

A P P E N D I XSynthesis of 3,3',-bibenzofuranyl
, dimethoxyl-5,5'-THEORETICAL

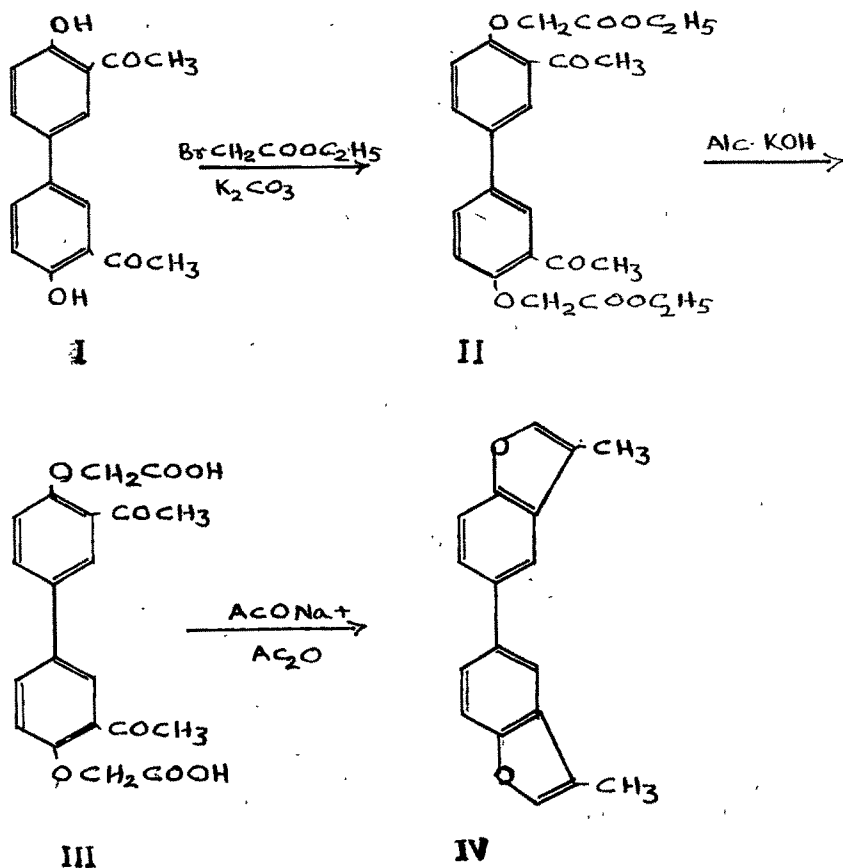
Furan, benzofuran, dibenzofuran and other furano derivatives form an important group of heterocyclic compounds. The representatives of this class of compounds are found to occur in vegetable kingdom extensively, mostly as glycosides, and some of them possess physiological properties and some others are commercially important. Khellin¹, Usnic acid², Pongamol³, Euparin⁴, Griseofulvin⁵ etc are some of the naturally occurring benzofuran derivatives.

Several bibenzofuran derivatives where two benzofuran nuclei are linked, are known in the literature. But all of them have been synthesised either by the action of metals on appropriate halogeno benzofurans or isolated as byproducts of other reactions^{6,7}.

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1. Clarke and Robertson., J.Chem.Soc., 1949, 302.
 2. Rochleder and Heldt., Ann., 48, 11 (1843).
 3. Seshadri et al., J.Chem.Soc., 1954, 1871 ;
1955, 2048.
 4. Kamthong and Robertson., Ibid., 1939, 925, 933.
 5. MacMillan et al., Ibid., 1952, 3949, 4002 ;
1953, 1697 ; 1954, 2585.
 6. Toda and Nakagawa., Bull.Chem.Soc., Japan., 34,
1000 (1961) ; C.A., 56, 2366 (1962).
 7. Hurd and Dowbenko., J.Am.Chem.Soc., 82, 3662 (1960).

It was thought of interest to see if the bibenzofuranyls could be synthesised by starting with a suitable biphenol derivative. The present work deals with the synthesis of 3,3'-dimethyl-5,5'-bibenzofuranyl starting with 4,4'-dihydroxy-3,3'-diacetylbiphenyl.

4,4'-Dihydroxy-3,3'-diacetyl biphenyl (I) on treatment with bromo acetic ester in the presence of anhydrous potassium carbonate in dry acetone gave 3,3'-diacetyl-4,4'-di(O-ethylacetate)biphenyl (II). This ester on hydrolysis with alcoholic sodium hydroxide gave the corresponding acid (III) which on refluxing with fused sodium acetate and acetic anhydride gave 3,3'-dimethyl-5,5'-bi-benzofuranyl (IV).



EXPERIMENTAL

Condensation of 4,4'-dihydroxy-3,3'-diacetyl biphenyl with bromoacetic ester : 3,3'-Diacetyl-4,4'-di-(O-ethyl acetate) biphenyl :- 4,4'-Dihydroxy-3,3'-diacetyl biphenyl (4.4 g. ; 0.01 mole) was dissolved in dry acetone (150 c.c.) and bromoacetic ester (7 c.c.) and anhydrous potassium carbonate (25 g.) were added and the reaction mixture refluxed over a steam bath for 6 hrs. The acetone was removed by distillation and the precipitate after washing with water was crystallised from benzene in white needles, m.p. 149° . Yield 6 g.

Analysis : 4.640 mg. of the substance gave 11.038 mg. of carbon dioxide and 2.442 mg. of water.

Found : C = 64.9 % ; H = 5.9 %.

$C_{24}H_{26}O_8$ requires : C = 65.1 % ; H = 5.9 %.

3,3'-Diacetyl-4,4'-di(O-acetic acid) biphenyl :- The above ester (3.9 g. ; 0.01 mole) was heated with 10 % alcoholic sodium hydroxide (10 % ; 50 c.c.) on a water bath at $60-70^{\circ}$. An intense red solution was obtained. It was acidified and the precipitated acid was purified by sodium bicarbonate treatment. It crystallised from acetic acid in white needles, m.p. 259° . Yield 2.5 g.

Analysis : 4.768 mg. of the substance gave 10.932 mg. of carbon dioxide and 2.076 mg. of water.

Found : C = 62.6 % ; H = 4.9 %.

$C_{20}H_{18}O_8$ requires : C = 62.2 % ; H = 4.7 %.

3,3'-Dimethyl-5,5'-bibenzofuranyl :- The above acid (1 g.) was mixed with acetic anhydride (20 c.c.) and freshly fused sodium acetate (6 g.) and refluxed gently over a wire gauze for 3 hrs. It was cooled and the product separated on pouring into water was collected and washed with sodium bicarbonate to remove any unreacted acid. It was then crystallised from petroleum ether in long stout needles, m.p. 73° .

Analysis : 4.736 mg. of the substance gave 14.228 mg. of carbon dioxide and 2.290 mg. of water.

Found : C = 82.0 % ; H = 5.4 %.

$C_{18}H_{14}O_2$ requires : C = 82.4 % ; H = 5.3 %.