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The Formation of a Propellane by the Oxidation of Biphenylene with Manganese(III) Acetate

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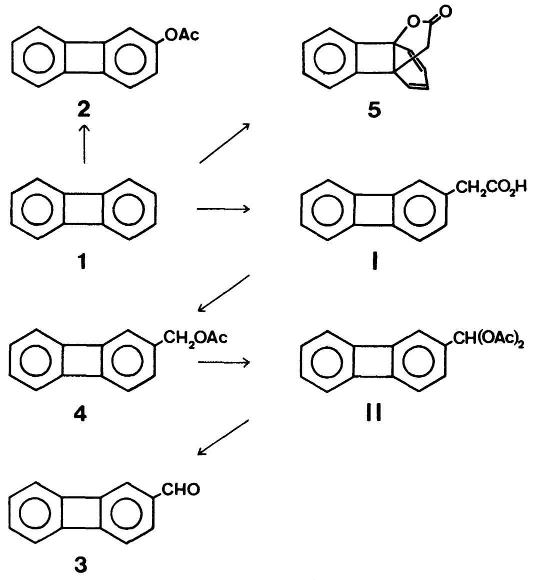
Synopsis. The reaction of biphenylene with manganese (III) acetate gave 2-acetoxybiphenylene, 2-formylbiphenylene, 2-(acetoxymethyl)biphenylene, and 7-oxa-10,11-benzotricyclo[4.3.2.0]undeca-2,4,10-trien-8-one. The reaction pathways are discussed.

Although a number of investigation of the reactions of biphenylene have been reported, the reaction of manganese(III) acetate with this compound was not known. In connection with our previous investigations of the radical reactions of manganese(III) acetate with various aromatic compounds,[1,2] the reaction of biphenylene with manganese(III) acetate was examined. The reaction of biphenylene with manganese(III) acetate in a molar ratio of 1 : 4 in boiling acetic acid containing 8 equivalents of acetic anhydride gave three products, **2**, **3**, and **4** (Table 1, Entry 2). Compounds **2** and **3** were found to be 2-acetoxybiphenylene and 2-formylbiphenylene respectively by studying their ^{1}H-NMR and IR spectra. The ^{1}H-NMR spectrum of Compound **4** in CCl_4 indicated the presence of an acetoxymethyl group [δ=2.00 (3H, s) and δ=4.80 (2H, s)] and seven aromatic protons centered at δ=6.65. The IR spectrum exhibited a carbonyl absorption at 1738 cm^{-1}. When **4** was oxidized with manganese(III) acetate, 2-formylbiphenylene (**3**) was obtained. Therefore, the structure of **4** was proved to be 2-(acetoxymethyl)biphenylene (Scheme 1). When the reaction was conducted in acetic acid containing a large amount of acetic anhydride, it gave **4** and **5** (Entry 3). The yield of **4** was much improved at the expense of the yields of **2** and **3**, and the maximum yield was obtained when the molar ratio was 1 : 4 (Entry 3). The structure of **5** was also elucidated by means of the study of its ^{1}H-NMR spectrum, which showed the presence of an AB system (δ=2.74 and 2.97 with a J value of 18.0 Hz), vinylic protons [δ=5.8—6.5 (4H, m)], and aromatic protons centered at δ=7.35 (4H, m). Its IR spectrum showed a carbonyl absorption at 1775 cm^{-1} characteristic of five-membered lactone. These spectral properties suggested that the structure is 7-oxa-10,11-benzotricyclo[4.3.2.0]-undeca-2,4,10-trien-8-one. The ^{13}C-NMR of **5** further confirmed the structure. The data are shown in the experimental part.

TABLE 1. OXIDATION OF BIPHENYLENE WITH MANGANESE (III) ACETATE IN ACETIC ACID CONTAINING ACETIC ANHYDRIDE AT THE REFLUX TEMPERATURE

Entry	Molar ratio of substrate : oxidant : Ac_2O	Time / min	Recovered substrate (%)	Product(yield/%)[a) 2	3	4	5
1	1 : 2 : 100	6	35			18	7
2	1 : 4 : 8	60	34	7	6	7	
3	1 : 4 : 100	9	26			23	10
4	1 : 6 : 100	9	12			12	5

a) Yields are based on the substrate used.



Scheme. 1.

It is well known that there are two reaction mechanisms operative in the manganese(III) acetate oxidation. One is the electron-transfer mechanism, which operates in the oxidation of aromatic compounds having ionization potentials below 8 eV.[3,4] The other is the free-radical mechanism, which operates in the reaction of compounds having higher ionization potentials.[4] Both mechanisms can compete in the reaction of some aromatic compounds under certain reaction conditions.[4] The free-radical mechanism predominates under anhydrous conditions and at high temperatures. It seems reasonable to assume that **2** was derived *via* the electron-transfer mechanism, by analogy to the oxidation of 2-methylnaphthalene, which gave 1-acetoxy-2-methylnaphthalene,[4] whereas the other products were formed *via* the free-radical mechanism. The fact that the acetoxymethyl group in **4** is located at the (2) position is in harmony with the results of the phenylation reaction of biphenylene, where 2-phenylbiphenylene is the major product, together with a minor quantity of 1-phenylbiphenylene.[5] It should be pointed out that there was no precedent for the formation of a lactone from an aromatic substrate in the oxidation by manganese(III) acetate. Interestingly, the lactone is a propellane and a derivative of the ring system (A), but it cannot isomerize to benzocyclooctene (B) (Fig. 1). Several reactions are known in which X-Y reagents add to biphenylene, and the product is nearly always a derivative of (B), as is shown in the reactions of biphenylene with nitric acid and acetic anhydride,[6] and with bromine,[7] and in the reaction of methoxybi-

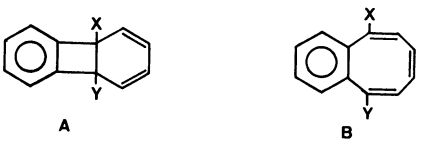


Fig. 1.

phenylene with bromine.[8] The formation of the acetoxymethyl group *via* the carboxymethyl group (I) in the oxidation by manganese(III) acetate has been well established,[4] and the further oxidation of **4** gave 2-(diacetoxymethyl)biphenylene (II), which yielded **3** on hydrolysis during the work-up procedure (Scheme 1).

Experimental

The ^{1}H-NMR spectra were recorded with a Hitachi R-24 NMR spectrometer, with TMS as the internal standard, while the proton-decoupled ^{13}C-FT NMR spectrum was measured at 22.5 MHz on a JEOL FX 90Q spectrometer (pulse width, 24 μs; spectral width 5000 Hz; data points, 8000; acquisition time 920 ms) in a 5-mm tube at 28 °C, using TMS as the internal reference. The IR spectra were taken for the chloroform solution on a JASCO IRA-1 grating spectrometer. The UV spectra were recorded for the methanol solution with a Hitachi EPS-3T spectrophotometer. The melting points were determined on a Yanagimoto micro-melting-point apparatus and were not corrected.

Oxidiation of Biphenylene with Manganese(III) Acetate. A typical procedure for the oxidation of biphenylene with manganese(III) acetate was as follows. A mixture of biphenylene[9] (2 mmol), manganese(III) acetate dihydrate,[3] acetic acid (20 ml), and acetic anhydride was heated under reflux for the time shown in the table until the color of the Mn(III) ion disappeared. Water (150 ml) was then added to the reaction mixture, and the solution was kept at room temperature overnight. The reaction mixture was extracted with benzene twice (30 ml of each portion), and then the benzene was removed *in vacuo*. The resulting semi-solid was separated on TLC, using chloroform as the developing solvent.

2-Acetoxybiphenylene (2): Mp 91—92 °C (light petroleum) (lit,[10] mp 91—92 °C); UV $\lambda_{\max}$ (ε) 245 (27900), 252 (46900), 330 (2980), 335_{sh} (3350), 344 (6270), 347_{sh} (5960), and 365 nm (8500); ^{1}H-NMR (CDCl$_3$) δ=2.23 (3H, s, OAc) and 6.2—6.9 (7H, m, aromatic).

2-Formylbiphenylene (3): Mp 80—81 °C (light petroleum) (lit,[11] mp 78—79 °C); IR 1700, 2720, and 2810 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=6.5—7.5 (7H, m, aromatic) and 9.61 (1H, s, CHO).

2-(Acetoxymethyl)biphenylene (4): Mp 63—64 °C (EtOH); IR 1738 cm^{-1} (OAc); UV $\lambda_{\max}$ (ε) 245.5 (28300), 254 (55000), 329.5_{sh} (2750), 335_{sh} (2910), 345.5 (5900), 347.5 (5660), 352.5_{sh} (4050), and 365 nm (8900). Found: C, 80.30; H, 5.32%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%.

7-Oxa-10,11-benzotricyclo[4.3.2.0]undeca-2,4,10-trien-8-one (5): Mp 125 °C (CCl$_4$); IR 1775 cm^{-1} (γ-lactone); UV $\lambda_{\max}$ (ε) 221_{sh} (3960), 228_{sh} (3120), 258_{sh} (1410), 264_{sh} (1860), 269.5 (2130), 276 (2050), and 285_{sh} (723); ^{13}C-NMR δ= 39.709 (-CH$_2$-), 51.736 (-$\underline{C}$-CH$_2$-), 84.837 (-C-O-), 121.080, 121.242, 121.513, 122.380, 124.059, 128.989, 129.260, 131.373 (four vinylic =CH- and four aromatic =CH-), 146.650 ($=\overset{|}{C}-$), 146.975 ($=\overset{|}{C}-$), and 175.308 (>C=O). Found: C, 79.86; H, 4.81%. Calcd for $C_{14}H_{10}O_2$: C, 79.98; 4.79%.

Oxidation of 2-(Acetoxymethyl)biphenylene (4) with Manganese(III) Acetate. A mixture of **2** (45 mg), manganese (III) acetate dihydrate (107 mg), acetic acid (2 ml), and acetic anhydride (0.1 ml) was heated under reflux for 20 min. The reaction mixture was diluted with water (20 ml) and then extracted with benzene. After the removal of the benzene *in vacuo*, the resulting mixture was separated on TLC, using benzene as the developing solvent, to give **3** (10 mg, 28%) and also unchanged **4** (15.6 mg, 35%) identical with authentic samples.

Oxidation of 2-(Acetoxymethyl)biphenylene (4) with Manganese(IV) Oxide. A mixture of **2** (45 mg), manganese (IV) oxide (1 g), and anhydrous diethyl ether (50 ml) was stirred at room temperature for 48 h. After the manganese (IV) oxide has been removed by filtration, the ethereal solution was concentrated and the resulting product was purified on TLC, using benzene as the developing solvent, to give **3** (20 mg, 56%).

References

1) K. Kurosawa and H. Harada, *Bull. Chem. Soc. Jpn.*, **52**, 2386 (1979).

2) H. Nishino, Ms. D. Thesis, Kumamoto University (1981).

3) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

4) E. I Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 138 (1969).

5) S. C. Dickerman, W. M. Feigenbaum, M. Fryd, N. Milstein, G. B. Vermont, I. Zimmerman, and J. F. W. McOmie, *J. Am. Chem. Soc.*, **95**, 4624 (1973).

6) J. W. Barton and K. E. Whitaker, *J. Chem. Soc., C*, **1968**, 1663.

7) J. W. Barton and K. E. Whitaker, *J. Chem. Soc., C*, **1968**, 28.

8) H. Kidokoro, M. Sato, and S. Ebine, *Abstracts of the 5th Joint Meeting of Basic Organic Chemistry*, 235 (1980).

9) F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, Coll. Vol. 5, 54 (1973).

10) J. M. Blatchly, D. V. Gardner, and J. F. W. McOmie, *J. Chem. Soc., C*, **1967**, 272.

11) J. F. W. McOmie and S. D. Thatte, *J. Chem. Soc.*, **1962**, 5298.