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Synthesis of sec.-undecylbenzene and sec.-dodecylbenzene by alkylation

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Abstract

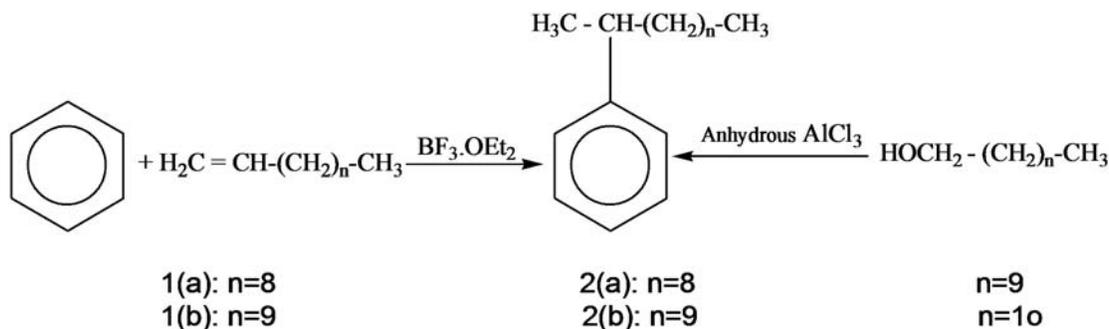
The title compounds were synthesized by the alkylation of benzene with olefins (undecene-1 and dodecene-1) in presence of borontrifluoride etherate and alcohols (undecan-1-ol and dodecan-1-ol) with anhydrous AlCl_3 . The effect of temperature, molar ratio of benzene to olefins & alcohols, amount of catalyst were studied. The highest yield was 73.6% in case of dodecene-1 and in case of undecene-1 was 70.6%. Dodecan-1-ol was found to be more reactive than undecan-1-ol but the yields were higher in olefins than alcohols.

Keywords: Alkylation; Benzene; Time; Molar ratio; Undecene-1; Undecanol-1; Dodecene-1; Dodecanol-1.

Introduction

Alkylbenzene can be used as intermediates for the detergents (Saha *et al.* 2001; Calcagno *et al.* 1970; Dimitrios 1964; Lebedev 1984), lubricating oils (Bataafsche, de 1952; Bataafsche de, 1952; Paul 1950) transformer oil (Ashimov, *et al.* 1966), plasticizers (Epshtein *et al.* 1964), pour-point depressant (Lebedev *et al.* 1960) and grease (Allison *et al.* 1953). Reactions of aromatic hydrocarbons with olefins were investigated by several authors (Pokzovskaya, 1959; Fredman, *et al.* 1957; Clausen *et al.* 1977). A few information are available in literature on the alkylation of aromatic hydrocarbons with cycloalkyl chlorides (Clausen *et al.* 1977). But studies on the alkylation of benzene with alcohols in the presence of anhydrous aluminium chloride are absent. We report here in the synthesis of the title compound (scheme 1).

ping funnel and a magnetic stirrer. Benzene (30 g) and catalyst mixture was heated to the desired temperature. Olefins; Undecene -1 (5.9231g or 38.462 mmol Expt no.- 4 from Table III) & Dodecene-1 (8.092 g or 48.075 mmol for Expt.no.-1 and 6.465 g or 38.409 mmol for Expt. no.-2) & alcohols; undecanol-1 (8.269 g or 48 mmol) & Dodecanol-1 (7.154 g or 38.462 mmol) was introduced separately into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the complete addition of olefins or alcohols separately the reaction mixture was stirred for an extended period of time (time of stirring) at the same temperature. The reaction mass was then cooled to room temperature, dissolved in a solvent, then washed with distilled water several times and distilled at atmospheric pressure. Unreacted reactants and solvent were distilled off



Scheme-1

Materials and methods

The reactions were carried out in a three-necked round bottomed flask fitted with a condenser, a thermometer, a drop-

and the yield was expressed as a percentage of theory. The residual product was finally distilled and its structure was

elucidated by physico-chemical and spectral means (IR, UV, ^1H NMR).

Results and discussion

The reaction of benzene with undecene-1 in the presence of borontrifluoride etherate under the conditions studied gave only sec.-undecylbenzene in 70.6% yield under the following reaction conditions: temperature = 80°C, molar ratio of benzene to undecene-1 = 10:1, amount of catalyst = 20% by wt. of benzene, time of addition = 2h and time of stirring = 1h.

Results of the reaction of benzene with dodecene-1 in the presence of borontrifluoride etherate are shown in Table I. The yield of the product (sec.-dodecylbenzene) increased from 71.3 to 73.6% on increasing the molar ratio of benzene to dodecene-1 from 8:1 to 10:1.

Table I. Alkylation of benzene with dodecene-1 in the presence of borontrifluoride etherate (temperature= 80°C, amount of catalyst = 20 % by wt. of benzene , time of addition = 2h and time of stirring = 1h).

Expt. No	Molar ratio of benzene to dodecene-1	% Yield of sec.-Dodecylbenzene
1	8:1	71.3
2	10:1	73.6

sec.-Undecylbenzene from undecan-1-ol:

sec.-Undecylbenzene has been obtained by the alkylation of benzene with undecan-1-ol in the presence of anhydrous aluminium chloride as catalyst. The influence of the variation of temperature, time of reaction, molar ratio of benzene to

undecanol-1 and amount of catalyst on the reaction of benzene with undecan-1-ol in the presence of anhydrous aluminium chloride as catalyst has been investigated. The temperature was varied from 60 to 80°C, molar ratio of benzene to undecan-1-ol from 5:1 to 10:1, amount of catalyst from 10 to 15 % by wt. of benzene and reaction time from 2 to 3h. Table II. shows the results. The yield of sec.-undecyl benzene, the product of the reaction increases with the increase of temperature (Expt. No. 1 and 2) , molar ratio of benzene to undecan-1-ol (Expt. No. 2, 5 and 6) , amount of catalyst (expt. No. 2 and 4) and time of reaction (Expt. No. 2 and 3). The sec.-undecylbenzene is obtained in 42.2% yield under the following reaction conditions : temperature = 80°C, molar ratio of benzene to undecan-1-ol = 10:1 , amount of catalyst = 15 % by wt. of benzene, time of addition = 2h and time of stirring = 1h.

sec.-Dodecylbenzene from dodecan-1-ol:

Benzene with dodecan-1-ol in the presence of aluminium chloride as catalyst produces sec.-dodecylbenzene. Table III shows the effects of the variation of parameters on the reaction of benzene with dodecan-1-ol in the presence of anhydrous aluminium chloride as catalyst. The reaction gives sec.-dodecylbenzene, the yield of which increases with the increase of temperature (Expt. No. 2 and 5) , molar ratio of benzene to dodecan-1-ol (Expt. No. 6 and 7). On further increasing the molar ratio of benzene to dodecan-1-ol, the yield of the product decreases (Expt. No. 7 and 8). The yield of the product also increases with the increase of amount of catalyst (Expt. No. 1 and 2) . The yield decreases when the amount of catalyst is increased further (Expt. No. 2 and 3) . The yield of the product decreases also when the reaction time is increased above three hours (Expt. No. 2 and 4) This happens due to the dealkylation of the product. Thus the best

Table II. Alkylation of benzene with undecan-1-ol in the presence of anhydrous aluminium chloride catalyst.

Expt. no.	Reaction conditions					
	Temperature °C	Molar ratio of benzene to undecan-1-ol	Amount of catalyst. % by wt. of benzene	Time of addition, h	Time of stirring, h	% Yield of sec.-Undecyl benzene
1	60	8:1	15	2	1	23.2
2	80	8:1	15	2	1	30.4
3	80	8:1	15	2	0	23.5
4	80	8:1	10	2	1	14.8
5	80	5:1	15	2	1	11.6
6	80	10:1	15	2	1	42.2

Table II. Alkylation of benzene with dodecan-1-ol in the presence of aluminium chloride catalyst.

Expt. no.	Reaction conditions					
	Temperature °C	Molar ratio of benzene to undecan-1-ol	Amount of catalyst. % by wt. of benzene	Time of addition, h	Time of stirring, h	% Yield of sec.-Undecyl benzene
1	80	10:1	10	2	1	15.2
2	80	10:1	15	2	1	31.3
3	80	10:1	20	2	1	22.5
4	80	10:1	15	2	2	17.4
5	60	10:1	15	2	1	24.6
6	80	6:1	15	2	1	13.2
7	80	8:1	15	2	1	45.4
8	80	12:1	15	2	1	29.8

yield of *sec.*-dodecylbenzene is obtained in 45.4% yield under the following reaction conditions : temperature = 80°C, molar ratio of benzene to dodecan-1-ol = 8.63:1 , amount of catalyst = 15 % by wt. of benzene, time of addition of dodecan-1-ol = 2h and time of stirring =1h (Expt. No. 7).

Characterisation of *sec.*-undecylbenzenes

sec.- Undecylbenzenes have been produced by the alkylation of benzene with undecan-1-ol. In the IR-spectrum of *sec.*-undecylbenzenes bands of 700cm⁻¹ and 720 cm⁻¹ are the characteristics of monosubstitued aromatic ring. Bands at 1600 cm⁻¹ and 2800-2900 cm⁻¹ indicate the presence of aromatic ring and alkylgroup respectively (Saha *et al.*, 2001). A weak band at 3045 cm⁻¹ was observed for CH aromatic.

In the ¹H NMR-spectrum of the product signals for five protons (5H) of the aromatic ring are observed at $\delta = 6.50-7.83$ ppm. Signals for all the hydrogens on the *sec.*-undecyl group except one on the alpha-position relative to the ring is observed at $\delta = 0.06-1.10$ ppm and six protons from two methyl groups present at the end of the chain in $\delta = 1.1-2.6$ ppm. Signal for the hydrogen on the alpha-position (-CH=) is observed at $\delta = 3.87-4.20$ ppm.

Since alkylation by benzene with different long chain alkylating agent is available in literatures (Anthonius *et al.*, 2003). This reaction is favorable to *p*-alkylation. Therefore we have not carried out the HPLC experiment this product.

sec.- Undecylbenzene shows absorption at $\lambda_{\max} = 287.0$ nm in 0.01 M methanol solution.

The product had b.p. 270°C, d_4^{20} 0.8311 n_D^{20} 1.4635 (MRD, Found : 77.085, Calc: 77.105).

Characterisation of *sec.*-dodecylbenzenes

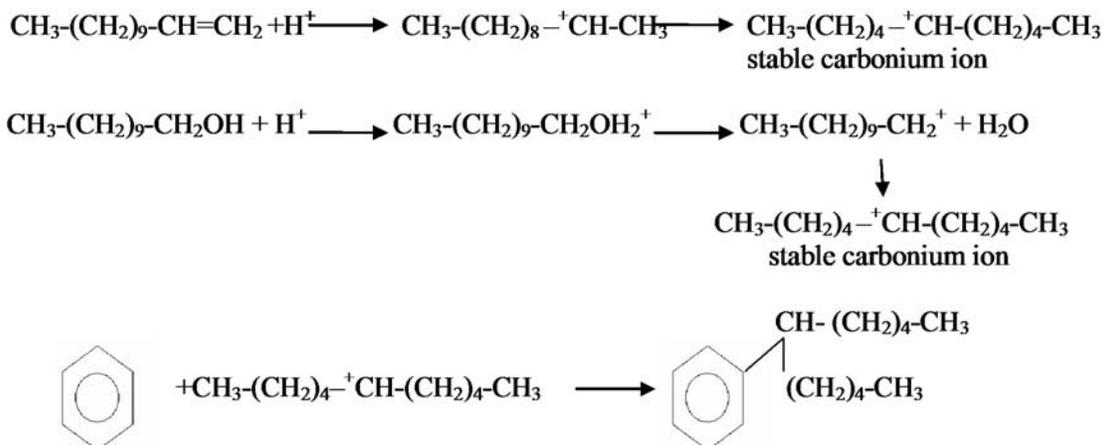
When benzene alkylated with dodecan⁻¹-ol produces *sec.*-dodecylbenzene. In the IR-spectrum of the product absorption bands at 700 cm⁻¹ and 720 cm⁻¹ indicate the presence of 5-adjacent C-H in the aromatic ring. The aromatic ring band is observed at 1600 cm⁻¹ and the bands of saturated alkyl group (C-H stretch) are observed at 2900 cm⁻¹ respectively. (Saha *et al.*). Spectrum signals for the aromatic ring protons are observed at $\delta = 6.66-7.33$ ppm. In the ¹H NMR-spectrum of *sec.*-Dodecyl benzenes show signals at $\delta = 6.20-7.80$ ppm for five protons (5H) of the aromatic ring. δ - values for all the 2 degree protons of the *sec.*- Dodecyl group except one on the alpha-position relative to the aromatic ring and six protons from two methyl groups present at alkyl chains $\delta = 0.6-1.1$ ppm respectively. Signal for the hydrogen of the alpha- position is observed at = 3.5-4.00 ppm.

In 0.001M petroleum ether solution the product absorbs at $\lambda_{\max} = 290.0$ nm in the UV-spectrum.

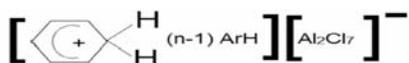
sec. - Dodecylbenzene had b.p. 302-306°C, d_4^{20} 0.8932, n_D^{20} 1.504 (MRD, Found : 81.697 , Calc. : 81.723).

Conclusion

sec.-Undecyl and dodecyl benzenes have been synthesized in high yield by the alkylation of benzene with olefins (undecene-1 & dodecene-1) & alcohols (undecanol-1 & dodecanol-1) respectively in the presence of borontrifluoride etherate and anhydrous aluminium chloride as catalysts. The products are the intermediates for detergents. Olefins (Undecene-1 & Dodecene-1) and catalyst borontrifluoride etherate were found to be more reactive in the reactions than alcohols (undecanol-& dodecanol-1) and anhydrous aluminium chloride.

Reaction mechanism

Aluminium chloride in the solid state is practically insoluble in hydrocarbons and does not strongly catalyze the reaction. However, as HCl is liberated aluminium chloride begins to be converted into a dark liquid substance which is also insoluble in excess hydrocarbon. This Gustavson complex possesses high catalytic activity and the reaction is gradually speeded up. It can be prepared by passing HCl on heating through a suspension of AlCl_3 in an aromatic hydrocarbon. The complex is a compound consisting of AlCl_3 and HCl with 1-6 molecules of an aromatic hydrocarbon. One of which is in a special structural state of a positive charged ion (a δ -complex), the remaining atoms forming the salvation shell:

**References**

- Anthonium J, Hoefnagel and Herman Van Bekkun(2003). Selective alylation of methyl benzene with cyclo hexane catalyzed by solid acids catalysis letters, **85** :1-2, 7-11.
- Ashimov MA, Refiev GD, Klionskaye and Kasimova RM (1966), Synthesis of surface active compounds and detergents from 100-250 fraction from petroleum cracking. *Azerb. Khim. Zh.* **1**:15-20.
- Ashimov MA, Mursalova MA and Kanzaveli SE (1969), Alkylation of benzene by a wide fraction of olefins (30 - 250°C), products of the cracking of n-olefins of trans-former oil, Dokl. Akad. Nauk. Azerb. **25** (7): 203..
- Allison JR and Nm. L Balack. (1953), Lubricating grease. *U.S.* **2** (628): 195-202.
- Bataafsche de NN (1952), Alkylated aromatic hydrocarbons suitable as a lubricating oil. *Dutch* **70**: 426.
- Bataafsche de NN (1952), Lubricants *Dutch* **71**: 112.
- Clausen CA and Matson G (1977), Principles of Industrial Chemistry, Willey Interscience Publication, p412.
- Calcagno BN Ferlazzo and Ghirgo M (1970) C9-C15 Alkylbenzene for detergents . *Ger. Offen.* **1**, 935, 750.
- Dimitrios VF (1964), n-Alkylbenzenes. *U.S.* **3**, 136, 824
- Epshtein AB and Filippychev GF (1964), Utilization of the alkylbenzene fraction obtained in the reduction of cumene as solvents. *Nefteperabotka I neftekhim. Nauchn. Tekhn. Sb.* **6**:33-36.
- Fredman BS, Morritz FL and Moroissey CK (1957) Alkylation of benzene and homologues with methylcyclohexenes. *J. Am. Chem. Soc.* **19**: 1165-1168.
- Lebedev NN (1984), Chemistry and technology of basic Organic and Petrochemical Synthesis, Mir, Publishers, Moscow, **1 and 2**: 638.
- Lebedev NN, Nicoleseu IV, Mircha I and Nikshin GI (1960), *Izvest. Akad. Nauk. USSR, Otdel. Khim.* **94**.
- Pokzovskaya ES (1959), Alkylation of alkylbenzenes with olefins and cyclopentene, *Neft. Akad.Nauk.SSSR.* **13**:3-10.
- Paul H (1950), Treatment for the improvement of lubricating oils. *U. S.* **2** (529) : 484
- Saha SK, Saha D and Saha M (2001), Alkylbenzenes for detergents. *Indian J. of Chemical Technology* , **8**: 25-27.

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