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# The Reaction of Benzofuran with Manganic Acetate

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**Synopsis.** The oxidation of benzofuran with manganic acetate in a mixture of acetic acid and acetic anhydride yielded four products: 2-(acetoxymethyl)benzofuran, 3a,8b-dihydrofuro[3,2-*b*]benzofuran-2(3*H*)-one, bis(2-benzofuranyl)methane, and 2-benzofuranylacetic acid.

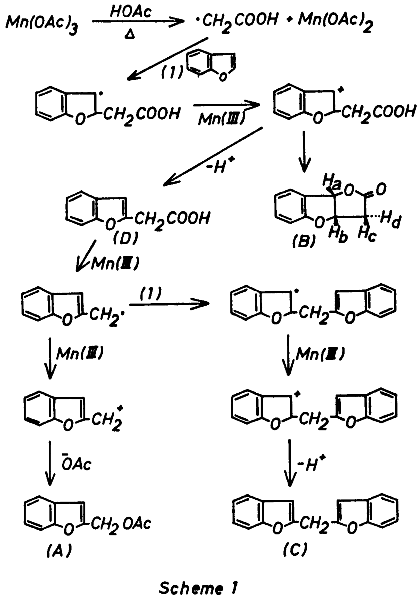
Previously, Heiba *et al.*[1] reported a novel one-step synthesis of γ-lactones by the reaction of olefins with manganic acetate in acetic acid; they suggested that a free radical mechanism involving the selective generation and oxidation of organic free radicals is present. The oxidation of aromatic hydrocarbons by manganic acetate was also described by the same authors.[2]

It is considered that benzofuran (I) possesses a generally aromatic character, plus some characteristics of an enol ether. The present investigation deals with the manganic acetate oxidation of I.

## Results and Discussion

In a mixture of acetic acid and acetic anhydride, I and manganic acetate were heated to reflux until the dark brown color of the Mn(III) had disappeared. 2-(Acetoxymethyl)benzofuran (**A**) and 3a,8b-dihydrofuro[3,2-*b*]benzofuran-2(3*H*)-one (**B**) were obtained as the main products and bis(2-benzofuranyl)methane (**C**) and 2-benzofuranylacetic acid (**D**) as the minor products.

In general, the thermolysis of manganic acetate leads almost exclusively to the formation of $\cdot CH_2COOH$ radical.[2,3] Spagnolo *et al.*[4] reported that, in I, the attack by the free radicals mainly occurs at the 2-position. Consequently, in the reaction of I with manganic acetate, the attack by the $\cdot CH_2COOH$ radical most likely occurs at the 2-position of I; this mechanism is shown in Scheme 1. The mechanism to account for the formation of **B** and **D** is similar to the one suggested for the olefin-manganic acetate oxidation.[1] Heiba *et al.*[2] reported that the oxidation of anisole with manganic acetate leads to the formation of a mixture of *o*-, *m*-, and *p*-methoxybenzyl acetate, and also suggested that *o*-, *m*-, and *p*-methoxyphenylacetic acid, formed primarily from the reaction of anisole with $\cdot CH_2COOH$ radicals, are the precursors of these products. Van Der Ploeg *et al.*[3] also showed that phenylacetic acid is decarboxylated by manganic acetate, leading to the formation of benzyl radicals. Therefore, the formation of **A** and **C** may well be attributed to the reaction of **D** with manganic acetate, followed by the formation of 2-benzofuranylmethyl radicals.



Scheme 1

## Experimental

The melting and boiling points are uncorrected. The IR and mass spectra were measured using a Hitachi 215 spectrophotometer and a Model RMU-6M mass spectrometer at 70 eV. The NMR spectra were obtained on a Hitachi Model R-22 (90 MHz), using tetramethylsilane as an internal standard (δ, ppm). Column chromatography was carried out on Kanto-Kagaku silica gel.

*Materials.* The preparation of the following compounds has already been reported: manganic acetate dihydrate[2] and benzofuran (I).[5]

*The Reaction of Benzofuran (I) with Manganic Acetate.* A solution of I (9.44 g, 0.08 mol) in 50 ml of acetic acid was refluxed under nitrogen with 5.36 g (0.02 mol) of manganic acetate dihydrate, in the presence of 12 ml of acetic anhydride, until the brown manganic color disappeared. The reaction mixture was diluted with water and extracted several times with ether. The ether extracts were then dried and evaporated. The residue was chromatographed on silica gel with hexane as the eluent.

The first elution with hexane gave 0.40 g (42%[6]) of **A**, bp 156—157 °C/16 Torr. Found: C, 69.61; H, 5.37%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%. IR spectrum (oil film): 3030, 1740 (C=O), 1590, 1240 (-OAc), 830, 810, 760, 750 $cm^{-1}$. NMR spectrum: δ 1.95 (s, 3H, $CH_3$), 5.10 (s, 2H, $CH_2$), 6.62 (s, 1H, H on $C_3$), 7.00—7.50 ppm (m, 4H, H on benzene ring). Mass spectrum *m*/*e* (rel. intensity): 190 (22) ($M^+$ for $C_{11}H_{10}O_3$), 148 (10) ($M^+-CH_2=C=O$), 131 (100) ($M^+-OAc$). The physical constants and IR and NMR spectra were identical with those of 2-(acetoxymethyl)benzofuran, which was prepared by acetylation of 2-benzofuranylmethanol.[7]

The second elution with hexane gave 0.37 g (21%[6]) of **B**, mp 111—112 °C (ethanol). Found: C, 68.03; H, 4.38%. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58%. IR spectrum (KBr): 3050, 3000, 2980, 1770 (C=O), 1610, 1480, 1240 (O–C=O), 1040, 740 $cm^{-1}$. NMR spectrum: δ 2.95 (s, 1H, $H_d$), 3.00 (d, 1H, $J_{b,c}=2$ Hz, $H_c$), 5.35 (d-d, 1H, $J_{a,b}=6$ Hz,

$J_{b,c}$=2 Hz, $H_b$), 5.99 (d, 1H, $J_{a,b}$=6 Hz, $H_d$), 7.00—7.50 ppm (m, 4H, H on benzene ring). Mass spectrum *m/e* (rel. intensity); 176 (65) ($M^+$ for $C_{10}H_8O_3$), 131 (100) (2-benzofuranyl-$CH_2^+$). After hydrolysis of **B** with potassium hydroxide solution, the treatment of the reaction product with hot acetic anhydride led to 2-benzofuranylacetic acid, mp 97—98 °C.[8] From these results, **B** was identified as 3a,8b-dihydrofuro[3,2-*b*]benzofuran-2(3*H*)-one.

The following elution with hexane–benzene (1: 1) gave 0.042 g (3%[6]) of **C**, mp 73—74 °C (methanol). Found: C, 82.43; H, 4.96%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. IR spectrum (KBr): 3050, 2930, 1600, 1580, 1445, 810, 790, 750 $cm^{-1}$. NMR spectrum: $\delta$ 4.18 (s, 2H, $CH_2$), 6.46 (s, 2H, H, on $C_3$ and $C_3'$), 7.10—7.50 ppm (m, 8H, H on benzene rings). Mass spectrum *m/e* (rel. intensity): 248 (15) ($M^+$ for $C_{17}H_{12}O_2$), 131 (100) (2-benzofuranyl-$CH_2^+$). **C** is identical in all respects with bis(2-benzofuranyl)methane, which was prepared by Wolff-Kishner reduction of bis(2-benzofuranyl) ketone.[9]

The elution with chloroform gave 0.032 g (0.2%[6]) of **D**, 2-benzofuranylacetic acid, mp 97—98 °C (lit,[7] mp 97—99 °C).

## References

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6) This calculation is based on the stoichiometry of 2 mol of manganic acetate/mol of **B** and **D** produced, and 4 mol of manganic acetate/mol of **A** and **C** obtained. This stoichiometry is required by the mechanism presented in this paper.

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