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A Study of a Condensation Product Obtained from 6-Methyl-3(2*H*)-benzofuranone and Acetic Anhydride

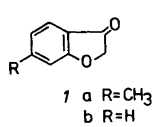
JAN BERGMAN and BÖRJE EGESTAD

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

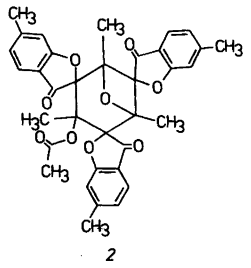
A reinvestigation of the condensation between 6-methyl-3(2*H*)-benzofuranone (*1a*) and acetic anhydride has been undertaken. The data obtained from ^{13}C NMR and UV measurements gave conclusive evidence that the compound obtained from this reaction is 1,1,1-tris(3-acetoxy-6-methylbenzofuran-2-yl)ethane (*4*).

In connection with the studies[1] of cyclocondensations of 3(2*H*)-benzofuranones we became interested in a trimeric condensation product originally reported by Bohlmann and Zdero.[2] The trimer, $C_{35}H_{30}O_9$, is readily obtained, albeit in modest yield, by treating 6-methyl-3(2*H*)-benzofuranone (*1a*) with acetic anhydride containing 1 % sulfuric acid. The highfield region of the ^1H NMR spectrum[2] of the trimer consists of three singlets [1.44 (9 H), 2.34 (3 H) and 2.44 (9 H)]. The German workers concluded that the trimer must be relatively symmetrical and suggested structure *2*. However, we felt that formation of an oxetane ring during the conditions given is unlikely and, furthermore, that the simplicity of the ^1H NMR spectrum requires a considerably more symmetrical structure, such as one with C_3-symmetry.

In their IR spectra 3(2*H*)-benzofuranones of type *1* display strong C=O stretching vibrations[3,4] at 1710 ± 10 cm^{-1}, whereas the trimer lacks such an absorption. Furthermore, 3(2*H*)-benzofuranones are known[5] to have a UV absorption band at around 325 nm, which is absent in the UV spectrum of the trimer. On the basis of the IR and UV spectra of the trimer, a structure such as *2* seems highly unlikely.



1 a R=CH$_3$
b R=H



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We have, therefore, further investigated the properties of the trimer and one related compound. The ^{13}C NMR spectrum of the trimer displays only 13 lines, supporting a highly symmetrical structure. The downfield signal at 167.70 ppm indicates a carboxylate carbon atom rather than a ketonic carbon atom. From the foregoing discussion, it seems likely that 3-acetoxy-2,6-dimethylbenzofurane (*3*)[6] could be used as a suitable model for the trimer.

The UV spectra of the acetate *3* and the trimer show a very close resemblance. The former com-

Table 1. ^{13}C NMR chemical shifts of trimer *4*, 3-acetoxy-2,6-dimethylbenzofurane (*3*) and 6-methyl-3(2*H*)-benzofuranone (*1a*).

Carbon	Trimer *4*	*3*	*1a*
$OCOCH_3$	167.70	168.09	
$OCOCH_3$	19.22	20.13	
C(2)	142.05	143.37	74.88
C(3)	131.38	130.05	199.08
C(3b)	120.85	121.03	118.84
C(4)	118.89	117.55	123.48
C(5)	124.42	124.08	123.48
C(6)	135.42	133.97	149.76
C(7)	111.89	111.55	113.53
C(7b)	152.50	152.70	174.44
C(6)–CH_3	21.64	21.41	22.32
C(2)–CH_3		10.96	
$C(2)_3C-CH_3$	41.36		
$C(2)_3C-CH_3$	23.32		

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pound displays a C=O stretching vibration at 1775 cm^{-1}, and the trimer one at 1770 cm^{-1}. The ^{13}C NMR spectra of the trimer, the acetate *3*, and 6-methyl-3(2*H*)-benzofuranone (*1a*) are compiled in Table 1. The signals were assigned on the basis of their multiplicity in the off-resonance spectra as well as the $^{13}C-^{1}H$ spin coupling constants. The close relationship between the acetate *3* and the trimer made it clear to us that the structure of the trimeric compound must be *4*.

The acetoxy proton resonance of the trimer (1.44 ppm) is shifted strongly upfield relative to those of the model compound *3*, which resonates at 2.27 ppm. The difference in chemical shift is as large as 0.83 ppm. Probably the acetoxy protons are forced into the shielding regions of the aromatic rings, due to steric crowding in the propeller-shaped molecule. This effect has been observed to some extent in related crowded triarylmethane derivatives (*cf.* Refs. 7 and 8).

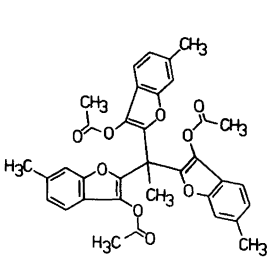
The rather unusual acetoxy proton resonance prompted us to investigate the ^{1}H NMR spectrum of tris(2-acetoxyphenyl)methane (*5*) as a model. However, this compound gave a resonance for the acetoxy protons at 2.03 ppm, which is nearly the same as for the uncrowded *o*-tolyl acetate.

The formation of the trimer *4* is most easily explained if one assumes that the benzofuranone *1a* is *C*-acetylated to give compound *6a*, followed by condensation of the latter with one mol of the parent compound *1a* to give the intermediate *7*, which then undergoes Michael addition of an additional mol of compound *1a*. After *O*-acetylation this would lead to the final product *4*. The two initial steps are the same as those suggested by Bohlmann and Zdero[2] to be involved in the formation of the purported compound *2*.

The proposed mechanism is supported by the fact that the treatment of one mol of 3-acetoxy-2-acetyl-6-methylbenzofurane (*6b*) with two mol of 3-acetoxy-6-methylbenzofurane (*8*) under otherwise unchanged conditions failed to yield the trimer *4* (TLC analysis). The *O*-acetylation must consequently occur in one of the last steps, most likely in the last step.

We have also investigated the possibility to obtain the parent ring system of the trimer *4* from 3(2*H*)-benzofuranone (*1b*), which however only yielded 3-acetoxy-2-acetylbenzofurane (*9*).

It should be added that the mass spectrometric fragmentation scheme of the condensation product, formulated by Bohlmann and Zdero[2] fits excellently with structure *4*.



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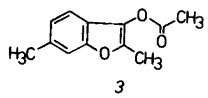

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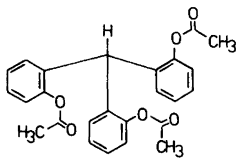

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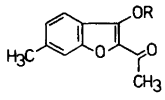
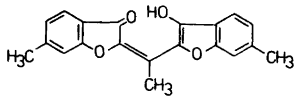


6 a R=H
b R=COCH$_3$



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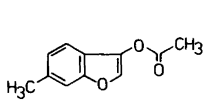

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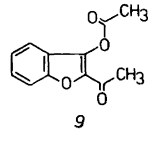

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EXPERIMENTAL

Melting points were determined on a micro hot stage apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 257 infrared spectrophotometer, the spectra being determined on KBr discs unless otherwise stated. UV spectra (solvent: ethanol) were recorded with a Hitachi 200 spectrophotometer. ^{1}H NMR spectra were obtained using a Varian EM-360 spectrometer (60 MHz) or a Bruker WP 200 spectrometer (200 MHz) and ^{13}C NMR spectra were obtained using a Varian XL-100A spectrometer (25.2 MHz). The samples were dissolved in $CDCl_3$.

6-Methyl-3(2*H*)-benzofuranone[9] (*1a*), 3(2*H*)-benzofuranone[9] (*1b*) and 3-acetoxy-6-methylbenzofuranone[6] (*8*) were prepared as described elsewhere.

1,1,1-Tris(3-acetoxy-6-methylbenzofuran-2-yl)-ethane (4). 6-Methyl-3(2*H*)-benzofuranone (*1a*) (2.7 g) in 30 ml acetic anhydride containing 0.3 ml sulfuric acid was kept at room temperature for 5 h. The white precipitate formed was collected and dried.

Yield 0.6 g (17 %), white crystals (diethyl ether–ethanol), m.p. 219–221 °C (lit.[2] m.p. 218 °C).

IR: 1785 (CO), 1770 (CO), 1364, 1210, 1146, 1080, and 810 cm^{-1}. IR($CHCl_3$): 1770 (CO) cm^{-1}. UV(log ε): 211 (5.01), 252 (4.74), 260 (4.77), 280 (4.42), 283 (4.43), and 289 (4.50) nm.

^{1}H NMR (200 MHz): δ 1.43 (9 H, s, $OCOCH_3$), 2.34 (3 H, s, $C-CH_3$), 2.45 (9 H, s, 3 $ArCH_3$), 7.04 (3 H, dd, *J* 1.4 and 8.0 Hz, 3 C(5)–*H*, 7.14 (3 H, dd, *J* 0.7 and 8.0 Hz, 3 C(4)–*H*), and 7.26 (3 H, dd, *J* 0.7 and 1.4 Hz, 3 C(7)–*H*). ^{13}C NMR: See Table 1.

3-Acetoxy-2,6-dimethylbenzofurane (3). A sample of this compound was generously supplied by Professor Cagniant.[6] IR(film): 1775 (CO), 1363, 1269, 1202, 1154, and 1132 cm^{-1}. UV(log ε): 207 (4.25), 213 (4.24), 250 (3.97), 255 (3.94), 282 (3.42), and 290 (3.39) nm.

^{1}H NMR(200 MHz): δ 2.23 (3 H, s, C(2)–CH_3), 2.27 (3 H, s, $OCOCH_3$), 2.36 (3 H, s, $ArCH_3$), 7.01 (1 H, dd, *J* 1.1 and 7.1 Hz, C(5)–*H*), 7.17 (1 H, dd, *J* 0.5 and 1.1 Hz, C(7)–*H*), and 7.18 (1 H, dd, *J* 0.5 and 7.1 Hz, C(4)–*H*). ^{13}C NMR: See Table 1.

3-Acetoxy-2-acetyl-6-methylbenzofurane (6b). This compound was prepared following the procedure given for 3-acetoxy-2-acetylbenzofurane by Geissman and Armen.[10] Colourless crystals (diethyl ether–light petroleum; b.p. 40–60 °C), m.p. 96–98 °C (lit.[2] m.p. 99 °C).

IR: 1783 (CO), 1680 (CO), 1573, 1380, 1358, 1192, 1160, and 824 cm^{-1}.

^{1}H NMR(60 MHz): δ 2.43, 2.47, 2.53, (9 H, 3 s, $ArCH_3$, $OCOCH_3$ and $COCH_3$) and 7.03–7.50 (3 H, m, Ar*H*).

Treatment of compound 6b *and compound* 8 *with acetic anhydride.* A solution of 3-acetoxy-6-methylbenzofurane (*8*) (0.21 g, 1.1 mmol) and 3-acetoxy-2-acetyl-6-methylbenzofurane (*6b*) (0.13 g, 0.56 mmol) in 5 ml acetic anhydride containing 0.05 ml sulfuric acid was kept at room temperature for 5 h. No precipitate was observed. The solution was treated with methanol and then neutralized with $NaHCO_3$. No trace of the trimer *4* could be detected by TLC (silica gel, diethyl ether–light petroleum; b.p. 40–60 °C, 1:1).

*Reaction of 3(2*H*)-benzofuranone in acetic anhydride.* 3(2*H*)-benzofuranone (*1b;* 0.9 g) in 10 ml acetic anhydride containing 0.1 ml sulfuric acid was kept at room temperature for 5 h. No precipitate was observed. The solution was treated with methanol, neutralized with $NaHCO_3$ and extracted with diethyl ether. The white crystals from the evaporated ether solution, m.p. 84–88 °C (diisopropyl ether) were shown to be 3-acetoxy-2-acetylbenzofurane (*9*) (lit.[10] m.p. 86–87 °C).

IR: 1775 (CO), 1679 (CO), 1570, 1380, 1195, 1165, and 761 cm^{-1}.

NMR(60 MHz): δ 2.33, 2.47 (6 H, 2 s, $OCOCH_3$ and $COCH_3$) and 7.00–7.53 (4 H, m, Ar*H*).

Tris(2-acetoxyphenyl)methane (5). Tri-*o*-anisylmethane[11,12] (1.2 g, 3.5 mmol) was treated[13] with BBr_3 (1 ml, 10.5 mmol) at −60 °C in dry CH_2Cl_2. The reaction mixture was stirred overnight and then poured into water. The solid formed was collected, dried (0.9 g), and without further characterization refluxed in a mixture of 10 ml acetic anhydride and 10 ml acetic acid for 2 h. When poured into water white crystals were formed, which were collected and dried. Yield 1.0 g (69 %), m.p. 151–153 °C (ethanol). Anal. $C_{25}H_{22}O_6$: C, H.

IR: 1760 (CO), 1485, 1450, 1370, 1205, 1095, 915, and 756 cm^{-1}.

NMR(60 MHz): 2.03 (9 H, s, 3 $OCOCH_3$), 5.80 (1 H, s, C*H*) and 6.67–7.37 (12 H, m, Ar*H*).

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