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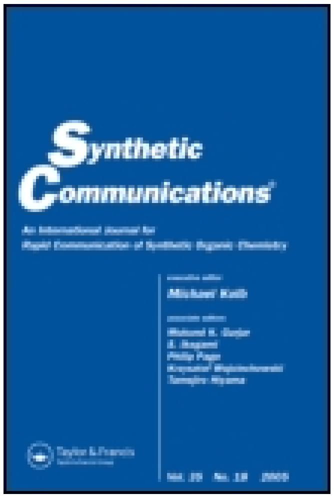

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AN EFFICIENT, FACILE, AND FAST SYNTHESIS OF 4-ALKOXY-4′-HYDROXYBIPHENYLS

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AN EFFICIENT, FACILE, AND FAST SYNTHESIS OF 4-ALKOXY-4′-HYDROXYBIPHENYLS

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ABSTRACT

A simple, fast and efficient method of synthesis of 4-alkoxy-4′-hydroxybiphenyls has been described. The reactions of 4,4′-dihydroxybiphenyl with appropriate alkyl halides were carried out over 3 h in DMSO in presence of solid powdered KOH.

In the field of liquid crystal (LC) chemistry biphenyl derivatives play a very important role as mesogenic units for the synthesis of thermotropic compounds.[1–7] Especially, monoalkoxybiphenols with long methylene chain are useful for their obtaining. There are many known liquid crystalline polyethers, polyesters and poly(ester imide)s containing such structure.[4,5]

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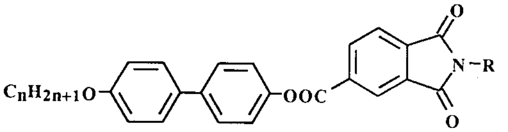
During the last few years we have been synthesising the new class of LC—low molecular ester imides carrying biphenyl moieties.[2,3]

The general formula of these compounds is given below:

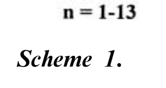


Usually, 4-alkoxy-4′-hydroxybiphenyls are obtained from 4,4′-dihydroxybiphenyl and proper aliphatic halides or tosyls.[1,2,7] The reactions occur in boiling methanol in the presence of dissolved KOH for over 16–20 h. Under these conditions the practical yields for typical mesogens ($n = 8$–11) do not exceed 30–40%. Due to large amounts of by-products, 4,4′-biphenyldiethers, produced in such case, separation and purification of monoalkylated derivatives are difficult and need multiple crystallisation of crude products. The 4-alkoxy-4′-hydroxybiphenyls (for $n = 1$–18) may be also prepared according to the five-step complex process described in the patent literature.[8]

Phase transfer catalysed reactions under basic conditions show higher selectivity of mono- vs. dialkylation due to the low effective concentration of the anions in the organic phase.[9,10] This findings prompt us to test the similar method for synthesis of monoethers from 4,4′-dihydroxybiphenyl-mesogens for liquid crystals preparation. The alkylation reactions were performed according to the Scheme given below. Powdered KOH makes the solid phase and DMSO solution of biphenol and proper alkyl halide composes the liquid phase in the reaction system (Sch. 1).

In this case the catalyst is not necessary, since efficient solvatation of K^+ cations with DMSO provides lipophilic cations, thus promoting transfer of the monophenolate anions into solution.[9,12] The similar mechanism is postulated when poly(ethylene glycol) is used as a solvent for alkylation of biphenols.[13]

As can be seen, efficiency of majority of the synthesis is higher than in the conventional method; for the compounds with the longest methylene



Scheme 1.

chain, suitable for liquid crystals preparation, the yields are almost doubled. Monoalkoxybiphenols with long methylene tail are slightly soluble in DMSO. It results that products of interest are removed from reaction medium and, in this way, diethers cannot form which simplifies the purification and separation processes and make the reaction yields higher. Also, the differences in solubility of products and by-products have a bearing on efficiency of crystallisation.

Great advantage of presented manner is shortening of reaction time, it is 3 h for alkyl bromides as starting substrates and even up to 2 h for iodides.

All compounds obtained are known, but not all their melting points are published, so on Fig. 1 we present temperature of the melt measured for compounds studied. The typical odd–even effect is observed on this plot.

In summary, this methodology consumes much less time and needs much less investment taking into account that due to high selectivity of the process, yields of the final products, particularly for the compounds useful for liquid crystals preparation ($n > 7$), are much higher than when traditional method is used.

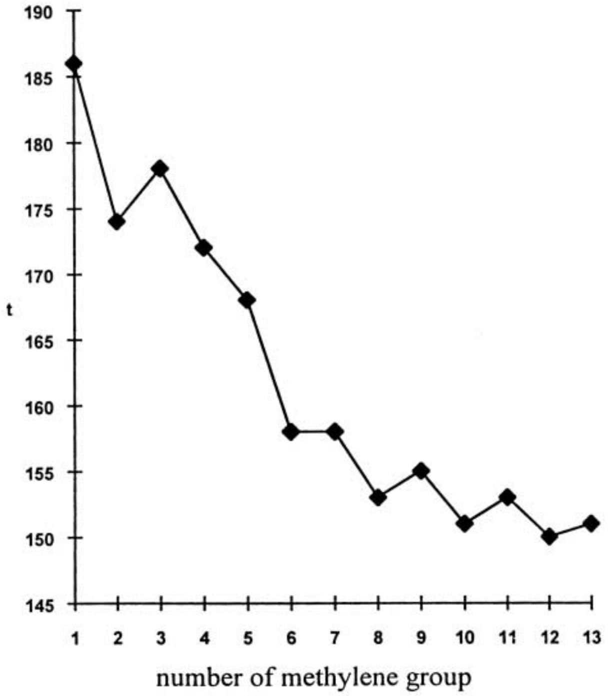


Figure 1. Odd–even effect of melting points (°C) of 4-alkoxy-4′-hydroxybiphenyls.

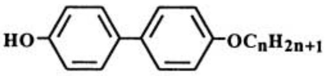
EXPERIMENTAL

General

All chemicals used were commercial products of analytical grade (Aldrich) and used without further purification. Melting points were taken in open capillary tubes on a Gallenkamp 5 apparatus and were uncorrected. The purity of 4-alkoxy-4′-hydroxybiphenyls was checked by TLC (Merck silica gel 60 plates) method using chloroform–methanol (v : v = 20 : 1) as an eluent. Though compounds are known their structures were confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$) and by elemental analysis. (Analysis indicated by symbols was within ± 0.4% of theoretical values).

4-Alkoxy-4′-hydroxybiphenyls: A round-bottomed flask equipped with a magnetic stirrer was charged with 9.3 g (0.05 m) of 4,4′-dihydroxybiphenyl and 50 mL of freshly distilled DMSO. Then 8.5 g (0.15 m) of powdered KOH was added. Next 0.05 m of proper alkyl bromide (for $n = 1, 2$ and 12 alkyl iodides were used, respectively) was added dropwise at such rate that the room temperature was kept. The mixture was vigorously stirred over 3 h and the course of reaction was followed by TLC. The 200 mL of

Table 1. Synthesis of 4-Alkoxy-4′-hydroxybiphenyls



n	Lit. M.P. (°C)	M.P. (°C)	R_f	Yields (%)	Purification
1	174[14]	186	0.56	55	Flash column chromatography
2		174	0.58	54	Flash column chromatography
3		178	0.58	40	Double crystallisation
4		172	0.58	43	Double crystallisation
5		167	0.59	45	Double crystallisation
6	147[15]	158	0.59	40	Double crystallisation
7		158	0.59	40	Double crystallisation
8	154[8]	153	0.60	45	Single crystallisation
9		155	0.60	64	Single crystallisation
10	151[2,8]	151	0.61	66	Single crystallisation
11		153	0.62	68	Single crystallisation
12		150	0.62	63	Single crystallisation
13		151	0.63	80	Single crystallisation

cold water and concentrate HCl (up to pH < 7) were added. The precipitate was filtered off and with care washed with water. For 4-methylenoxy and 4-ethylenoxybiphenols the crude product was purified by flash column chromatography (SiO_2) using $CHCl_3$ as an eluent. For $n = 3$–7 the crude product was crystallised from methanol two times. The other precipitates were crystallised from methanol only once. The appropriate yields are given in Table 1.

As an example, for 4-decyloxy-4′-hydroxybipenyl the ^{1}H NMR data are given below: 0.89 (m, 3H), 1.28 (m, 12H), 1.80 (m, 4H), 3.99 (*t*, 2H, $J = 6.6$ Hz), 6.99–7.55 (m, 8H), 8.34 (s, 1H).

The R_f values for all compounds listed in Table 1 were in the range 0.56–0.63.

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