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Acylcobalt salophen complexes. Homolytic decomposition to salicyl aldehyde esters

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Abstract

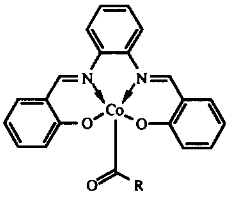
Irradiation of acylcobalt salophen complexes leads to salicyl aldehyde ester products resulting from cobalt-to-oxygen migration.

1. Discussion

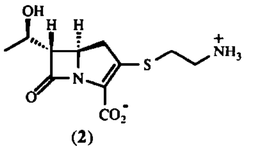
In earlier work we have described the synthesis of a range of novel alkyl, vinyl, aryl, oxy and aminyl acylcobalt salophen complexes, *i.e.* **1**, and demonstrated their uses in carbon-to-carbon bond forming reactions, including syntheses of cycloalkanones and β-lactams, *e.g.* thienamycin, **2** [1,2]. In other studies, with arylmethyl-substituted acylcobalt salophens, we have shown that carbon-to-cobalt bond homolysis is accompanied by *in situ* decarbonylation, producing new alkyl radical centres which can be intercepted by radical trapping agents, leading to functionalised noralkanes *i.e.g.* **3** → **4** [3].

In neither of the aforementioned investigations did we observe the co-formation of 1,2-dione by-products resulting from competitive coupling reactions between the acyl radical intermediates. This feature presumably reflects the greater ease of reaction between the acyl radical intermediates and the more reactive radical acceptor molecules used in the reactions. In connection with a quite separate study involving polycarbonyl compounds, we have now examined the independent chemistry of a number of acylcobalt complexes, under a range of homolytic cleavage conditions, with a view to the synthesis of 1,2-dicarbonyl compounds.

Thus, when a solution of the acylsalophen **1a** was heated in dichloromethane or benzene, under anaerobic conditions, it was recovered (70–90%) unchanged.



(1)



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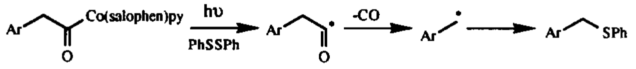

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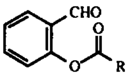
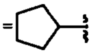
(4)



(5)

a; R = CMe_3 b; R = Et c; R = C_5H_{11} d; R = CH_2CMe_3

e; R =  f; R = $CHMe_2$

When the same acylcobalt salophen in dichloromethane was *irradiated* with a 300 W sunlamp at 25°C, however, the only monomeric organic product isolated was the salicyl aldehyde ester **5a**, in 26% yields. Likewise, irradiation of the related alkylacyl cobalt salophen complexes **1b** → **1f** led to the corresponding esters **5b** → **5f**. In neither instance were we able to detect the co-formation of 1,2-dione products in any of these reactions.

Although rearrangement reactions within coenzyme B_{12} model complexes are known [4], the homolytic

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cleavage of cobalt salophen complexes leading to products resulting from cobalt-to-oxygen migrations, *i.e.* **1** → **5**, is without precedent. This study suggests that some of the modest yields reported in the literature for synthetic work with cobalt salophens [1,2] could be accounted for by taking into consideration competitive migrations of the type described here and elsewhere [4].

2. Experimental details

2.1. *Photolysis of acylcobalt(III) salophen complexes at room temperature. General procedure*

A solution of the acylcobalt complex [1] in dry distilled dichloromethane was irradiated under nitrogen at room temperature using a 300 W sunlamp (*d* 10–20 cm) for 8–40 h. The progress of the reaction was monitored by TLC, and interrupted when all the starting material had disappeared. The mixture was filtered through a short pad of silica, and the filtrate was then concentrated *in vacuo* to leave a residue which was purified by column chromatography (silica; dichloromethane).

2.2. *2-Formylphenyl 2,2-dimethylpropanoate (5a)*

According to the general procedure, tertiary butanoylcobalt(III) salophen complex (249 mg, 0.544 mmol) in dichloromethane (10.0 ml) was irradiated for 36 h to afford the aldehyde ester (29 mg, 26%) as a pale yellow oil; ν_{max} (film) 2977, 2936, 2874, 1755, 1698, 1605m 1582 and 1104 cm^{-1}; δ(H) $CDCl_3$ (400-MHz) 10.15 (1H, s, C*H*O); 7.90 (1H, dd, *J* 7.8, 1.6 Hz, Ar*H*CHO); 7.62 (1H, ddd, *J* 7.8, 7.7, 1.6 Hz, Ar*H*H); 7.37 (1H, ddd, *J* 7.8, 7.7, 1.6 Hz, Ar*H*H), 7.14 (1H, d, *J*7.7 Hz, Ar*H*O) and 1.42 (9H, s, $(CH_3)_3$); δ(C) $CDCl_3$ (100 MHz) 176.1, 152.0, 127.8, and 38.9 (qC), 187.8, 134.7, 129.5, 125.7, and 122.8 (CH) and 26.6 (CH_3) (Found: M^+ 206.0953. $C_{12}H_{14}O_3$ calc.: *M* 206.0943)

2.3. *2-Formylphenyl propanoate* (**5b**)

According to the general procedure, a solution of propanoylcobalt(III) salophen complex (197 mg, 0.383 mmol) in dichloromethane (10.0 ml) was irradiated for 24 h. Chromatography (silica; hexane 80% EtOAc 20%) afforded the pure aldehyde ester (11.8 mg, 17%) as a colourless oil; δ(H) $CDCl_3$ (400 MHz) 10.1 (1H, s, C*H*O); 7.89 (1H, dd, *J* 7.7, 1.6 Hz, Ar*H*CHO); 7.63 (1H, ddd, *J* 7.7, 7.5, 1.6 Hz, Ar*H*H); 7.40 (1H, ddd, *J* 7.7, 7.5, 1.7 Hz, Ar*H*H); 7.19 (1H, d, *J* 7.5, Hz, Ar*H*O); 2.71 (2H, q, *J* 7.5 Hz, CH_2) and 1.31 (3H, t, *J*7.5 Hz, CH_3) (Found: M^+ 178.0627 $C_{10}H_{10}O_3$ calc.: *M*, 178.0630), and also gave the corresponding benzoic acid (1.3 mg, 2%) as an amorphous solid, m.p. 82.0–84.0°C, ν_{max} ($CHCl_3$) 3400–2700, 1759, 1704, 1609 and 1149 cm^{-1}; δ(H) $CDCl_3$ (400 MHz) 8.11 (1H, d, *J* 7.7 Hz, Ar*H*CO_2H); 7.62 (1H, t, *J* 7.9 Hz, Ar*H*H); 7.35 (1H, t, *J* 7.7 Hz, Ar*H*H); 7.13 (1H, d, *J* 7.9 Hz, Ar*H*O); 2.65 (2H, q, *J* 7.5 Hz, CH_2) and 1.28 (3H, t, *J* 7.5 Hz, CH_3); δ(C) $CDCl_3$ (68 MHz) 173.1, 169.5, 151.4, 134.8, 132.5, 126.1, 124.0, 122.2, 27.7 and 8.8 (Found: M^+ 194.0553. $C_{10}H_{10}O_4$ calc.: *M* 194.0579).

2.4. *2-Formylphenyl hexanoate* (**5c**)

According to the general procedure, a solution of hexanoylcobalt(III) salophen complex · $0.5Ch_2Cl_2$ (202 mg, 0.393 mmol) in dichloromethane (10.0 ml) was irradiated for 13 h to give the aldehyde ester (17.8 mg, 21%) as a colourless oil; ν_{max} (film) 3080, 2958, 2932, 1767, 1698, 1605 and 1267 cm^{-1}; δ(H) $CDCl_3$ (250 MHz) 10.1 (1H, s, C*H*O); 7.89 (1H, dd, *J* 7.7, 1.4 Hz, Ar*H*CHO); 7.64 (1H, ddd, *J* 8.2, 7.7, 1.4 Hz, Ar*H*H); 7.39 (1H, ddd, *J* 8.2, 7.7, 1.7 Hz, Ar*H*H); 7.18 (1H, dd, *J* 8.2, 1.7 Hz, Ar*H*O); 2.67 (2H, t, *J* 7.4 Hz, COCH_2); 1.80 (2H, m, CH_2); 1.41 (4H, m, 2 × CH_2) and 0.94 (3H, t, *J* 6.9 Hz, CH_3); δ(C) $CDCl_3$ (100 MHz) 188.63, 172.04, 151.9, 135.3, 130.8, 128.2, 126.3, 123.5, 34.1, 31.3, 24.4, 22.3 and 13.9 (Found: M^+ 220.1108. $C_{13}H_{16}O_3$ calc.: *M* 220.1099).

2.5. *2-Formylphenyl 3,3-dimethylbutanoate* (**5d**)

According to the general procedure, a solution of 3,3-dimethylbutanoylcobalt(III) salophen complex (312 mg, 0.490 mmol) in dichloromethane (10.0 ml) was irradiated for 15 h to give the aldehyde ester (21.1 mg, 20%) as a colourless oil; ν_{max} (film) 2959, 2871, 1764, 1698, 1605, 1582, 1277 and 1108 cm^{-1}; δ(H) $CDCl_3$ (250 MHz) 10.16 (1H, s, C*H*O); 7.90 (1H, dd, *J* 7.6, 1.7 Hz, Ar*H*CHO); 7.64 (1H, ddd, *J* 7.6, 7.4, 1.7 Hz, Ar*H*H); 7.39 (1H, ddd, *J* 7.6, 7.4, 1.7 Hz, Ar*H*H); 7.19 (1H, dd, *J* 7.4, 1.7 Hz, Ar*H*O); 2.56 (2H, s, CH_2) and 1.16 (9H, s $(CH_3)_3$); δ(C) $CDCl_3$ (100 MHz) 170.4, 152.0, 128.2, and 31.0 (qC), 188.6, 135.2, 130. 3, 126.3 and 123.5 (CH), 47.4 (CH_2) and 29.6 (CH_3) (Found: M^+ 220.1108. $C_{13}H_{16}O_3$ calc.: *M* 220.1099).

2.6. *2-Formylphenyl cyclopentylmethanoate* (**5e**)

According to the general procedure, cyclopentylcarbonylcobalt(III) salophen complex (33.4 mg, 0.071 mmol) in dichloromethane (10.0 ml) was irradiated for 10 h to give the aldehyde ester (2.3 mg, 15%) as a pale yellow oil; δ(H), $CDCl_3$ (400 MHz) 10.15 (1H, s, C*H*O); 7.90 (1H, dd, *J* 7.5, 1.7 Hz, Ar*H*CHO); 7.63 (1H, ddd, *J* 7.6, 7.5, 1.7 Hz, Ar*H*H); 7.52 (1H, ddd, *J* 7.6, 7.5, 1.0 Hz, Ar*H*H); 7.18 (1H, dd, *J* 7.6, 1.0 Hz, Ar*H*O): 3.09 (1H, m, C*H*CO) and 2.2–1.5 (8H, m, 4 × CH_2) (Found: M^+ 218.0944. $C_{13}H_{14}O_3$ calc.: *M* 218.0943).

2.7. *2-Formylphenyl 2-methylpropanoate* (**5f**)

According to the general procedure, a solution of 2-methylpropanoylcobalt(III) salophen complex (279 mg, 0.526 mmol) in dichloromethane (10.0 ml) was irradiated for 40 h to afford a mixture of the aldehyde ester and the corresponding benzoic acid; δ(C) $CDCl_3$ (100 MHz) 175.4, 175.2, 170.1, 152.1, 151.4, 128.2 and 122.5 (qC), 188.6, 135.3, 134.7, 132.5, 130.5, 126.3, 126.0, 124.0, 123.4, 34.2 and 34.2 (CH), 18.9 and 18.8 (CH_3) of the mixture. Chromatography (silica; hexane 80%EtOAc 20%) gave the pure aldehyde ester (4 mg, 4%) as a colourless oil; δ(H) $CDCl_3$ (400 MHz) 10.10 (1H, s, C*H*O); 7.89 (1H, dd, *J* 7.6, 1.7 Hz, Ar*H*CHO); 7.62 (1H, ddd, *J* 7.9, 7.6, 1.7 Hz, Ar*H*H); 7.38 (1H, ddd, *J* 7.9, 7.6, 1.7 Hz, Ar*H*H); 7.17 (1H, d, *J* 7.9 Hz, Ar*H*O); 2.92 (1H, quin., *J* 7.0 Hz, $CH(CH_3)_2$); 1.37 (6H, d, *J* 7.0 Hz, $CH(CH_3)_2$) (Found: M^+ 192.0796 $C_{11}H_{12}O_3$ calc.: *M* 192.0786), and the benzoic acid derivative (17.4 mg, 16%) as a white crystalline solid, m.p. 88.0–92.5°C, ν_{max} (Nujol) 3400–2600, 1752, 1705, 1607 and 1274 cm^{-1}; δ(H) $CDCl_3$ 8.11 (1H, dd, *J* 7.9, 1.6 Hz, ArHCO_2H); 7.61 (1H, ddd, *J* 7.9, 7.8, 1.6 Hz, Ar*H*H); 7.34 (1H, ddd, *J* 7.9, 7.8, 1.6 Hz, Ar*H*H); 7.11 (1H, d, *J* 7.8 Hz, Ar*H*O); 2.86 (1H, quin., *J* 7.0 Hz, $CH(CH_3)_2$) and 1.34 (6H, d, *J* 7.0 Hz, $(CH_3)_2$); δ(C) $CDCl_3$ (100 MHz) 175.5, 170.2, 151.5 and 122.5 (qC), 134.8 132.6, 126.1 and 124.1 (CH) and 18.9 (CH_3) (Found: C, 63.12; H, 6.05%; M^+ 208.0796. $C_{11}H_{12}O_4$ calc. C, 63,45; H, 5.81%; *M* 208.0736).

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