2-methoxy-2,3-dihydrobiphenylene (**13a**) or 2,4a-diacetoxy-3-methoxy-2,4a-dihydrobiphenylene (**13b**). However, the structure **13a** is preferred because compound **13** showed a symmetrical A_2B_2 pattern due to aromatic protons in the ^{1}H-NMR spectrum. Also, the δ values calculated[6] for H-1 and H-4 in **13a** are the same (6.0) and they agree with the experimental value (6.0), whereas the values calculated for H-1 and H-4 in **13b** (4.95 and 6.0 respectively) differ by about 1 ppm. The compound **13** was stable in $CDCl_3$ solution, but when the solution contained HCl (or DCl), it was converted to a new compound, **14**, which showed a new carbonyl carbon at δ 197.722 and a methylene carbon at δ 41.164 in its ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum indicated the presence of =CH–CO–CH_2–CH=unit. These spectroscopic properties suggest the structure of 5,10-diacetoxy-7(8*H*)-benzocyclooctenone (**14**) (Scheme 1).

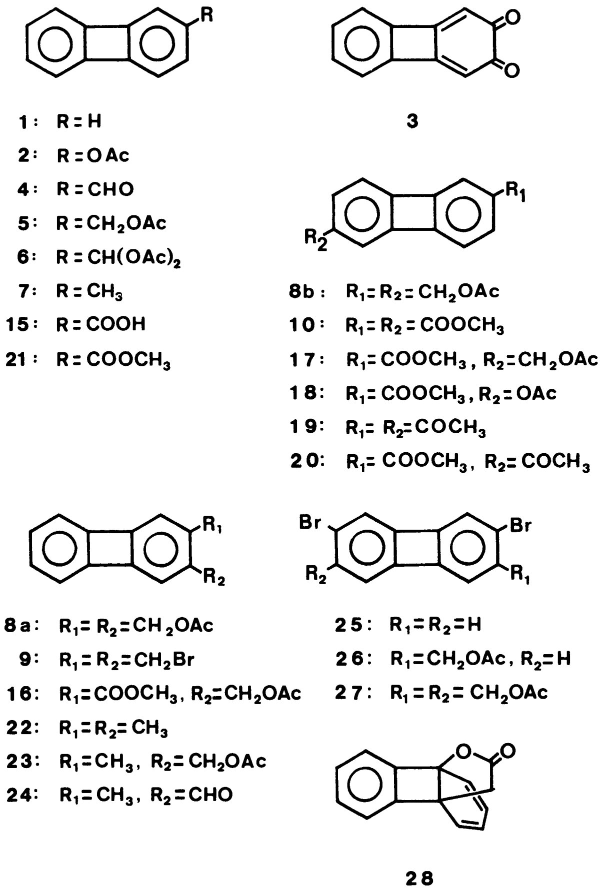


Fig. 1.

When 2-carboxybiphenylene[3] (15) was oxidized with $Pb(OAc)_4$ and $Mn(OAc)_3$, followed by treatment with diazomethane, three compounds, **16**, **17**, and **18**, were obtained (Table 3, Entries 1—4). The structures of these compounds were elucidated by spectroscopic evidence, by conversion to a known compound, and by synthesis. The structure of **16** was confirmed by reducing it with $LiAlH_4$ and then acetylating it to give a bis(acetoxymethyl)biphenylene which was identical with **8a**. In the same way, the structure of compound **17** was confirmed by converting it into the bis(acetoxymethyl) compound **8b**. The structure of **18**, which could not be obtained as a pure substance, was confirmed by an unambiguous synthesis. The Baeyer-Villiger oxidation of 2-acetyl-6-(methoxycarbonyl)biphenylene (**20**) which was obtained from 2,6-diacetylbiphenylene (**19**) gave **18**. When 2-(methoxycarbonyl)biphenylene[3] (**21**) was oxidized with $Pb(OAc)_4$ and with $Mn(OAc)_3$, it gave again **16**, **17**, and **18** in slightly modified yields (Table 3, Entries 5 and 6).

Oxidation of 2,3-dimethylbiphenylene[4] (**22**) with $Mn(OAc)_3$ in the molar ratio of 1:2 gave 2-acetoxymethyl-3-methylbiphenylene (**23**) and 2-formyl-3-methylbiphenylene[4] (**24**) (Table 4, Entry 1). When the molar ratio was increased to 1:4, the products were **23**, **24**, and **8a** together with very small amounts of the other substitution products which could not be separated. The structure of **23** was proved by its ^{1}H-NMR spectrum which showed the presence of six aromatic protons, one $ArCH_2$ and $ArCH_3$ group.

Bromination of biphenylene with *N*-bromosuccinimide (molar ratio 1:2) in *N,N*-dimethylformamide gave a mixture of dibromobiphenylenes. 2,7-Dibromobiphenylene (**25**) (the less soluble isomer) was obtained by fractional crystallization of the mixture. However, it is easier to isolate **25** if the bromination of biphenylene is carried out in two steps, *i.e. via* monobromobiphenylene. The orientation of **25** was proved by treatment with butyllithium and then with methyl iodide, which gave 2,7-dimethylbiphenylene. Oxidation of 2,7-dibromobiphenylene (**25**) with $Mn(OAc)_3$ gave mono(acetoxymethyl) compound **26** and a much lower yield of the bis(acetoxymethyl) compound **27** (Table 4, Entry 3). The structures of **26** and **27** were

TABLE 3. OXIDATIONS OF 2-CARBOXYBIPHENYLENE (**15**) AND 2-(METHOXYCARBONYL)BIPHENYLENE (**21**) WITH $Pb(OAc)_4$ AND $Mn(OAc)_3$ IN ACETIC ACID AT THE REFLUX TEMPERATURE

Entry	Substrate	Oxidant	Molar ratio	Time / min	Recovered substrate (%)	Product(yield/%)[a]		
						16	**17**	**18**
1	**15**	$Pb(OAc)_4$	1 : 1	30	56[b]	5	4	3
2	**15**	$Pb(OAc)_4$	1 : 2	30	33[b]	4	4	4
3	**15**	$Pb(OAc)_4$	1 : 3	20	23[b]	6	4	4
4	**15**	$Mn(OAc)_3$	1 : 6	50	31[b]	2	2	6
5	**21**	$Pb(OAc)_4$	1 : 2	35	39	10	4	7
6	**21**	$Mn(OAc)_3$	1 : 4	180	51	11	7	4

a) Yields are based on the amount of the substrate used. b) Isolated as methyl ester.

Table 4. Oxidations of 2,3-dimethylbiphenylene (**22**) and 2,7-dibromobiphenylene (**25**) with $Mn(OAc)_3$ at the reflux temperature

Entry	Substrate	Molar ratio of substrate : oxidant : Ac_2O	Recovered substrate (%)	Product (yield/%)[a]
1	**22**	1 : 2 : 100	15	**23**(33), **24**(10)
2	**22**	1 : 4 : 100	0	**23**(4), **24**(14), **8a**(14)[b]
3	**25**	1 : 3.7 : 90	29	**26**(23), **27**(2)
4	**25**	1 : 5.5 : 90	21	**26**(28), **27**(4)

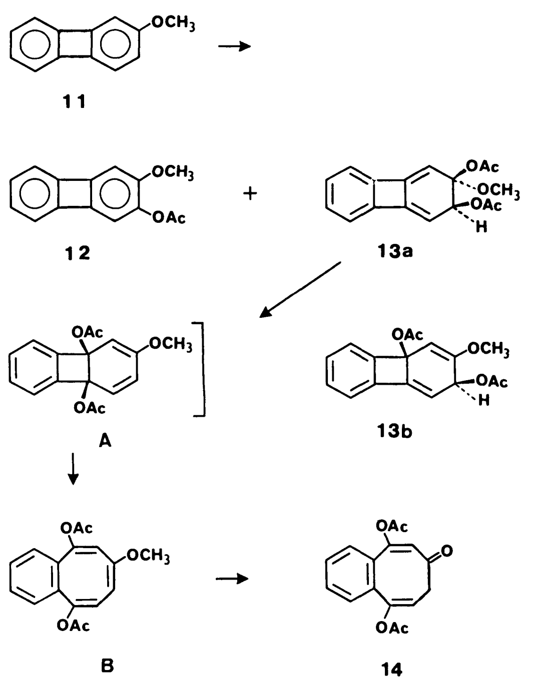
a) Yields are based on the amount of the substrate used. b) Yield was estimated from its ^1H-NMR spectrum.

determined by their ^1H-NMR spectra. In each experiment, there were many unidentified products which could not be separated.

Discussion

The oxidation of biphenylene (**1**) with $Mn(OAc)_3$ gives a mixture of 2-substituted biphenylenes and an addition product, namely the propellane **28** (0—10% yield).[1] The latter is presumably formed by attack of the $^{\bullet}CH_2COOH$ radical at position 4a of biphenylene, followed by cyclization. The formation of **4** and **5** in the reaction of **1** with $Pb(OAc)_4$ indicates that this acetate also yielded the $^{\bullet}CH_2COOH$ radical in minor quantity, but it could not afford any of the propellane **28**. The reaction of **5** with $Pb(OAc)_4$ gave **4** in a 35% yield, together with 2-(diacetoxymethyl)biphenylene **6** (14%). It seemed that **2** might be a precursor for **3**; therefore, the reaction of **2** with $Pb(OAc)_4$ was also carried out, but it gave **3** (3%) and unchanged **2** (19%). The result indicates that **2** cannot be the major precursor because of the poor yield of **3** from **2**. We hoped that $Mn(OAc)_3$ oxidation of biphenylene containing either electron-donating (CH_3) or electron-withdrawing substituents (COOH, $COOCH_3$, and Br) would give higher yields of propellane. However, we were not able to detect any propellane type of products from the substituted biphenylenes, but we obtained acetoxymethylated-biphenylenes as the major product in each case. Our results show that the incoming groups, OAc and CH_2COOH (and thence CH_2OAc, $CH(OAc)_2$, CHO),[7] always enter at β-positions (2,3,6,7) of the biphenylene nucleus. This is further evidence of the unreactivity of the α-positions (1,4,5,8) towards substitution by free radicals, by electron-transfer mechanism, and by electrophilic reagents. On the other hand, the reactions of **7** and **22** with $Mn(OAc)_3$ occurred at the methyl group rather than in the biphenylene nucleus, giving acetoxymetyl- and formyl-derivatives.

Several reactions have been reported in which X-Y reagents add to biphenylene and give products with ring-enlargement, for example in the reaction of biphenylene with HNO_3 and Ac_2O[8] and in the reaction of methoxybiphenylene with Br_2.[9] However, as far as we know, compound **13a** is the first example of a stable 2,3-adduct isolated from an addition reaction of biphenylene. It has been reported that aliphatic vinyl ether, CH_2=CHOR, reacts with $Pb(OAc)_4$ at room temperature to give diacetate, *e.g.* CH_2=CHOR gives $AcOCH_2CH(OR)OAc$.[10] In 2-methoxybiphenylene (**11**), the $C_{(2)}$–$C_{(3)}$ bond is more like a double-bond than the $C_{(1)}$–$C_{(2)}$ bond is, and the CH_3O–$C_{(2)}$–$C_{(3)}$ system may behave like a vinyl ether. The proposed rearrangement of **13a** to A involves the 1,3-migration of two acetoxyl groups. Similar [3,3] sigmatropic changes have been recorded, *e.g.* the reversible isomerization of 6-acyloxy-2,4-cyclohexadienes into 4-acyloxy-2,5-cyclohexadienes by heating them in chloroform or pyridine.[11] Now the thermal [3,3] sigmatropic rearrangement of allylic acetates proceeds suprafacially *via* a 6-membered transition state;[11] hence the two acetoxyl groups in **13a** must be *cis* as shown.[12] The rearrangement of **13a** into A could take place either in two-steps, *e.g.* *via* **13b**, or in one step *via* simultaneous 1,3-migration of two acetoxyl groups. However both paths (one-step and two-step) have the same stereochemical requirements and lead to the same conclusion concerning the relative stereochemistry of **13a** and A. The intermediate, B, is an enol ether and, as expected,[8] undergoes very rapid acid-catalyzed hydrolysis to the ketone **14**. In conclusion, it was shown that the reaction of biphenylenes having electron-withdrawing groups



Scheme 1.

with $Mn(OAc)_3$ and $Pb(OAc)_4$ yielded acetoxymethylated derivatives, whereas the methyl group was oxidized in the reaction of methyl substituted biphenylenes. The reaction of 2-methoxybiphenylene with $Pb(OAc)_4$ provided the first example of a stable 2,3-adduct in the addition reaction of biphenylene.

Experimental

The ^1H-NMR spectra at 60 MHz and 200 MHz were recorded with a Hitachi-Perkin-Elmer R 24 (or JEOL PMX 60) and with a JEOL FX 200 spectrometer, respectively, with TMS as internal reference. The ^{13}C-NMR spectra at 22.5 MHz were obtained on a JEOL FX 90Q spectrometer. The IR spectra were taken on a JASCO IR A-1 grating spectrometer. The high-resolution Mass spectra were recorded on an A.E.I. MS 902 spectrometer (VG2AB electronics and ion source) with direct inlet at 75 ev. The melting points were determined with a Yanagimoto micro-melting point apparatus and were not corrected.

Oxidation with $Pb(OAc)_4$. The typical procedure for the oxidations of biphenylene[13] and its derivatives was as follows. A mixture of a biphenylene (1 mmol) and $Pb(OAc)_4$ in acetic acid (15 ml) was heated or stirred until the solution became negative to a wet KI-starch paper. The reaction mixture was then diluted with water (15 ml) and extracted with chloroform. After removal of the chloroform *in vacuo*, the resulting mixture was separated on TLC (Wakogel B10) with chloroform as the developing solvent. In the case of the oxidation of 2-carboxybiphenylene, the products were treated with diazomethane in diethyl ether and then separated. Yields are summarized in Tables 1, 2, 3, and 4.

*Oxidation Products of Biphenylene (**1**).* 2-Acetoxybiphenylene (**2**), mp 91—92 °C (lit,[5] mp 91—92 °C), 2,3-biphenylenedione (**3**), mp 213—216 °C (from light petroleum) (lit,[14] 216—217 °C), and 2-formylbiphenylene (**4**), mp 80—82 °C (light petrolem) (lit,[15] mp 78—79 °C). The ^1H-NMR and IR spectra were identical with those of authentic samples.[1,16]

*Oxidation Products of 2-Acetoxymethylphenylene[1] (**5**).* *2-Formylbiphenylene (**4**)*: **4** (35%) was obtained as a mixture with **5** (28%); the yields were estimated from its ^1H-NMR spectrum.

*2-(Diacetoxymethyl)biphenylene (**6**)*: Mp 154—155 °C (CCl_4); 14%; IR($CHCl_3$) 1760 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.00 (6H, s, 2×OAc), 6.5—6.7 (7H, m, aromatic), and 7.42 (1H, s, –CH<); MS *m/z* (rel intensity) 43 (40), 151 (37), 179 (48), 180 (78), 181 (100), 223 (3), and 282.0890 (64, M^+). Calcd for $C_{17}H_{14}O_4$: M, 282.0892.

*Oxidation Products of 2-Methylbiphenylene[4] (**7**).* 2-Formylbiphenylene (**4**) and 2-acetoxymethylbiphenylene (**5**) were obtained as a mixture.

*Oxidation Products of 2-Methoxybiphenylene[3] (**11**).* *2-Acetoxy-3-methoxybiphenylene (**12**)*: Mp 125.4—126.4 °C (hexane) (lit,[17] mp 111—112 °C); 5%; IR ($CHCl_3$) 1760 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.23 (3H, s, OAc), 3.77 (3H, s, OCH_3), 6.26 (1H, s, $H_{(1)}$ or $H_{(4)}$), 6.40 (1H, s, $H_{(4)}$ or $H_{(1)}$), and 6.2—6.7 (4H, m, $H_{(5)}$–$H_{(8)}$); MS *m/z* (rel intensity) 126.0476 (22), 180.0443 (91), 198.9746 (100), 240.0834 (28, M^+). Calcd for $C_{15}H_{12}O_3$: M, 240.0774.

r-*2*,c-*3-Diacetoxy-2-methoxy-2,3-dihydrobiphenylene (**13a**)*: Mp 137.5—138.5 °C (methanol); 9%; IR ($CHCl_3$) 1640 (C=C) and 1760 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.15 (6H, s, 2×OAc), 3.50 (3H, s, OCH_3), 4.95 (1H, d, *J*=6.0 Hz, –CH<), 6.0 (2H, m, 2×–CH=), and 7.2—7.4 (4H, m, aromatic). The doublet at δ 4.95 collapsed to a singlet on irradiation of the signals at δ 6.0; ^{13}C-NMR ($CDCl_3$) δ=21.126 (2×$OCO\underline{C}H_3$), 55.281 (OCH_3), 96.615 (–CH<), 116.789 (=CH–), 119.000 (=CH–), 127.709 (=CH–), 127.913 (=CH–), 128.594 (=CH–), 128.866 (=CH–), 135.874, 136.044, 145.672, 149.218 153.394, 168.941 ($O\underline{C}OCH_3$), and 169.723 ($O\underline{C}OCH_3$); MS *m/z* (rel intensity, formula) 182.0413 (20, $C_{12}H_6O_2$), 183.0433 (32, $C_{12}H_7O_2$), 197.0589 (30, $C_{13}H_9O_2$), 198.0637 (100, $C_{13}H_{10}O_2$), 199.0704 (20, $C_{13}H_{11}O_2$), 201.0507 (16, $C_{12}H_9O_3$), 215.0721 (35, $C_{13}H_{11}O_3$), 216.0789 (27, $C_{13}H_{12}O_3$), and 258.0941 (10, $C_{15}H_{14}O_4$). Found: C, 67.86; H, 5.41%. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37%.

*5,10-Diacetoxy-7(8*H*)-benzocyclooctenone (**14**)*: IR (CH_2Cl_2) 1670, 1690, 1725, and 1775 cm^{-1} (OAc); ^1H-NMR (200 MHz, $CDCl_3$) δ=2.192 (6H, s, 2×OAc), 2.769 (1H, dd, *J*=12.94 and 10.36 Hz, $-\underline{H}CH-$), 3.019 (1H, ddd, *J*=12.94, 7.42, and 1.71 Hz, $-\underline{H}CH-$), 5.813 (1H, dd, *J*=10.36 and 7.42 Hz, $H_{(9)}$), 6.290 (1H, d, *J*=1.71 Hz, $H_{(6)}$), and 7.492 (4H, m, aromatic); ^{13}C-NMR ($CDCl_3$) δ=20.956 (q, $OCO\underline{C}H_3$), 21.160 (q, $OCO\underline{C}H_3$), 41.162 (t, $-CH_2-$), 115.700 (d, =CH–), 123.457 (d, =CH–), 126.859 (d, =CH–), 128.492 (d, =CH–), 129.206 (d, =CH–), 130.023 (d, =CH–), 133.527 (s, $=\overset{|}{C}-$), 134.071 (s, $=\overset{|}{C}-$), 147.815 (s, $=\overset{|}{C}-$), 156.422 (s, $=\overset{|}{C}-$), 168.125 (s, $O\underline{C}OCH_3$), 169.111 (s, $O\underline{C}OCH_3$), and 197.722 (s, >C=O); MS *m/z* (rel intensity) 43 (100), 128 (17), 156 (23), 157 (20), 159 (86), 160 (76), 174 (22), 184 (24), 202.0622 (51, calcd for $C_{12}H_{10}O_3$: 202.0630), and 244.0738 (25, calcd for $C_{14}H_{12}O_4$: 244.0735).

*Oxidation Products of 2-Carboxy-[3] (**15**) and 2-(Methoxycarbonyl)biphenylene[3] (**21**).* *2-Acetoxymethyl-3-(methoxycarbonyl)biphenylene (**16**)*: Mp 96.7—97.7 °C (methanol); IR ($CHCl_3$) 1710 ($-COOCH_3$) and 1725 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.10 (3H, s, OAc), 3.82 (3H, s, OCH_3), 5.33 (2H, s, $-CH_2O-$), 6.75 (5H, m, $H_{(4)}$-$H_{(8)}$), and 7.12 (1H, s, $H_{(1)}$); MS *m/z* (rel intensity) 43 (11), 151 (18), 179 (17), 207 (100), 239 (10), 282.0899 (37, M^+). Calcd for $C_{17}H_{14}O_4$: M, 282.0892.

*2-Acetoxymethyl-6-(methoxycarbonyl)biphenylene (**17**)*: Mp 95.5—96.6 °C (methanol); IR ($CHCl_3$) 1710 ($-COOCH_3$) and 1735 cm^{-1} (OAc): ^1H-NMR ($CDCl_3$) δ=2.05 (3H, s, OAc), 3.80 (3H, s, OCH_3), 4.88 (2H, s, $-CH_2O-$), 6.5—6.9 (4H, m, $H_{(4)}$, $H_{(5)}$, $H_{(7)}$, and $H_{(8)}$), 7.20 (1H, d, *J*=1.0 Hz, $H_{(1)}$), and 7.52 (1H, dd, *J*=6.0 and 1.0 Hz, $H_{(3)}$); MS *m/z* (rel intensity) 43 (14), 223 (70), 240 (25), and 282.0894 (100, M^+). Calcd for $C_{17}H_{14}O_4$: M, 282.0892.

*2-Acetoxy-6-(methoxycarbonyl)biphenylene (**18**)*: Mp 134—137 °C (metanol); IR ($CHCl_3$) 1725 ($-COOCH_3$) and 1760 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.25 (3H, s, OAc), 3.80 (3H, s, OCH_3), 6.5—6.8 (4H, m, $H_{(4)}$, $H_{(5)}$, $H_{(7)}$, and $H_{(8)}$), 7.20 (1H, d, *J*=1.0 Hz, $H_{(1)}$), and 7.60 (1H, dd, *J*=6.0 and 1.0 Hz, $H_{(3)}$); MS *m/z* (rel intensity) 167 (14), 195 (22), 226.0642 (100, M^+ −42, calcd for $C_{14}H_{10}O_3$: 226.0630), and 268.0733 (13, M^+). Calcd for $C_{16}H_{12}O_4$: M, 268.0735.

*Oxidation of 2-Methylbiphenylene (**7**) with $Mn(OAc)_3$.* A mixture of **7** (1 mmol) and $Mn(OAc)_3\,2H_2O$[18] in acetic acid (20 ml) was heated under reflux for the time shown in Table 2 until the color of the Mn(III) ions disappeared. The reaction mixture was worked up in a manner similar to that described in the oxidation with $Pb(OAc)_4$. 2-Formylbiphenylene (**4**) and 2-acetoxymethylbiphenylene (**5**) were obtained as a mixture, yields of which were estimated from the ^1H-NMR as shown in Table 2.

*2-(Diacetoxymethyl)biphenylene (**6**)*: Mp 154—155 °C

*2,3-Bis(acetoxymethyl)biphenylene (**8a**)*: Mp 88—89 °C (ethanol); IR (CCl_4) 1742 cm^{-1} (OAc); ^1H-NMR ($CDCl_3$) δ=2.00 (6H, s, 2×OAc); 4.91 (4, s, 2×$-CH_2O-$), and 6.62 (6H, br. s, aromatic); MS *m/z* (rel intensity) 43 (22), 165 (26), 194 (100), 296.1038 (17, M^+). Calcd for $C_{18}H_{16}O_4$: M, 296.1048.

*2,6-Bis(acetoxymethyl)biphenylene (**8b**)*: Mp 104—105.5 °C (ethanol); IR ($CHCl_3$) 1742 cm^{-1} (OAc); ^1H-NMR (CCl_4) δ=2.00 (6H, s, 2×OAc), 4.74 (4H, s, 2×$-CH_2O-$), 6.56 (6H, m, aromatic); MS *m/z* (rel intensity) 43 (23), 152 (10), 165 (28), 178

(19), 195 (12), 237 (77), 254 (11), and 296.1030 (100, M$^+$). Calcd for $C_{18}H_{16}O_4$: M, 296.1048.

Preparation of 2,3-Bis(acetoxymethyl)biphenylene (8a). a) From 2,3-bis(bromomethyl)biphenylene (9): A mixture of 2,3-bis(bromomethyl)biphenylene[17] (258 mg) and anhydrous sodium acetate (205 mg) in acetic acid was refluxed for 3 h, then allowed to stand for 60 h. Water (50 ml) was added and the mixture was extracted with toluene (2×25 ml). The toluene was evaporated and the residue was separated by TLC on silica gel with chloroform as eluent. The major component was collected and recrystallized from aqueous ethanol. The product (162 mg, 55%), mp 88—89 °C was identical (IR, ^{1}H-NMR and Mass) with compound **8a**.

b) From 2-acetoxymethyl-3-(methoxycarbonyl)biphenylene (16): A mixture of **16** (60 mg), anhydrous tetrahydrofuran (10 ml), and lithium aluminium hydride (200 mg) was stirred at room temperature for 2 h. After ethyl acetate (1 ml) and 3M (1M=1 mol dm^{-3}) hydrochloric acid (100 ml) had been added to the mixture, it was extracted with ethyl acetate. After removal of the ethyl acetate, the resulting liquid was treated with acetic anhydride (1 ml) in pyridine (1 ml) overnight. The mixture was poured into water and the precipitate was collected, and recrystallized from methanol, giving **8a** (45 mg, 72%), mp 89—90 °C.

Oxidation of 2,6-Diacetylbiphenylene (19) by King's Method.[19] A mixture of 2,6-diacetylbiphenylene[20] (**19**) (460 mg, 2 mmol), iodine (1.1 g, 4 mmol), and pyridine (30 ml) was heated on a steam bath for 1 h, then kept at room temperature for 12 h. The brown precipitate was collected by filtration and washed with water. The solid was boiled for 2 h with water (10 ml) and 10% sodium hydroxide (15 ml), then poured into water (50 ml). The mixture was extracted with diethyl ether to remove non-acidic material. The aqueous solution was acidified with hydrochloric acid and the yellow precipitate was collected and dried at 100 °C. This solid (275 mg) did not melt below 350 °C. A mixture of the solid (250 mg) and boron trifluoride–methanol complex (14% BF_3, 12 ml) in methanol (20 ml) was refluxed for 6 h. The solution was cooled, poured into a saturated aqueous solution of sodium hydrogencarbonate, then extracted with diethyl ether. Evaporation of the ethereal solution gave a yellow solid (130 mg) which was separated by preparative TLC (silica gel) in benzene, the plate being eluted four times to achieve good separation. The band with lowest R_f value gave a yellow solid (6 mg, 1.5%) mp 256 °C identified as 2,6-diacetylbiphenylene (mixed mp and IR spectrum). The middle band gave 2-acetyl-6-(methoxycarbonyl)biphenylene (**20**) as a yellow solid (93 mg, 20% overall), mp 180—181 °C; IR (Nujol mull) 1670 and 1722 cm^{-1}; UV (C_2H_5OH) λ_{max} (log ε) 216 (3.76), 266 (4.32), 279 (4.42), 326^{sh} (3.04), 339^{sh} (3.34), 342 (3.34), 354^{sh} (3.61), 357 (3.62), and 374 nm (3.87); ^{1}H-NMR ($CDCl_3$) δ=2.42 (3H, s, $COCH_3$), 3.79 (3H, s, OCH_3), 6.69 (2H, d, $H_{(4)}$ and $H_{(8)}$), 7.19 (1H, d, $H_{(1)}$), 7.24 (1H, d, $H_{(5)}$), 7.45 (1H, dd, $J_{1,3}$=1.0 and $J_{4,5}$=7.5 Hz, $H_{(3)}$), and 7.58 (1H, dd, $J_{5,7}$=1.0 and $J_{7,8}$=7.5 Hz, $H_{(7)}$). Found: C, 75.98; H, 4.68%. Calcd for $C_{16}H_{12}O_3$: C, 76.19; H, 4.76%. The band with the highest R_f value gave 2,6-bis(methoxycarbonyl)biphenylene (**10**) (30 mg, 6% overall) as a yellow solid, mp 210—212 °C (lit,[21] mp 223—225 °C); IR (Nujol mull) 852, 902, and 1715 cm^{-1}; UV (C_2H_5OH) λ_{max} log ε) 216 (4.16), 262^{sh} (4.67), 269 (4.75), 277^{sh} (4.62), 322^{sh} (3.25), 330^{sh} (3.38), 334 (3.51), 338 (3.52), 347 (3.78), 3.52 (3.79), and 369 nm (3.98); ^{1}H-NMR ($CDCl_3$) δ=3.77 (6H, s, 2×OCH_3), 6.76 (2H, d, $H_{(4)}$ and $H_{(8)}$), 7.31 (2H, d, $H_{(1)}$ and $H_{(5)}$), and 7.65 (2H, dd, $J_{1,3}$=1.0 and $J_{3,4}$=7.5 Hz, $H_{(3)}$ and $H_{(7)}$).

Preparation of 2,6-Bis(acetoxymethyl)biphenylene (8b). a) From 2,6-bis(methoxycarbonyl)biphenylene[21](10): 2,6-Bis(methoxycarbonyl)biphenylene (100 mg), when reduced and acetylated in a manner similar to the above, yielded **8b** (86 mg, 78%), mp 105—106.4 °C.

b) From 2-acetoxymethyl-6-(methoxycarbonyl)biphenylene (17): 2-Acetoxymethyl-6-(methoxycarbonyl)biphenylene (**17**) (80 mg) was similarly treated with lithium aluminium hydride and then acetic anhydride to give **8b** (40 mg, 47%), mp 104—106 °C.

Preparation of 2-Acetoxy-6-(methoxycarbonyl)biphenylene (18) from 2-Acetyl-6-(methoxycarbonyl)biphenylene (20). A mixture of **20** (10.4 mg) and *m*-chloroperbenzoic acid (22 mg) in deuteriochloroform (0.3 ml) was kept at 36 °C for 6.5 h. The reaction mixture was passed through a short alumina column eluting with chloroform. After removal of the chloroform, the resulting solid was recrystallized from methanol, giving **18** (7.6 mg, 69%), mp 147—148 °C.

Oxidation of 2,3-Dimethylbiphenylene[4] (22) with Mn(OAc)$_3$. A mixture of **22** (170 mg, 0.94 mmol) and $Mn(OAc)_3 2H_2O$ (500 mg, 1.86 mmol) in acetic acid (20 ml) and acetic anhydride (10 ml) was heated under reflux until the brown color of the solution had changed to yellow. Water (150 ml) was added and the mixture was allowed to stand overnight. The mixture was extracted with toluene (2×100 ml). The toluene extracts were evaporated to dryness. TLC on silica gel, with chloroform as eluent, showed two components, whose R_f values were 0.75 and 0.59, and a third component, R_f 0.55 (visible under UV light), which overlapped the component with R_f value 0.59. The mixture was partially separated on a column of silica gel (35 g) using chloroform as eluent. The fractions corresponding to R_f values 0.59—0.55 were separated by chromatography several times on TLC plates (0.5 mm thickness of silica gel). The compound with R_f value 0.75 was unchanged compound **22**.

When the experiment was repeated using 1.01 g instead of 500 mg of $Mn(OAc)_3$, a new component (with R_f value 0.38) was obtained. The results are summarized in Table 4.

2-Acetoxymethyl-3-methylbiphenylene (23): R_f value 0.59; mp 62—64 °C (from aqueous ethanol); ^{1}H-NMR ($CDCl_3$) δ= 2.02 (3H, s, OAc), 2.10 (3H, s, CH_3), 4.82 (2H, s, -CH_2O-), and 6.30—6.80 (6H, m, aromatic); MS *m/z* (rel intensity) 165 (12), 178 (100), 179 (60), 238.0976 (45, M$^+$). Calcd for $C_{16}H_{14}O_2$: M, 238.0994.

2-Formyl-3-methylbiphenylene (24): R_f value 0.55; mp 141—143 °C (lit,[4] 136—138 °C), identified by its ^{1}H-NMR spectrum.[4]

2,3-Bis(acetoxymethyl)biphenylene (8a): R_f value 0.38; This was not obtained pure, but its ^{1}H-NMR spectrum (apart from impurities) was identical with that of an authentic sample.

Preparation of 2,7-Dibromobiphenylene (25). (In collaboration with Dr. M. E. Cracknell) A mixture of biphenylene (4.57 g) and *N*-bromosuccinimide (4.50 g) in dry *N*,*N*-dimethylformamide (50 ml) was stirred at room temperature for 3 h. The mixture was diluted with water (100 ml) and stirred for 3 h more. The crude product was collected, dried, and sublimed at 90 °C/0.5 mmHg (1 mmHg≈133.322 Pa) and gave 2-bromobiphenylene (5.55 g, 80%) as yellow crystals, mp 63—65 °C (lit,[20] mp 64—65 °C). A mixture of 2-bromobiphenylene (2 g) and *N*-bromosuccinimide (1.54 g) in *N*,*N*-dimethylformamide (50 ml) was stirred at room temperature for 20 h. The mixture was poured into ice water, and the solid was collected and dried in a vacuum desiccator. The crude product was fractionally crystallized from methanol and gave 2,7-dibromobiphenylene (**25**) (0.28 g, 10%) as yellow plates, mp 137—138 °C; ^{1}H-NMR ($CDCl_3$) δ=6.37 (2H, dd, $H_{(4)}$ and $H_{(5)}$), 6.65 (2H, m, $J_{1,3}$=1.2 and $J_{1,4}$= 0.8 Hz, $H_{(1)}$ and $H_{(8)}$), and 6.83 (2H, dd, $J_{3,4}$=6.8 Hz, $H_{(3)}$, $H_{(6)}$). Found: C, 46.39; H, 2.13%. Calcd for $C_{12}H_6Br_2$: C, 46.49; H, 1.95%.

Conversion of 2,7-Dibromobiphenylene (25) into 2,7-Dimethylbiphenylene. 2,7-Dibromobiphenylene (1 g) was dissolved in sodium-dried diethyl ether (40 ml) and cooled to 0

°C under an atmosphere of nitrogen. Butyllithium (10 ml) was added and the solution was stirred for 5 min. Methyl iodide (4.6 g) was added to the solution, giving some precipitates. The uncovered reaction mixture was left stirring overnight. Water was added and the solution was extracted with diethyl ether. The organic layer was washed with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The solution was filtered and then the solvent was evaporated off. The resulting solid was recrystallized from ethanol to give 2,7-dimethylbiphenylene (197 mg, 34%), mp 113—114 °C (lit,[22] mp 115 °C). The ^{1}H-NMR spectrum was identical with that reported.

*Oxidation of 2,7-Dibromobiphenylene (**25**) with $Mn(OAc)_3$.* A mixture of **25** (340 mg) and $Mn(OAc)_3 2H_2O$ (1.08 g) in acetic acid (20 ml) and acetic anhydride (9.3 ml) was heated under reflux until the color of the solution had changed from brown to yellow. The products were isolated and separated as described for the oxidation of 2,3-dimethylbiphenylene. The experiment was repeated using 1.62 g in place of 1.08 g $Mn(OAc)_3 2H_2O$. The yields for both experiments are shown in Table 4.

*2-Acetoxymethyl-3,6-dibromobiphenylene (**26**)*: Mp 133—134 °C (ethanol); ^{1}H-NMR δ=2.14 (3H, s, CH_3), 5.01 (2H, s, $-CH_2O-$), 6.55 (1H, dd, $H_{(8)}$), 6.72 (1H, d, $J_{1,4}$=0.4 Hz, $H_{(1)}$), 6.79 (1H, dd, $J_{5,7}$=1.5 and $J_{5,8}$=0.7 Hz, $H_{(5)}$), 6.87 (1H, br. s, $H_{(4)}$), and 6.97 (1H, dd, $J_{7,8}$=7.4 Hz, $H_{(7)}$). Found: C, 47.59; H, 2.82: Br, 41.56%. Calcd for $C_{15}H_{10}Br_2O_2$: C, 47.16; H, 2.64; Br, 41.83%.

*2,7-Bis(acetoxymethyl)-3,6-dibromobiphenylene (**27**)*: Mp153—154 °C (ethanol); ^{1}H-NMR ($CDCl_3$) δ=2.08 (6H, s, $2\times CH_3$), 4.97 (4H, s, $2\times$-CH_2O-), 6.67 (2H, s, $H_{(1)}$ and $H_{(8)}$), and 6.77 (2H, s, $H_{(4)}$ and $H_{(5)}$); MS m/z (rel intensity) 43 (27), 163 (11), 209 (11), 331 (98), 332 (19), 333 (100), 334 (18), 395 (18), 452 (18, M^+), 453.9235 (45, M^+), and 456 (19, M^+). Calcd for $C_{18}H_{14}O_4\,^{79}Br^{81}Br$: M, 453.9238.

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