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

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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-butyl dibenzofurans (ς). The AlCl₃ catalyzed reaction of ς₆ (R = CH₃) in boiling toluene gave 2-hydroxydibenzofuran (ξ) in 79% yield. The mechanism of the formation of ξ from ς was also discussed.

2-Hydroxydibenzofuran (ξ), 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 ξ from 2,2'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl (2) in only two steps. The starting material 2 was prepared by oxidative coupling³ of 2,4-di-tert-butylphenol (1) which is commercially available.

It has been previously reported that¹ chlorination of 2 with sulfuryl chloride afforded the biscyclohexadienones 3 and 4.
On the contrary, bromination of 2 with excess bromine (3.5 mole/l mole of 2) in alcohols such as methanol and ethanol gave the corresponding 1-bromo-2-alkoxy-4,5,7-tri-tert-butyl dibenzofurans (ς) 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-butyl dibenzofuran \((6)\) 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 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 \( \text{AlCl}_3 \) catalyzed reaction of \( 5 \) in aromatic solvent might afford the desired 2-hydroxydibenzofuran \( 7 \).

Indeed, conversion of \( 5 \) into the desired \( 7 \) was achieved in 79\% yield by \( \text{AlCl}_3 \) catalyzed reaction in refluxing toluene; bromotoluenes \( (8) \) and tert-butyltoluene \( (2) \)

\[ \text{AlCl}_3 \text{ in toluene} \text{ refluxed for 3 h} \]
were formed as side products. However, under the mild conditions as is shown in Scheme 1, one or two tert-butyl groups on 5 were selectively removed to afford 1-bromo-2-methoxy-4-tert-butyl-(\(\text{V}\))\(^7\) and 1-bromo-4,5-di-tert-butyl-dibenzofuran (\(\text{V}\))\(^8\) in 74 and 71% yields together with \(\text{II}\), respectively.

Based on the above results, the mechanism of formation of \(\text{V}\) from \(\text{I}\) 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 (\(\text{V}\)) reacted with alcohols to give the corresponding 4-alkoxy derivatives (\(\text{V}\), (\(\text{V}\)).
Compound $\delta$ should be an intermediate of the formation of product $\gamma$ in the bromination of $\alpha$ under the used conditions.

REFERENCES AND NOTES


4. $\delta_a$: 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).

$\delta_b$: 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).


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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