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A New Convenient Synthesis of 4′-(trans-4-Pentylcyclohexyl)-4-cyanobiphenyl

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A convenient method of obtaining 4′-(trans-4-pentyl-cyclohexyl)-4-cyanobiphenyl from valeryl chloride, cyclohexene and biphenyl is described. The total yield is 4.1%.

Keywords: Synthesis; 4′-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl; nematic liquid crystal

INTRODUCTION

4′-(trans-4-Pentylcyclohexyl)-4-cyanobiphenyl, an important single liquid crystal, like other trans-1, 4-substituted hexane derivative liquid crystals [1, 2], has low viscosity and wide phase transition temperature range (C → N 95.5°C, N → I 222.5°C, K → N 50.99 $J \cdot g^{-1}$). It is the main component of many nematic mixtures, such as E_{100} and E_{110}. The only method of obtaining it reported [3] is illustrated by the following scheme:

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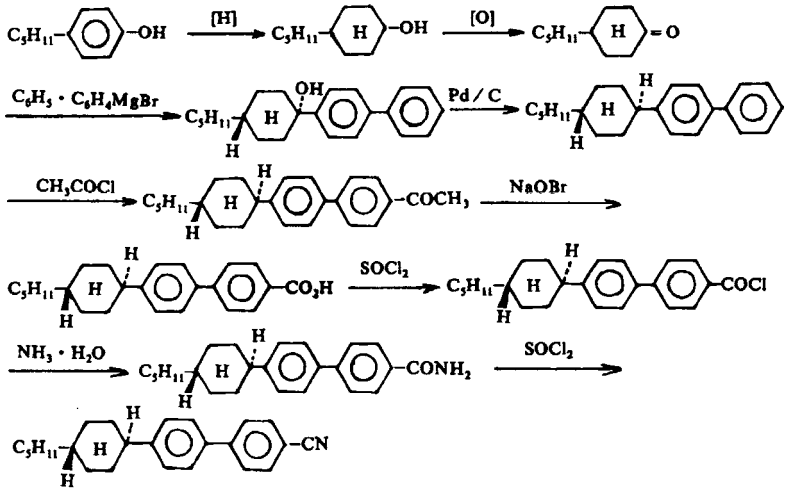
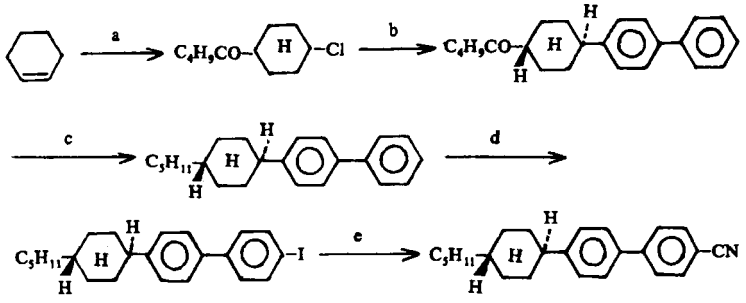


But, this synthesis route is laborious and the total yield is low (1.9%). Today, we report an convenient and simple synthesis of 4′-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl from valeryl chloride, cyclohexene and biphenyl.



a) C_4H_9COCl, $AlCl_3$ b) $C_6H_5 \cdot C_6H_5$, $AlCl_3$
c) $H_2N \cdot NH_2$, KOH d) I_2, HIO_3, CH_3COOH e) CuCN, DMF

This method has the advantages of mild reaction conditions, short reaction time, high yield, and easy work-up.

EXPERIMENTAL

^1H NMR spectra was recorded in $CDCl_3$ containing TMS as internal reference with a JEOL FX-90Q spectrometer. IR spectra was obtained on a 60SXR-FT spectrometer. The phase transition temperature was determined by a Perkin-Elmer DSC-2C differential scanning calorimeter.

Synthesis of 4-(trans-4-Pentylcyclohexyl)biphenyl

(a) [4] 500 ml of dry CH_2Cl_2 and 160 g(1.2 mol) of anhydrous $AlCl_3$ were mixed, cooled to 5°, then 120.5 g (1 mol) of valeryl chloride were added dropwise. Next, the mixture was cooled to $-30°$ and at that temperature 82 g (1 mol) of cyclohexene were added dropwise. When this operation was terminated, cooling was interrupted and the mixture left to get heated to about 10°. Then it was poured onto crushed ice. The organic phase was separated and the aqueous one was extracted with 100 ml of CH_2Cl_2. The combined organic phases were washed twice with 5% HCl, several times with water and dried over anhydrous $MgSO_4 \cdot CH_2Cl_2$ was removed on a Rotavap. The dark, oily residue was diluted in the flask with 100 ml petroleum benzine and evaporated again to remove the solvent of residue CH_2Cl_2.

(b) 800 ml of cyclohexane, 160 g (1.2 mol) of anhydrous $AlCl_3$ and 616 g (4 mol) of biphenyl were mixed thoroughly in a flask placed on a water bath. Next, the product of cyclohexene acylation obtained in step a was slowly added (1.5 hour) dropwise. Gaseous HCl was evolved and the temperature was increased automatically to about 35°. Then the mixture was heated for 4 hrs at 45–50°, colled, poured onto ice. The organic layer was separated and washed with 5% HCl and water. Excess biphenyl and cyclohexane were removed by steam-distillation. The resultant dark, oily liquid contains 4-(trans-4-valerylcyclohexyl)biphenyl.

(c) 400 ml of diethylene glycol, 165 g (ca 3 mol) of KOH, 232 g (ca 3.75 mol) of 80% hydrazine hydrate and the product from step b were refluxed at 130° for 3 hrs. Then the temperature was slowly raised and the volatile components were distilled off until the temperature in the flask achieved 220°. The refluxing was continued for 3 hrs. After cooling the mixture was diluted with water and extracted with petroleum benzine (4 × 200 ml). The extract was washed with water, diluted 5% H_2SO_4 and the 75–80% H_2SO_4. Then the extract was washed with water again (5 × 200 ml) and dried over anhydrous $MgSO_4$. The petroleum benzine was removed on a Rotovap. The residue was distilled under reduced pressure (220–270°/20 Pa)

to give an oily product containing about 70% of 4-(trans-4-Pentylcyclohexyl)-biphenyl.

Synthesis of 4-Iodo-4′-(trans-4-pentylcyclohexyl)biphenyl

(d) 112 ml of CH_3COOH, 34 ml of 15% (V:V) H_2SO_4, 9 g of HIO_3, 13 g of I_2, 46 ml of CH_2ClCH_2Cl and 39 g of the product from step C were mixed and heated to reflux for 8 hrs. The unreacted iodine was removed by adding dropwise a solution of 10% Na_2SO_3. The mixture was cooled and filtered to give a crude product, which was recrystallized from ethanol to give 28 g of a pure product (GC 96%).

Synthesis of 4′-(trans-4-Pentylcyclohexyl)-4-cyanobiphenyl

(e) 96 ml of DMF, 8.8 g of CuCN and 28 g of 4-iodo-4′-(trans-4-pentyl cyclohexyl) biphenyl were mixed and heated to reflux for 10 hrs under N_2 protection. The DMF was distilled off and the residue was extracted with petroleum benzine (2×200 ml). The extract was washed with 100 ml of 25% $NH_3 \cdot H_2O$, water and dried over anhydrous $CaCl_2$ and then filtered through a silica gel column. The petroleum benzene was distilled off and the residue was distilled under reduced pressure to give a crude product, which was recrystallized from methanol to give 13.8 g of a pure product, m.p. 97.4°, GC > 99.5%, ^{1}H NMR($CDCl_3$): δ 7.66–7.24 (m, 8H), δ 2.37–2.66 (m, 1H), δ 3.899–1.84 (m, 20H), IR (KBr): 3060, 3029, 2959, 2921, 2849, 2229, 1604, 1490 cm^{-1}.

Anal. Calcd for $C_{24}H_{29}N$: C, 86.96; H, 8.82. Found: C, 86.93; H, 8.82.

The phase transition temperatures were: K 97.4° N 222.5° I. The total yield with respect to cyclohexene used was 4.1%.

RESULTS AND DISCUSSION

The Synthesis method proposed in the present work is simple, and involves easily available and cheap substrates. The intermediates do not have to be of high purity. In steps b and c, the nonpurified reaction products are used. In steps d, an enriched by distillation hydrocarbon fraction containing on the average 70–85% of 4-(trans-4-pentylcyclohexyl)biphenyl was used with a very good result. Acylation of cyclohexene (step a) is best to conduct in CH_2Cl_2 or CS_2. The powdered $AlCl_3$ should be used as otherwise more side

products are formed due to the insolubility of $AlCl_3$ complexes with acid chloride in this solvent. The crude product obtained in step c is very difficult to separate, and we did not succeed to seperate neither pure 4-(trans-4-pentylcyclohexyl)biphenyl nor any other components by distillation. For isolation of the fraction enriched in 4-(trans-4-pentylcyclohexyl)-biphenyl a 40 cm Vigreux column was used, and the distillation was conducted very slowly. The first pure substance was obtained after the crude product obtained in step c was iodinated. Pure 4-iodo-4′-(trans-4-pentylcyclohexyl)biphenyl was obtained by crystallizing the crude product obtained in step d from ethanol.

The melting and clearing points of 4′-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl obtained by the above described method are in agreement with those given in Ref. [3].

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