DUJASE Vol. 3(1) 31-33, 2015 (January)

Alkylation of *p*-chlorophenol with olefins in the presence of perchloric acid

Mohammad Kamruzzaman and Manoranjan Saha

Department of Applied Chemistry and Chemical Engineering, University of Dhaka,

Dhaka-1000, Bangladesh.

E-mail: mkzamandu@gmail.com

Received on 24. 11. 2013. Accepted for publication on 14.07. 2014.

Abstract

2-Alkyl-4-chlorophenols have been synthesized in high yield by the reaction of *p*-chlorophenol with cyclopentene, cyclohexene, cyclooctene and octane-1 in the presence of perchloric acid as catalyst. The effects of the variation of reaction parameters such as temperature, molar ratio of *p*-chlorophenol to olefin, amount of catalyst and time of reaction were investigated. The optimum conditions for the production of 2-alkyl-4-chlorophenols phenol have been determined. The yield of the products increased with the increase of each of the above-mentioned parameters.

Keywords : Alkylation, *p*-chlorophenol, olefins, perchloric acid

1. Introduction

The alkylation of aromatic substrates is important in many sectors of the chemical industry. Alkylchlorophenols and their derivatives are the most effective antioxidants and multifunctional stabilizers in fuels, lubricating oils and wide variety of oxygen sensitive materials [1-6]. They are also strong herbicides, bactericides, insecticides etc. [7-13]. Reactions of chlorophenols with olefins, alcohols and alkylhalides in the presence of several acidic catalysts have been studied [10,14-27]. But no attempt has ever been made to study the reactions in the presence of perchloric acid as catalyst.

In the present work, alkylation of *p*-chlorophenol with cyclopentene, cyclohexene, cyclooctene and octane-1 in the presence of perchloric acid as catalyst has been investigated and the yield of 2-alkyl-4-chlorophenol optimized using a set reaction parameters.

2. Experimental

Chemicals used in this work were purchased from Merck Chemicals Co. and were used without further purification unless stated. Perchloric acid was used as catalyst.

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a stirrer. *p*-Chlorophenol-catalyst mixture was charged into the flask, heated to the temperature of the experiment, then olefin was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. The reaction mixture was stirred for another period of time (time of stirring) at the same temperature after the addition of the total amount of olefin. The reaction mass was then cooled to room temperature and neutralized with an equivalent amount of 10% KOH solution. The neutralized reaction mass was then dissolved in diethyl ether, washed with distilled water several times and dried with anhydrous magnesium sulfate. Unreacted reactants and solvent were distilled off at atmospheric pressure. The product thus obtained was subjected to fractionation by distillation and characterized by physico-chemical and spectral means.

3. Results and Discussion

The reaction of *p*-chlorophenol with cyclohexene in the presence of perchloric acid was investigated over the temperature range of 100-140°C. Molar ratio of *p*-chlorophenol to cyclohexene was varied from 4:1 to 8:1, reaction time from 3 to 4 h and amount of catalyst from 1 to 5% by wt. of *p*-chlorophenol. As can be seen from Table 1, the yield of 2-cyclohexyl-4-chlorophenol, the product of the reaction, increased with the increase of temperature (Expt. No. 1, 2, 3 and 4), molar ratio of *p*-chlorophenol to cyclohexene (Expt. No. 4, 5 and 6), amount of catalyst (Expt. No. 6, 7, 8 and 9) and reaction time (Expt. No. 6 and 10).

Therefore, the following conditions may be considered as optimum (yield = 96.1%) for the production of 2-cyclohexyl-4-chlorophenol: temperature = 140°C, molar ratio of *p*-chlorophenol to cyclohexene = 8:1, amount of perchloric acid = 5% by wt. of *p*-chlorophenol, time of addition = 2 h and time of stirring = 2 h.

The reactions of *p*-chlrophenol with cyclopentene, cyclooctene and octane-1 in the presence of perchloric acid were carried out under the above mentioned conditions to obtain 2-alkyl-4-chlorophenol in 95.3%, 96.9% and 91.3% yield, respectively.

The UV-spectrum of 2-cyclohexyl-4-chlorophenol showed a strong absorption at $\lambda_{max.}$ = 296.6 nm in 0.01 M petroleum ether solution.

In the IR spectrum of 2-cyclohexyl-4-chlorophenol, absorption band at 3400 cm^{-1} showed the presence of –OH group. Bands at 805 cm^{-1} and 870 cm^{-1} accounted for 1,2,4-trisubstituted aromatic ring. Bands at 650 cm^{-1}, 2870-2930 cm^{-1} and 1600 cm^{-1} were observed for, saturated C–H, C–Cl stretch and benzene ring $C=C$, respectively.

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

Expt. No	Reaction Conditions					% Yield of 2-cyclohexyl-4-chlorophenol
	Temp., °C	Molar ratio of *p*-chlorophenol to cyclohexene	Amount of catalyst, % by wt. of *p*-chlorophenol	Time of addition, h	Time of stirring, h	
1	100	4:1	5	2	1	69.3
2	110	4:1	5	2	1	72.4
3	120	4:1	5	2	1	75.3
4	140	4:1	5	2	1	82.4
5	140	6:1	5	2	1	86.3
6	140	8:1	5	2	1	94.4
7	140	8:1	1	2	1	68.5
8	140	8:1	2	2	1	86.3
9	140	8:1	3	2	1	91.2
10	140	8:1	5	2	2	96.1

In the ^{1}H NMR-spectrum of the product, chemical shifts of the aromatic ring protons were observed at δ = 6.40-7.40 ppm. All the protons of the cyclohexyl group except one on the α-position relative to the aromatic ring were observed at δ = 0.62-2.36 ppm and one proton on the α-position was observed at δ = 2.40-3.37 ppm. Chemical shift for the –OH group proton was observed at δ = 5.21 ppm.

2-Cyclohexyl-4-chlorophenol had b.p. 307°C, d_4^{20} 1.1375 and n_D^{20} 1.5400.

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

In the IR spectrum of 2-cyclopentyl-4-chlorophenol, absorption bands at 820 cm^{-1} and 880 cm^{-1} accounted for 1,2,4-trisubstituted aromatic ring. Bands at 640 cm^{-1}, 1600 cm^{-1}, 2870-2920 cm^{-1} and 3400 cm^{-1} were observed for C–Cl, benzene ring C=C, saturated C–H and –OH group, respectively.

The ^{1}H NMR-spectrum of 2-cyclopentyl-4-chlorophenol showed signals at δ = 6.35-7.11 ppm for the aromatic ring protons. Signals for all the protons of the cyclopentyl group except one on the α-position relative to the aromatic ring were observed at δ = 1.37-2.21 ppm, while the signal for the proton on the α-position was observed at δ = 2.89-3.40 ppm. Chemical shift for the –OH group proton was observed at δ = 5.10-6.00 ppm.

2-Cyclopentyl-4-chlorophenol had b.p. 278°C, d_4^{20} 1.1616 and n_D^{20} 1.5445.

The UV-spectrum of 2-cyclooctyl-4-chlorophenol in 0.01 M petroleum ether solution showed a strong absorption at $\lambda_{max.}$ = 295.2 nm.

The IR spectrum of 2-cyclooctyl-4-chlorophenol showed the absorption bands at 640-680 cm^{-1}, 1600 cm^{-1} and 800-900 cm^{-1} for C–Cl stretch, aromatic ring C=C and 1,2,4-trisubstituted benzene ring, respectively. Absorption band at 3400 cm^{-1} showed the presence of –OH group, band at 2950 cm^{-1} was accounted for saturated C–H stretch.

The ^{1}H NMR-spectrum of 2-cyclooctyl-4-chlorophenol showed signals at δ = 6.53-7.73 ppm for the aromatic ring protons. Signals for all the protons of the cyclooctyl group except one on the α-position relative to the aromatic ring were observed at δ = 0.69-3.30, ppm, while the signal for the proton on the α-position was observed at δ = 3.40-3.96 ppm. Chemical shift for the –OH group proton was observed at δ = 5.30-6.43 ppm.

2-Cyclooctyl-4-chlorophenol had b.p. 309°C, d_4^{20} 1.1313 and n_D^{20} 1.5570.

The UV-spectrum of 2-*sec.*-octyl-4-chlorophenol showed a strong absorption at $\lambda_{max.}$ = 298.8 nm in 0.01 M petroleum ether solution.

In the IR spectrum of 2-*sec.*-octyl-4-chlorophenol, bands at 2870 cm^{-1} and 2920 cm^{-1} showed saturated C–H in the sec.-

octyl group, while the bands at 650 cm^{-1}, 1600 cm^{-1}, 840-880 cm^{-1} and 3400 cm^{-1} accounted for C–Cl, aromatic ring C–C, 1,2,4-trisubstituted benzene ring and –OH group, respectively.

In the ^1H NMR-spectrum of 2-*sec*.-octyl-4-chlorophenol, chemical shifts for the aromatic ring protons and–OH group proton were observed at $\delta = 6.30\text{-}7.10$ ppm and $\delta = 5.17$ ppm, respectively. Signals for all the protons on the *sec*.-octyl group except one on the α-position relative to the aromatic ring were observed at $\delta = 0.63\text{-}2.07$ ppm, while the signal for the proton on the α-position was observed at $\delta = 3.73\text{-}4.10$ ppm.

2-*sec*.-Octyl-4-chlorophenol had b.p. 308°C, d_4^{20} 1.0452 and n_D^{20} 1.5218.

4. Conclusion

The yield of alkylation of *p*-chlorophenol with olefins in the presence of perchloric acid was optimized and the alkylated products were thoroughly characterized. Results of this study indicated that the effects of temperature, molar ratio of *p*-chlorophenol to olefins, amount of catalyst and time of reaction were significant. All these variables significantly affected the yield of 2-alkyl-4-chlorophenols. Optimum yield of the products were obtained under the reaction conditions of a temperature of 140°C; an 8:1 molar ratio of *p*-chlorophenol to olefin, a 5% by weight perchloric acid of *p*-chlorophenol, a 2 h time of addition of olefin and a 2 h time of stirring of the reaction.

References

1. Starnes, W.H., 1972, "Unusual antioxidant behavior of hindered chlorophenols in metal containing systems", Tetrahedron Lett. 25, pp 34743-34746.
2. Harry, E.A., 1951, "Halo-alkylphenol stabilizers for synthetic rubbers", US Patent, 2560044.
3. Orloff, H.D. and J.P. Napolitano, 1964, "Stabilizes organic material", US Patent, 3146273.
4. Farbenfabriken Bayer, A.G., 1954, FRG Patent, 912862.
5. Lee, D.H., 1967, "Mineral lubricating oil containing bisphenol, detergent and phosphite additive", US Patent, 3296134.
6. Herman, D.K. and C.K. Edwin, 1949, "Oxygen inhibitors", US Patent, 2469469.
7. Weintraub, R.L., W.J. Brown and J.A. Trone, 1945, "Herbicidal activity", J. Agr. Food. Chem. 2(19), pp 996-999.
8. Okazaki, K., H. Kato and R. Matsui, 1951, "Relation between bactericidal and insecticidal activities", J. Pharm. Soc. Japan 71, 195.
9. Newman, M.S., W. Fones and M. Renoll, 1947, "New compounds as plant-growth regulators", J. Am. Chem. Soc. 69(3), pp 718-723.
10. Akhmedov, K.Kh., M.K. Tyraeva and A.R. Abdurasuleva, 1978, "Alkylation of 2-and 4-chlorophenols", Dokl. Akad. Nauk. Uzb. SSR. 10, pp 47-48.
11. Klarmann, E., 1938, "Monoalkylchlorophenols", US Patent, 2139550.
12. Mills, L.E., 1940, "Alkylated halo-phenols", US Patent, 2176010.
13. Mills, L.E., 1941, "Tertiary halo-phenols", US Patent, 2221807.
14. Kasyanov, V.V., F.F. Muganlinskii and M. Saha, 1984, "Study of alkylation of chlorophenol by cyclohexene", Azerb. Khim. Zh. 5, pp 14-18.
15. Kasyanov, V.V., F.F. Muganlinskii and M. Saha, 1984, "Kinetics and mechanism of alkylation of chlorophenol by cyclohexene", Kinet. Katal. 25(1), pp 13-17.
16. Mircea, J., M. Maria and Nicolac, 1970, "Cyclohexyl chlorophenols", Bull. Soc. Chim. France 11, pp 4004-4006.
17. Saha, M. and V.V. Kasyanov, 1981, Alkylation of *p*-chlorophenol by cycloolefins in the presence of sulfuric acid", Sintezi Prevrashen. Geteroatomsoderzh. Organ. Soedin. Baku, pp 26-34.
18. Saha, M., 1986, "Studies on the reaction of 2,4-dichlorophenol with cyclohexene", Bangladesh J. Sci. Res. 4(1), pp 83-92.
19. Saha, M., 1990, "Reaction of *p*-chlorophenol with cyclopentene", J. Bangladesh Acad. Sci. 14(2), pp 241-245.
20. Saha, M., S.K. Ghosh, M.B. Zaman, H.N.M.E. Mahmud, M.A.B. Sarker, Y.N. Jolly and S. Chowdhury, 1996, "Cycloalkylation of *p*-chlorophenol with cycloalkenes in the presence of borontrifluoride etherate", Bangladesh J. Sci. Ind. Res. 31(3), pp 1-8.
21. Zavgorodnii, S.V, 1952, "Reaction of *p*-chlorophenol with cyclohexene", Zh. Obsh. Khim. 22(11), 1995-1997.
22. Abdurasuleva, A.R. and L.G. Mjalvskaya, 1959, "Condensation of *p*-chlorophenol with cyclohexanol", Zh. Obsh. Khim. 29, pp 4025.
23. Saha, M. and M.B. Zaman, 1989, "Cyclohexylation of *p*-chlorophenol", Dhaka Univ. Stud. 37(2), pp 153-158.
24. Saha, M., S. Biswas and N. Nahar, 1993, "Cycloalkylation of *p*-chlorophenol", Bangladesh J. Sci. Ind. Res. 28(2), pp 150-153.
25. Saha, M. and R.K. Roy, 1989, "Reaction of *p*-chlorophenol with cyclohexanol", Bangladesh J. Sci. Ind. Res. 24(1-4), pp 41-45.
26. Turaeva, M.K., K.N. Akhmedov and A.R. Abdurasuleva, 1975, "Alkylation of 2-and 4-chlorophenols, 4-chloroanisole by alkylhalides in the presence of salts of iron and zinc", Ruk. Dep. VINITI. Tashkent. pp 3172-3175.
27. Turaeva, M.K., K.N. Akhmedov and A.R. Abdurasuleva, 1976, "Alkylation of phenols and their ethers in the presence of small amount of catalysts; Alkylation of 3-chlorophenol, 3-chloroanisole with alkylhalides in the presence of iron salts", Deposited Doc. VINITI. pp 3010-3036.