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CYCLOCONDENSATION OF 3(2*H*)-BENZOFURANONE

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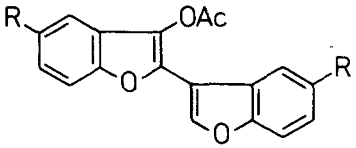
In 1911 Fries and Pfaffendorf[1] reported that 3-acetoxy-2,3´-bibenzofuranyl (1a), an acetylated condensation product from 3(2*H*)-benzofuranone (2a), when treated with HCl in HOAc (100 °C/8h, sealed tube) was transformed into a high-melting pale orange-red compound, with the composition $(C_8H_4O)_n$. The German workers proposed structure 3a (*s*-tetrakis-2:3-benzofuranocyclooctatetraen) for this compound on the basis of elemental analysis and mode of formation.

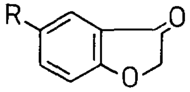
Several years later Baker and Banks[2] suggested, on the basis of a molecular weight determination (Rast) that products of this type should have the trimeric structure 4 rather than the tetrameric structure 3. To account for this they suggested, quite reasonably, that the starting material (1) underwent deacetylation and retro-aldolization followed by a cyclocondensation of the formed 3(2*H*)-benzofuranone with compound 1.

We have now repeated these condensations and determined the molecular weights by high-resolution MS[3] of the products obtained and studied the NMR-spectrum (270 MHz)[4] of the condensation product derived from compound 1b, which (in agreement with the original proposal) gave conclusive evidence for the general structure 3 for these products.[5] No trace of the trimeric compounds 4 could be detected in the cyclocondensation of compound 1a or 1b.

The structure 4a has also been assigned[6] to a yellow compound obtained in low yield by refluxing 3(2*H*)-benzofuranone (2a) in pyridine. However, this yellow compound ($C_{32}H_{18}O_6$, M^+=498.1103) was identical with a product formed in traces along with compound 3a. By changing the condition for the reaction from sealed tube at 100 °C to reflux at atomspheric pressure this yellow compound was the major solid product formed (albeit still in low yield). This compound has now been shown to have structure 5, by X-ray diffraction analysis.

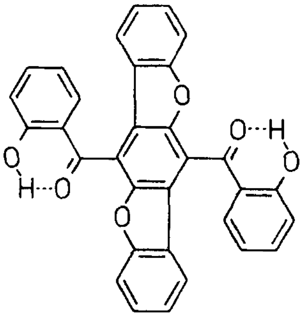


1



2

a R=H
b $R=CH_3$



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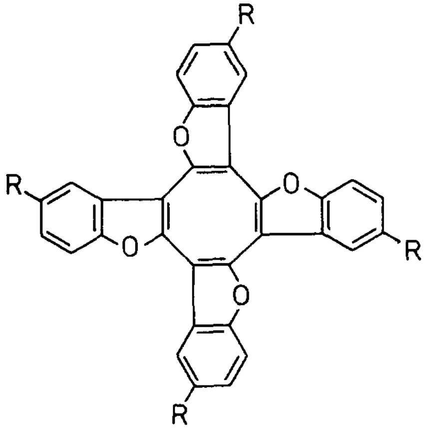

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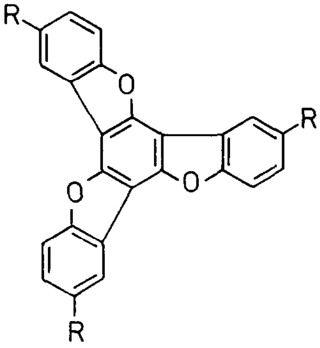
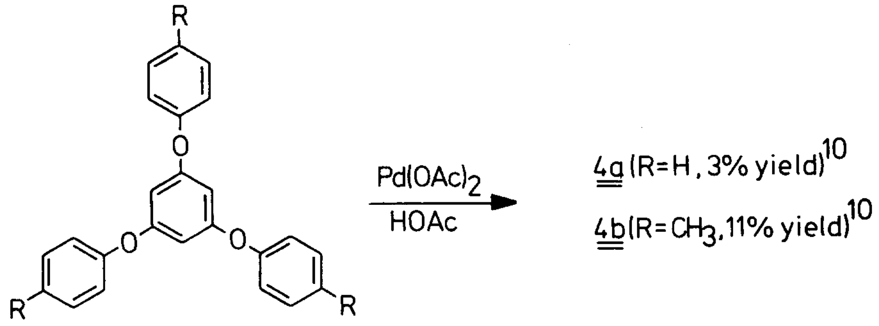


4

By treating 3(2*H*)-benzofuranone (2a)[7] with HCl in HOAc (100 °C/8h, sealed tube) it was possible to obtain the novel trimeric compound *s*-tris-2:3-benzofuranobenzene (4a) and compound 3a in the ratio 2:1, together with small amounts of compound 5. This mixture could be separated by gradient sublimation (330 °C/10 mm Hg).

The trimeric structure 4 was confirmed by an independent synthesis starting with the appropriate 1,3,5-triphenoxybenzenes (6).[8] (For related syntheses of dibenzofurans, see ref. 9.)



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

Acknowledgement: We thank Dr. H.-E. Högberg, Stockholm, for his interest in this work and Dr. O. Wennerström, Göteborg, for recording the 270 MHz NMR spectrum.

REFERENCES AND NOTES

1. K. Fries and W. Pfaffendorf, *Berichte* 44, 114 (1911).

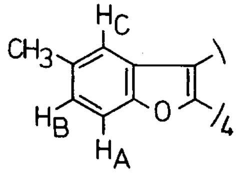
2. (a) Baker and Banks[2b] condensed compound 1b and claimed that the product had the composition $C_{27}H_{18}O_3$, which is in agreement with compound 4b.

(b) W. Baker and R. Banks, *J. Chem. Soc.*, 279 (1939).

3. (a) *s*-Tetrakis-2:3-benzofuranocyclooctatetraen, (3a): M.p. 383 °C (differential scanning calorimetry). High resolution MS gave M^+=464.1041 (calculated 464.1048 for $C_{32}H_{16}O_4$. MS: 466 (7), 465 (35), 464 (100), 436 (10), 435 (28), 232.5 (10), 232 (27), 217 (8). Only peaks higher than 5% of the base peak are listed.

(b) *s*-Tetrakis-2:3-(5-methylbenzofurano)-cyclooctatetraen, (3b): M.p. 428 °C (differential scanning calorimetry). High resolution MS gave M^+=520.1677 (calculated 520.1675 for $C_{36}H_{24}O_4$). MS: 522 (9), 521 (41), 520 (100), 491 (7), 477 (7), 260.5 (9), 260 (28), 238 (6). Only peaks higher than 5% of the base peak are listed.

4. NMR (270 MHz, $CDCl_3$): δ = 2.48 (12H, s, $ArCH_3$), 7.18 (4H, q, H_B), 7.47 (4H, d, H_A) and 7.59 (4H, d, H_C). J_{AB} = 8.5 Hz, J_{BC} = 1.5 Hz.



5. (a) The formation of 8-membered rings in cyclocondensations has been recorded before.[5b]

   (b) H. Erdtman and H.-E. Högberg, *Chem. Commun.*, 773 (1968). H.-E. Högberg, *Acta Chem. Scand.* 26, 309 (1972).

6. J.N. Chatterjea, *J. Ind. Chem. Soc.* 36, 69 (1959).

7. (a) The 3(2*H*)-benzofuranone was prepared according to Higginbotham and Stephen[7b] from phenoxyacetyl chloride, generously supplied by BASF AG, Ludwigshafen, Germany. For two new synthetic methods, see refs. 7c and 7d.

   (b) L. Higginbotham and H. Stephen, *J. Chem. Soc.* 117, 1534 (1920).

   (c) P. Cagniant and G. Kirsch, *Comptes rendus* 282C, 993 (1976).

   (d) D.R. Amick, *J. Het. Chem.* 12, 1051 (1975).

8. (a) Compound 6a was prepared according to Ullmann and Sponagel[8b] from 1,3,5-tribromobenzene and phenol, m.p. 108-110 °C (lit. m.p. 110 °C, after dest. 112 °C[9b]). Compound 6b was prepared in the same manner from 1,3,5-tribromobenzene and *p*-cresol, m.p. 97-99 °C (Spengler and Koll reported[9c] the following data: b.p. 163-169 °C/0.001 mm Hg, n_D^{20} = 1.6073).

   (b) F. Ullmann and P. Sponagel, *Berichte* 38, 2211 (1905). F. Ullmann and P. Sponagel, *Ann.* 350, 102 (1906).

   (c) G. Spengler and M. Koll, *Deut. Luft.-Raumfahrt,* Forschungsber. 68-86 (1968).

9. (a) B. Åkermark, L. Eberson, E. Jonsson and E. Petterson, *J. Org. Chem.* 40, 1365 (1975).

   (b) A. Shiotani and H. Itatani. *J. Chem. Soc. Perkin I,* 1236 (1976) and references therein.

10. (a) *s*-Tris-2:3-benzofuranobenzene, (4a): M.p. 344-346 °C. High resolution MS gave M^+= 348.0780 (calculated 348.0786 for $C_{24}H_{12}O_3$). MS: 350 (5), 349 (27), 348 (100), 319 (5), 263 (5), 174.5 (7), 174 (21), 131.5 (7). Only peaks higher than 4% of the base peak are listed.

    (b) *s*-Tris-2:3-(5-methylbenzofurano)-benzene, (4b): M.p. 280-282 °C. High resolution MS gave M^+=390.1262 (calculated 390.1256 for $C_{27}H_{18}O_3$). MS: 391 (7), 390 (24), 377 (7), 376 (24), 363 (9), 362 (34), 361 (7), 349 (26), 348 (100), 263 (7), 174.5 (7), 174 (22). Only peaks higher than 6% of the base peak are listed.

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