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The Reactions of 2-Hydroxystilbenes with Lead Tetraacetate and Manganic Acetate

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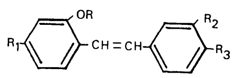
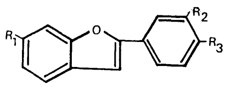
Synopsis. Four 2-hydroxystilbenes (Ia∼Id) were oxidized with lead tetraacetate to give corresponding 3-arylbenzofurans (IIa∼IId) in moderate yields. IId and IIe were also obtained by the reactions of Id and Ie respectively with manganic acetate in poor yields.

In the reactions of lead tetraacetate and manganic acetate with phenolic compounds, an oxidative cyclization has been observed when a compound possesses a hydroxy group and an aromatic or a vinylic hydrogen which are located in spatially suitable positions.[1-4] It is now demonstrated that 2-hydroxystilbenes gave 2-arylbenzofurans with lead tetraacetate in moderate yields.

When 4′-methoxy-2-hydroxystilbene(Ib), prepared from salicylaldehyde and 4-methoxybenzyl-triphenylphosphonium chloride by the Wittig reaction, was treated with lead tetraacetate, a compound (IIb) was isolated. This compound (IIb)(mp 146 °C), $C_{15}H_{12}O_2$, showed no absorption in the hydroxyl region (3500 cm^{-1}) in its IR spectrum. The NMR spectrum of this compound did indicate, however, the presence of a *p*-substituted phenyl group[δ 6.87 (d, 2H) and δ 7.73)(d, 2H)(AA′XX′-system)], a methoxy group [δ 3.80 (s, 3H)], four aromatic protons [δ 7.0—7.6 (m, 4H)], and a singlet [δ 6.80 (1H)]. These spectroscopic properties indicated that the structure of this compound is 2-(4′-methoxyphenyl)-benzofuran.



Ia–e (R=H)
IIIa–d (R=OAc)



IIa–e

a $R_1=R_2=R_3=H$
b $R_1=R_2=H$, $R_3=OCH_3$
c $R_1=OCH_3$, $R_2=R_3=H$
d $R_1=R_3=OCH_3$, $R_2=H$
e $R_1=H$, $R_2=R_3=OCH_3$

Three other 2-hydroxystilbenes (Ia, Ic and Id) were prepared, their reactions with lead tetraacetate gave 2-arylbenzofurans (IIa, IIc and IId). The results are shown in Table 1. It seems that the reaction of 2-hydroxystilbenes with lead tetraacetate can be used as a convenient one-step synthesis of 2-arylbenzofurans, although the yields are not very good and depend on the reaction temperature and solvent used.

The reaction of 2-hydroxystilbenes with manganic acetate also yielded 2-arylbenzofurans (IId and IIe) in poor yields.

Experimental

The NMR spectra were recorded in a deuteriochloroform solution by means of a Hitachi R-24 NMR spectrometer, with tetramethylsilane as the internal reference; The IR spectra were recorded in a chloroform solution by means of a JASCO IRA-1 grating spectrometer; The UV spectra were measured for a methanol solution by means of a Hitachi EPS-3T spectrophotometer. The melting points were determined by means of a Yanagimoto hot-stage apparatus and are uncorrected.

Preparation of 2-Hydroxystilbenes. The general procedure for the preparation of 2-hydroxystilbene was as follows. Benzyl-triphenylphosphonium chloride[5] (22 mmol) was treated with sodium ethoxide, prepared from metallic sodium (20 mmol) and ethanol (50 ml). To this solution we then added 2-hydroxybenzaldehyde (15 mmol), and the solution was heated at 90 °C with stirring until all the aldehyde had disappeared. After the removal of the ethanol *in vacuo*, the residue was triturated with water and extracted with benzene. The benzene layer was washed with aqueous sodium bisulfite, and the benzene was removed *in vacuo*. The product was then purified through a silica column [a mixture of Wakogel C 100 (180 g) and B 10 (20 g)], eluted with benzene, and recrystallized from benzene; it could thus be characterized as an acetate. Thus, 2-hydroxystilbene (Ia) (mp 137—138 °C(lit,[6] mp 147 °C)) was obtained in a in 66% yield. ν_{max}: 3580 and 3300 cm^{-1} (OH); $\lambda_{max}(\varepsilon)$: 304 (35000) and 316 nm (25300). 2-Acetoxystilbene (IIIa) (mp 54 °C(lit.[7] mp 54 °C)). ν_{max}: 1760 cm^{-1}. 2-Hydroxy-4′-methoxystilbene (Ib); mp 145—146 °C; 23% yield. ν_{max}: 3580 and 3300 cm^{-1} (OH); $\lambda_{max}(\varepsilon)$: 310 (36,100) and 324 nm(23,600). Found: C, 79.61; H, 6.41%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%. 2-Acetoxy-4′-methoxy-

Table 1. Oxidation of 2-hydroxystilbene with lead tetraacetate

Compd.	Reaction conditions				Benzofuran (%)
	Molar ratio of I : oxidant	Solvent	Temperature (°C)	Time (min)	
Ia	1 : 1.5	C_6H_6	17	5	IIa(21)
Ib	1 : 1.5	C_6H_6	17	15	IIb(25)
Ic	1 : 1.5	AcOH	18	300	IIc(13)
Ic	1 : 1.5	C_6H_6	18	40	IIc(24)
Id	1 : 1.5	C_6H_6	17	15	IId(4)

stilbene (IIIb); mp 75.8 °C; ν_{max}: 1760 cm^{-1}(OAc). Found C, 75.99; H, 6.03%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%. 2-Hydroxy-4-methoxystilbene (Ic); mp 117—118 °C; 56% yield. ν_{max}: 3580 and 3300 cm^{-1}(OH); $\lambda_{max}(\varepsilon)$: 316 (32,400) and 329 nm(27,100). Found: C, 79.62; H, 6.38%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%. 2-Acetoxy-4-methoxystilbene (IIIc); mp 156 °C; ν_{max}: 1760 cm^{-1}(OAc). Found: C, 75.80; H, 6.02%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%. 4,4′-Dimethoxy-2-hydroxystilbene (Id); mp 168—169 °C; 44% yield. ν_{max}: 3500 cm^{-1}(OH); $\lambda_{max}(\varepsilon)$: 319 (36700) and 332 nm (29600). Found: C, 74.83; H, 6.33%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%. 2-Acetoxy-4,4′-dimethoxystilbene (IIId); mp 140 °C; ν_{max}: 1760 cm^{-1}(OAc). Found: C, 72.23; H, 6.22%. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%. 3′,4′-Dimethoxy-2-hydroxystilbene (Ie): mp 109 °C; 21% yield. ν_{max}: 3580 and 3300 cm^{-1}(OH); $\lambda_{max}(\varepsilon)$: 316 (33,600) and 327 nm(25,500). Found: C, 75.09; H, 6.31%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

Oxidation of 2-Hydroxystilbene with Lead Tetraacetate. The general procedure for the oxidation of 2-hydroxystilbenes was as follows. 2-Hydroxystilbene (4.4 mmol) was heated with lead tetraacetate (6.6 mmol) in a solvent (70 ml) with stirring for a period of time as is shown in the table. After the removal of the solvent *in vacuo*, the residue was triturated with water and extracted with chloroform. The crude products were purified either on silica plates or through a silica column, with chloroform as the eluting solvent, and then recrystallized from ethanol. Ia gave 2-phenylbenzofuran (IIa) (mp 118 °C(lit,[8] mp 120 °C)) in a 21% yield. ν_{max}: 1560, 920 and 880 cm^{-1}; $\lambda_{max}(\varepsilon)$: 290 (19,000), 300 (16,800) and 327 nm(18,800); δ: 6.92(s, -CH) and 7.0—8.0(m, 9H). Ib gave 2-(4′-methoxyphenyl)benzofuran (IIb) (mp 146 °C) in a 25% yield. ν_{max}: 1570, 920 and 880 cm^{-1}; $\lambda_{max}(\varepsilon)$: 294 (21,400), 303 (20,000) and 331 nm(24,400). Found: C, 80.19; H, 5.57%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.29%. Ic gave 6-methoxy-2-phenylbenzofuran (IIc) (mp 81 °C) in a 24% yield. ν_{max}: 1560, 960 and 920 cm^{-1}; $\lambda_{max}(\varepsilon)$: 293 (18,200), 300 (17,600) and 331 nm(23,100); δ: 3.79 (s, OCH$_3$), 6.85(s, -CH) and 6.8—7.8 (m, 8H, aromatic). Found: C, 80.04; H, 5.45%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.29%. Id gave 6-methoxy-2-(4′-methoxyphenyl)benzofuran (IId) (mp 159 °C (lit,[9] mp 159 °C)) in a 4% yield. ν_{max}: 1560, 960 and 920 cm^{-1}; $\lambda_{max}(\varepsilon)$: 295 (22,500) and 334 nm(26,000); δ: 6.89(d, 2H) and 7.67 (d, 2H)(*p*-substituted phenyl), 3.79(s, OCH$_3$), 3.80(s, OCH$_3$), 7.33(d, 1H) and 6.8—7.0 (m, 2H)(aromatic), and 6.73(s, 1H, vinylic).

The oxidation of 2-hydroxystilbenes with manganic acetate was also carried out in a similar manner. Id gave IId (3%) and IIId (13%). Ie yielded 2-(3′,4′-dimethoxyphenyl)-benzofuran (IIe) (5%); mp 112—114 °C. ν_{max}: 1570, 920 and 880 cm^{-1}; $\lambda_{max}(\varepsilon)$: 294 (14500) and 333 nm(20800); δ: 3.89(s, OCH$_3$), 3.94(s, OCH$_3$), 6.89(s, -CH) and 6.8—7.7 (m, 7H, aromatic). Found: C, 75.28; H, 5.35%. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%.

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