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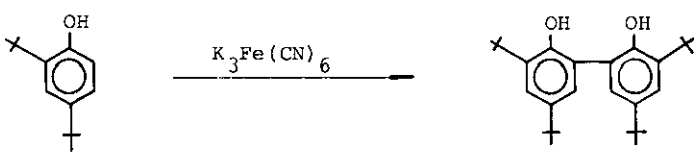
Abstract —— Bromination of 2,2'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl (2) with bromine in alcohols such as methanol and ethanol afforded the corresponding 1-bromo-2-alkoxy-4,5,7-tri-tert-butyldibenzofurans (5). The $AlCl_3$ catalyzed reaction of 5a (R = CH_3) in boiling toluene gave 2-hydroxydibenzofuran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

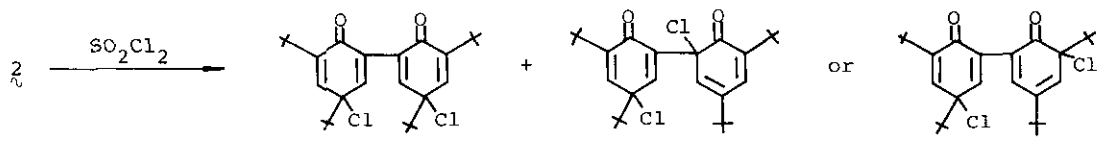
The starting material 2 was prepared by oxidative coupling[3] of 2,4-di-tert-butylphenol (1) which is commercially available.



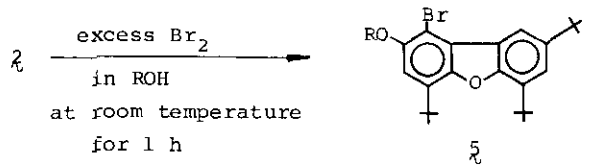
1 2

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,



3 4a 4b

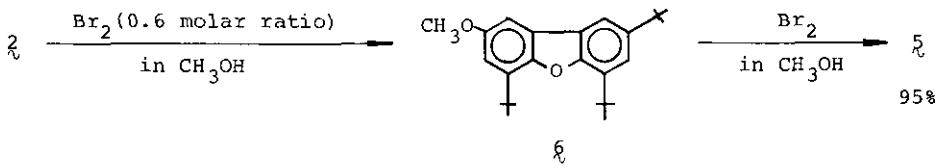


5

a: R = CH_3; 68%

b: R = CH_3CH_2; 44%

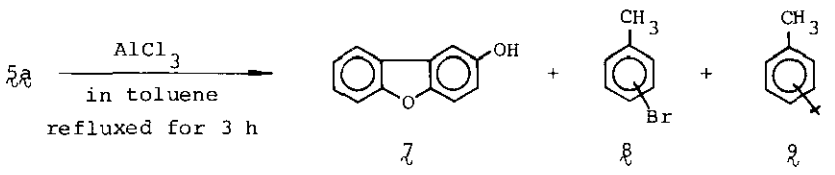
bromination of 2 in methanol with small amount of bromine afforded 2-methoxy-4,5,7-tri-tert-butyldibenzofuran (6)[5] together with a large amount of recovered 2. It was also found that bromination of 6 in methanol with bromine afforded 5 in 95% yield.



6

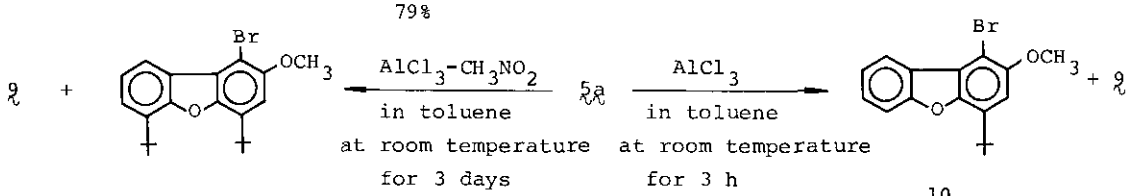
It has been reported that[6] tert-butyl and bromo groups could be used as a positional protective group for the selective preparation of some aromatic compounds. These results suggest that the $AlCl_3$ catalyzed reaction of 5 in aromatic solvent might afford the desired 2-hydroxydibenzofuran (7).

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)



7 8 9

79%



11 10

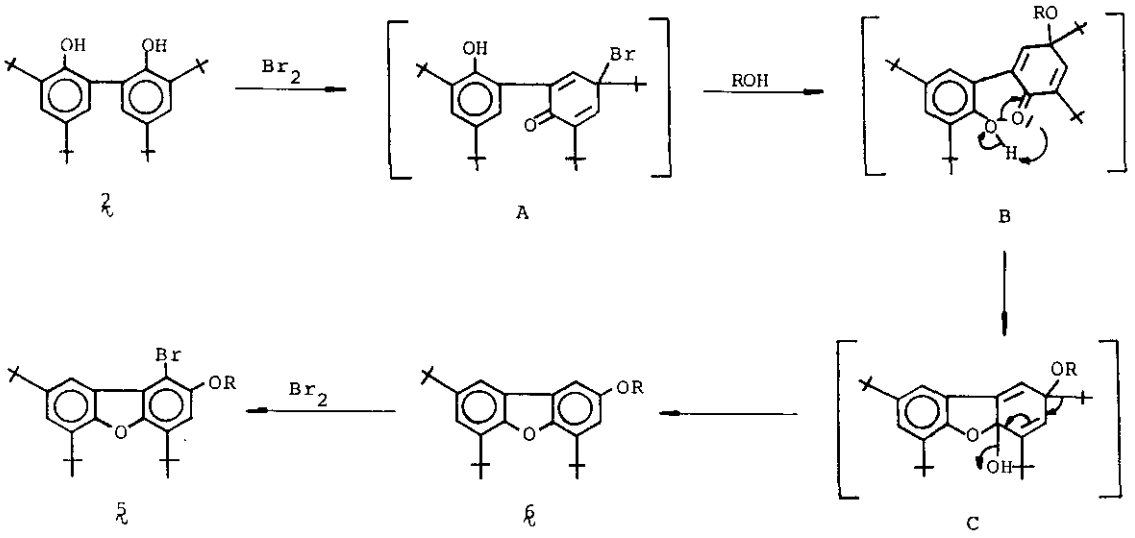
71% 74%

Scheme 1

were formed as side products.

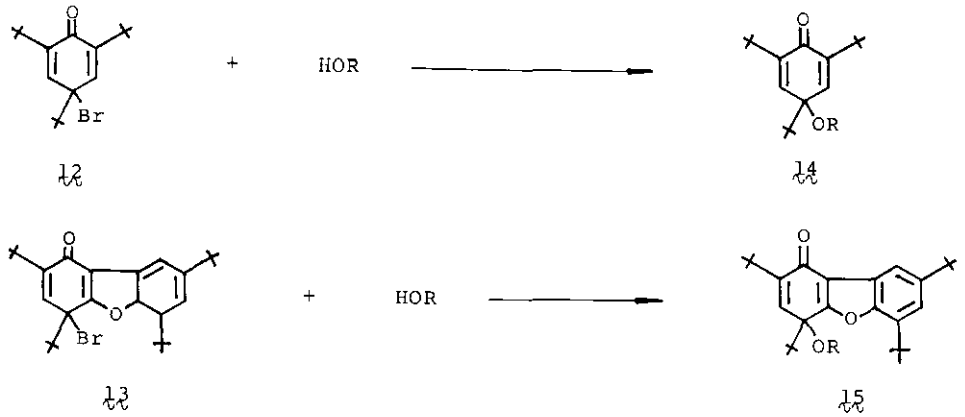
However, under the mild conditions as is shown in Scheme 1, one or two tert-butyl groups on 5a were selectively removed to afford 1-bromo-2-methoxy-4-tert-butyl-(10)[7] and 1-bromo-4,5-di-tert-butyl-dibenzofuran (11)[8] in 74 and 71% yields together with 9, respectively.

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.



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

REFERENCES AND NOTES

1. Selective Preparation; 32. Part 31. M. Tashiro, G. Fukata, and H. Yoshiya, submitted to J. Org. Chem..
2. H. Gilman, P. R. Van Ess, J. Am. Chem. Soc., 1939, 61, 1365.
3. E. Müller, R. Mayer, B. Narr, A. Rieker, and K. Scheffer, Liebigs Ann. Chem., 1961, 645, 25.
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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