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A CONVENIENT PREPARATION OF 2-HYDROXYDIBENZOFURAN FROM 2,2'-DIHYDROXY-3,3',5,5'-TETRA-TERT-BUTYLBIPHENYL IN TWO STEPS[1]

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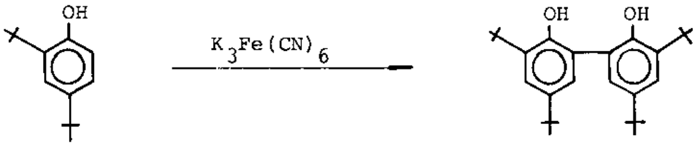
Abstract —— Bromination of 2,2'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl (2) with bromine in alcohols such as methanol and ethanol afforded the corresponding 1-bromo-2-alkoxy-4,5,7-tri-tert-butyldibenzofurans (5). The $AlCl_3$ catalyzed reaction of 5a (R = CH_3) in boiling toluene gave 2-hydroxydibenzofuran (7) in 79% yield. The mechanism of the formation of 5 from 2 was also discussed.

2-Hydroxydibenzofuran (7), a benzofuran derivative of some importance, has hitherto been prepared from readily available starting materials only by laborious method.[2] We wish to report here a convenient synthesis of 7 from 2,2'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl (2) in only two steps.

The starting material 2 was prepared by oxidative coupling[3] of 2,4-di-tert-butylphenol (1) which is commercially available.

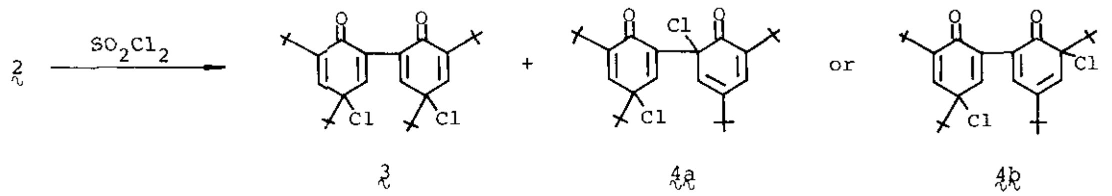


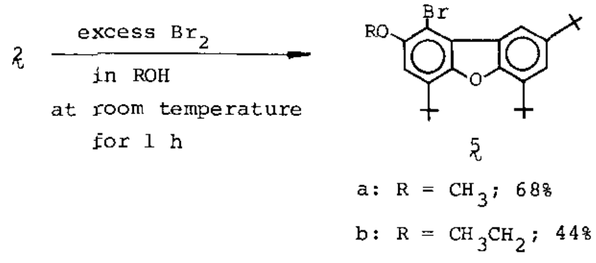
1

2

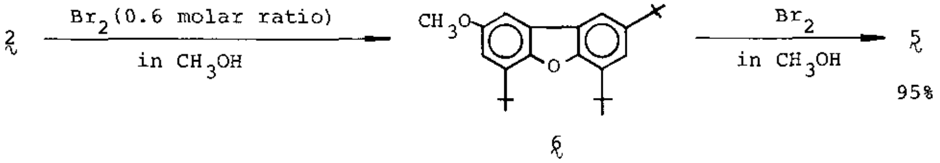
It has been previously reported that[1] chlorination of 2 with sulfuryl chloride afforded the biscyclohexadienones 3 and 4.

On the contrary, bromination of 2 with excess bromine (3.5 mole/1 mole of 2) in alcohols such as methanol and ethanol gave the corresponding 1-bromo-2-alkoxy-4,5,7-tri-tert-butyldibenzofurans (5)[4] in 68 and 44% yields, respectively. However,



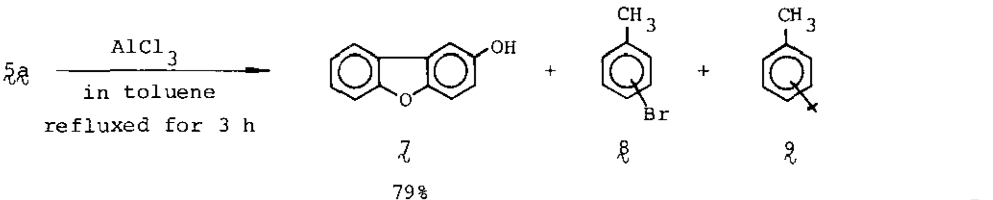


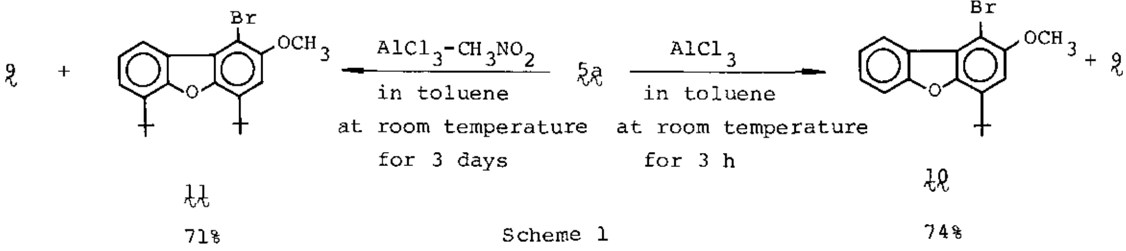
bromination of 2 in methanol with small amount of bromine afforded 2-methoxy-4,5,7-tri-tert-butyldibenzofuran (6)[5] together with a large amount of recovered 2. It was also found that bromination of 6 in methanol with bromine afforded 5 in 95% yield.



It has been reported that[6] tert-butyl and bromo groups could be used as a positional protective group for the selective preparation of some aromatic compounds. These results suggest that the $AlCl_3$ catalyzed reaction of 5 in aromatic solvent might afford the desired 2-hydroxydibenzofuran (7).

Indeed, conversion of 5a into the desired 7[2] was achieved in 79% yield by $AlCl_3$ catalyzed reaction in refluxing toluene; bromotoluenes (8) and tert-butyltoluene (9)



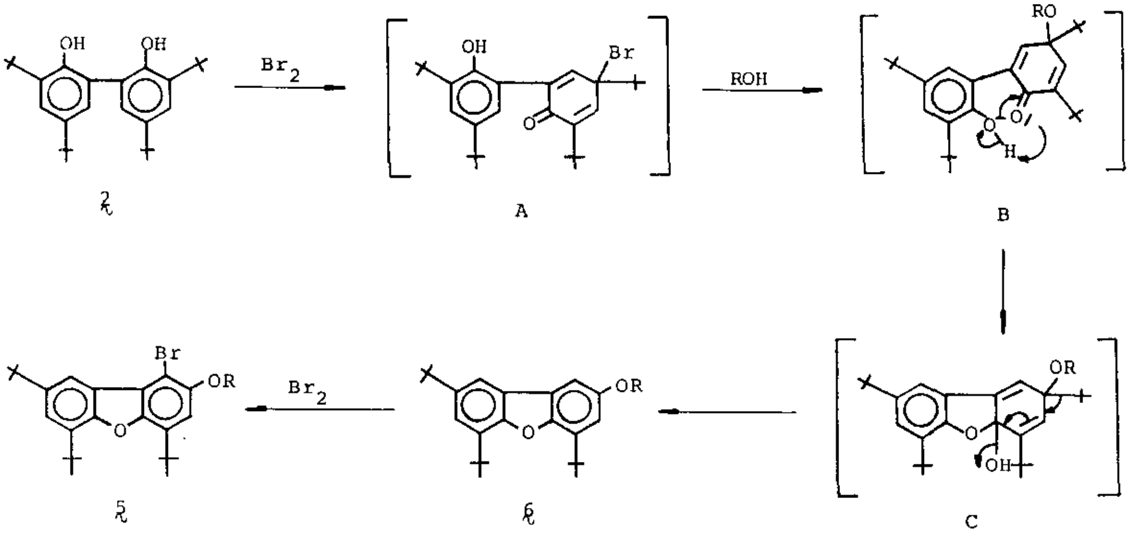


Scheme 1

were formed as side products.

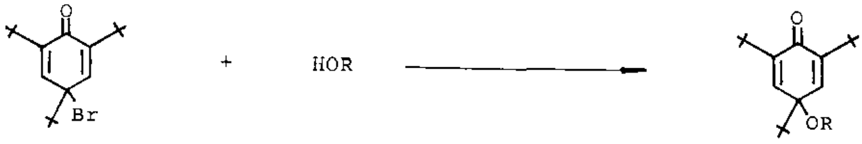
However, under the mild conditions as is shown in Scheme 1, one or two tert-butyl groups on 5a were selectively removed to afford 1-bromo-2-methoxy-4-tert-butyl-(10)[7] and 1-bromo-4,5-di-tert-butyl-dibenzofuran (11)[8] in 74 and 71% yields together with 9, respectively.

Based on the above results, the mechanism of formation of 5 from 2 might be proposed as is shown in the following Scheme 2.

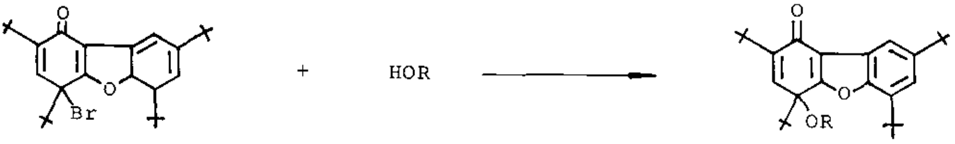


Scheme 2

Conversion of intermediate A into intermediate B seems to be reasonable because[1,9] 4-bromo-cyclohexa-2,5-dien-1-ones 12, 13 reacted with alcohols to give the corresponding 4-alkoxy derivatives 14, 15.



12 14



13 15

Compound **6** should be an intermediate of the formation of product **5** in the bromination of **2** under the used conditions.

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4. **5a**: colorless plates (methanol), mp 138-140°C, NMR ($CDCl_3$) δ 1.44, 1.57 and 1.59 (each 9H, s), 3.99 (3H, s), 7.05 (1H, s), 7.52 and 8.57 (each 1H, d, J = 2 Hz). **5b**: colorless plates (ethanol), mp 139.5-140.5°C, NMR ($CDCl_3$) δ 1.44, 1.56 and 1.59 (each 9H, s), 1.53 (3H, t, J = 6 Hz), 4.15 (2H, q, J = 6 Hz), 6.97 (1H, s), 7.43 and 8.48 (each 1H, d, J = 2.5 Hz).
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7. Colorless prisms (hexane), mp 150-151°C, NMR ($CDCl_3$) δ 1.55 (9H, s), 3.97 (3H, s), 7.06 (1H, s), 7.26-7.71 (3H, m), 8.58-8.72 (1H, m).
8. Colorless plates (methanol), mp 148.5-149.5°C, NMR ($CDCl_3$) δ 1.56 (18H, s), 3.95 (3H, s), 6.98 (1H, s), 7.24-7.43 (2H, m), 8.46 (1H, dd, 7.75 Hz, 2 Hz).
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