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Synthesis of 2-Cycloalkyl-4-chlorophenols

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Abstract

2-Cycloalkyl-4-chlorophenols were synthesized in high yield by the alkylation of *p*-chlorophenol with cyclopentanol and cyclohexanol in the presence of perchloric acid as catalyst. The effects of the variation of temperature, molar ratio of *p*-chlorophenol to cycloalcohols, time of reaction and amount of catalyst on the reactions were also studied.

Keywords: Chlorophenol, Cyclopentanol, Cyclohexanol, Perchloric acid, 2-Cycloalkyl-4-chlorophenols

I. Introduction

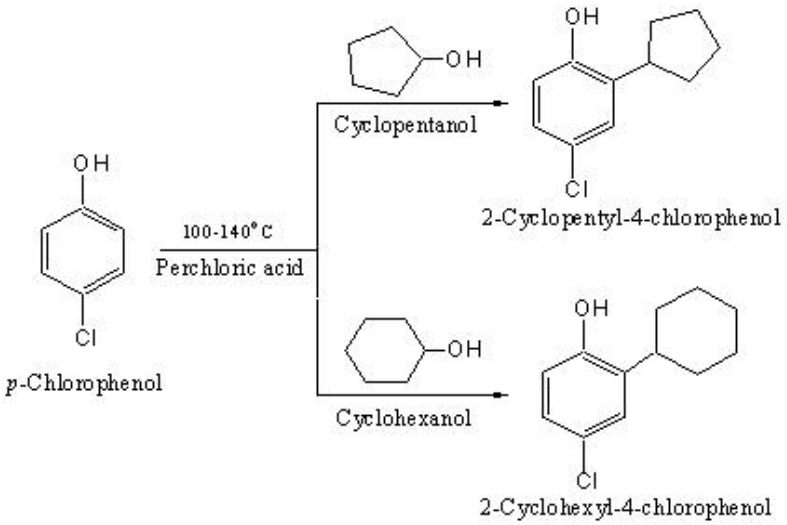
Friedel Craft's reaction was investigated more than hundred years ago, still the reaction is in the attention of many investigators. This is because of the fact that the products of the alkylation reaction have found wide practical utilization in different fields. Undoubtly, alkylation is one of the most popular techniques for transferring of an alkyl group from one molecule to another to produce new functional molecules. Among the alkylation reactions, cycloalkylation is very important by which cyclic ring structures can be introduced. Alkylchlorophenols and their derivatives are excellent antioxidants for fuels, lubricating oils and wide variety of polymeric materials.[1-3] Cycloalkylchlorophenols also stabilize synthetic rubber.[4,5] Moreover, some of the derivatives are good herbicides, bactericides, and insecticides.[6-8]

Cycloalkylation of chlorophenols with cycloalkenes,[9-13] halides[14-17] and cycloalcohols[18-20] have been investigated in the presence of protic and aprotic acid by several authors. In 1984, Kasyanov et al.[9] reported alkylation of chlorophenol by cyclohexene. In 1996, Saha et al.[13] reported cycloalkylation of *p*-chlorophenol with cycloalkenes in the presence of brontrifluoride etherate. On the other hand, Turaeva et al.[17] reported alkylation of phenols and chlorophenols with alkylhalides in terms of quantitative usage of iron salt catalyst. This survey revealed that studies on the reactions in the presence of perchloric acid have not yet been reported from any research group for the synthesis of cycloalkylchlorophenols.

In the present work, cycloalkylation of *p*-chlorophenol with cyclopentanol and cyclohexanol in the presence of perchloric acid as catalyst has been investigated.

II. Materials and Methods

All reactants and reagents were purchased from Merck, Germany and used as received (without further purification). A three necked round bottomed flask fitted with a stirrer, a condenser, a thermometer and a dropping funnel was used to



Scheme 1. Chemical reaction scheme for alkylation of *p*-chlorophenol with cyclopentanol and cyclohexanol in the presence of perchloric acid.

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perform the designed reaction. The reactant, *p*-chlorophenol and catalyst, perchloric acid were first charged into the flask and heated to the desired temperature and then cycloalcohol (cyclopentanol or cyclohexanol) was introduced dropwise to the mixture for a certain period of time (time of addition) while constant stirring was executed. When the addition of total amount of cycloalcohol was finished, the reaction mixture was stirred for another 1 to 2 h (time of stirring) at the same temperature. The reaction mass was then cooled to room temperature, dissolved in ether and neutralized. After washing with distilled water several times, the reaction mixture was subjected to distillation. At atmospheric pressure all unreacted reactants and solvent were distilled off. The products were then characterized by spectral means.

III. Results and Discussion

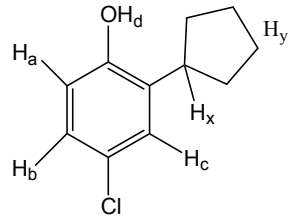
The reactions of *p*-chlorophenol with cyclohexanol in the presence of perchloric acid was investigated over the temperature range of 100-140^{o}C as shown in the Scheme 1. Molar ratio of *p*-chlorophenol to cyclohexanol was varied from 4:1 to 8:1, reaction time from 2 to 4 h and the amount of catalyst from 2 to 5 % by wt. of *p*-chlorophenol. The reaction gave 2-cyclohexyl-4-chlorophenol. The yield of 2-cyclohexyl-4-chlorophenol increased with the increase of temperature (entry 1 & 5), molar ratio of *p*-chlorophenol to cyclohexanol (entry 2 & 3), amount of catalyst (entry 3 & 5) and time of reaction (entry 4 & 5) as shown in Table 1. Thus the best yield (96%) of the 2-cyclohexyl-4-chlorophenol was obtained under the following reaction conditions: temperature = 140^{o}C, molar ratio of *p*-chlorophenol to cyclohexanol = 8:1, amount of catalyst = 5% by wt. of *p*-chlorophenol, time of addition = 2 h and time of stirring = 2 h.

One the other hand, 2-Cyclopentyl-4-chlorophenol was obtained in 94.8% yield by the alkylation of *p*-chlorophenol with cyclopentanol in the presence of perchloric acid under the following reaction conditions: temperature = 140^{o}C, molar ratio of *p*-chlorophenol to cyclopentanol = 8:1, amount of perchloric acid = 5% by wt. of *p*-chlorophenol, time of addition = 2 h and time of stirring = 2 h.

Table. 1. Alkylation of *p*-chlorophenol with cyclohexanol in the presence of perchloric acid

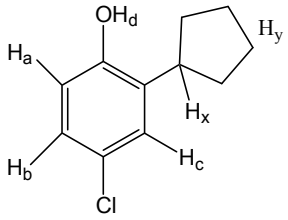
Entry	Reaction condition					Yield, %
	Temp. (^{o}C)	Molar ratio of chlorophenol to cyclohexanol	Catalyst, % by wt. of chlorophenol	Time of addition, h	Time of stirring, h	
1	100	8:1	5	2	2	75.6
2	140	8:1	5	2	2	54.2
3	140	8:1	5	2	2	70.0
4	140	8:1	5	2	0	83.7
5	140	8:1	5	2	2	96.0

Table. 2. ^{1}H-NMR spectral analyses of 2-cyclopentyl-4-chlorophenol in $CDCl_3$

2-Cyclopentyl-4-chlorophenol	Protons	Chemical shift (δ) ppm	Ratio of integrator readings
	a,b,c	6.35-7.11	3
	d	5.23	1
	x	2.89-3.40	1
	y*	1.37-2.21	8

y* represents all the hydrogens on cyclopentane ring except one on position 1(i.e. x)

Table. 3. ^{1}H-NMR spectral analyses of 2-cyclohexyl-4-chlorophenol in $CDCl_3$

2-Cyclopentyl-4-chlorophenol	Protons	Chemical shift (δ) ppm	Ratio of integrator readings
	a,b,c	6.40-7.41	3
	d	5.21	1
	x	2.40-3.37	1
	y*	0.62-2.23	10

y* represents all the hydrogens on cyclohexane ring except one on position 1(i.e. x)

The UV-spectrum of 2-cyclopentyl-4-chlorophenol showed strong absorption at λ_{max} 297.8 nm in 0.01 M petroleum ether solution..

In the FT-IR spectrum of 2-cyclopentyl-4-chlorophenol, absorption peak at 3350 cm^{-1} showed the presence of –OH group. Bands at 1600 cm^{-1}, 2870-2900 cm^{-1}, and 640 cm^{-1} were observed for benzene ring C=C, saturated C-H and C-Cl stretch, respectively. Bands at 820 cm^{-1} and 880 cm^{-1} accounted for the 1, 2, 4-trisubstituted aromatic ring.

The UV-spectrum of 2-cyclohexyl-4-chlorophenol showed strong absorption at λ_{max} = 298.0 nm in 0.01 M petroleum ether solution.

In the FT-IR spectrum of 2-cyclohexyl-4-chlorophenol, bands at 805 cm^{-1} and 870 cm^{-1} showed 1, 2, 4-trisubstituted benzene ring. Absorption band at 3400 cm^{-1} accounted for the presence of –OH group. Bands at 1600 cm^{-1}, 2850-2900 cm^{-1}, and 650 cm^{-1} were observed for benzene ring saturated C-H and C-Cl stretch, respectively.

Table 2 and 3, show the spectral analyses of 2-cyclopentyl-4-chlorophenol and 2-cyclohexyl-4-chlorophenol with ^{1}H-NMR spectroscopy, respectively. In Table 4, the physicochemical properties (boiling point, density and refractive index) of the products are presented.

C=C

Table. 4. Physicochemical properties of 2-cycloalkyl-4-chlorophenols

Parameters	2-Cyclopentyl-4-chlorophenol	2-Cyclohexyl-4-chlorophenol
Boiling point (°C)	278	306
Density (d_4^{20})	1.1680	1.1252
Refractive index (n_D^{20})	1.5560	1.5426

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