

Shape Selective Alkylation of Biphenyl with 1-octene on ((Al+C₃H₇Cl)+C₂H₄) Catalysts

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ABSTRACT: Alkylation of biphenyl with 1-octene was investigated using ((Al+C₃H₇Cl)+C₂H₄) catalysts. The catalytic activity of ((Al+C₃H₇Cl)+C₂H₄) for the alkylation was studied at different temperatures, mol ratios of biphenyl to 1-octene, reaction times and catalyst concentrations. It was shown that using this catalyst has more advantageous than another catalysts. Experiments show that by increasing temperature the alkylation process accelerates and the amounts of obtained octylbiphenyls increases. It is observed that selectivity of mono-octylbiphenyls increases by increasing catalyst concentration and mol ratio of biphenyl to 1-octene. Optimum conditions were determined for mono-, di- and poly-octylbiphenyls.

KEY WORDS: Shape-selectivity, ((Al+C₃H₇Cl)+C₂H₄) catalyst, Alkylation of biphenyl, 1-octene, Catalytic activity

INTRODUCTION

Alkylation of aromatic compounds to prepare substituted arylalkyles is an important area of fine chemical synthesis. The use of this class of reaction for substituting aromatic rings is due to the high regioselectivity towards the substitution p-positions. Traditionally, Friedel-Crafts alkylation of aromatic compounds is carried out with classic Lewis acid catalysts such as AlCl₃, BF₃, etc. However, these acids do not behave as true catalysts since they are consumed in stoichiometric amounts due to the formation of an adduct, and the ensuing separation of the product by hydrolysis generates a great deal of environmentally unfriendly waste.

Biphenyls have both the properties of high thermodynamic stability and high reactivity so they are

alkylated with different alkylation compounds such as alcohols, olefins and alkyl halogens. A mixture of ortho-, meta- and para-alkylbiphenyls is formed during the alkylation. These alkylbiphenyls are used in the preparation of plastic and polyester materials due to their superior characteristics [1,2].

Different catalysts are used in alkylation reactions. Jana Horniakova et al.[3] studied the alkylation of biphenyl with t-butanol in aqueous environment by using HY and H β zeolites and showed that HY zeolites are more active than H β zeolites. Great attention has been devoted in the recent years to the isopropylation reaction of biphenyl in the liquid phase with propylene over dealuminated mordenite zeolites[4-8] and highly dealuminated mordenites impregnated with cerium[9-11].

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The results, especially showed that these dealuminated mordenites constitute the best catalysts for the selective production of the linear 4,4'-diisopropylbiphenyl derivatives, reviewed recently by Sugi [12,13].

More specifically, the alkylation of biphenyl with 1-octene is a reaction of practical interest since it may produce mono-, di- and polyoctylbiphenyl, an important intermediate in the preparation of polymers.

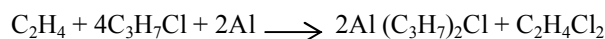
In the present paper, the alkylation of biphenyl with 1-octene has been studied by using a catalyst. Experimental results showed that biphenyl is alkylated with 1-octene easily and different alkyl derivatives of biphenyl are formed. The effects of some parameters (temperature, molar ratio of biphenyl to 1-octene, reaction time and catalyst concentration) on the process and on the

formation of alkylbiphenyls are investigated.

EXPERIMENTAL

Materials

$((Al + C_3H_7Cl) + C_2H_4)$ was used as catalyst in the experiment. Propyl chloride is added to aluminium powder and then the mixture reacts with ethylene in liquid phase to obtain the catalyst. Catalytic reaction is as follows:



Biphenyl and 1-octene (with 99% purity) were used as raw materials. Boiling points, density and index of refraction of 1-octene were 121-122°C, 0,715 g/cm³ and 1,408 respectively. 99% pure ethylene and pure nitrogen were used.

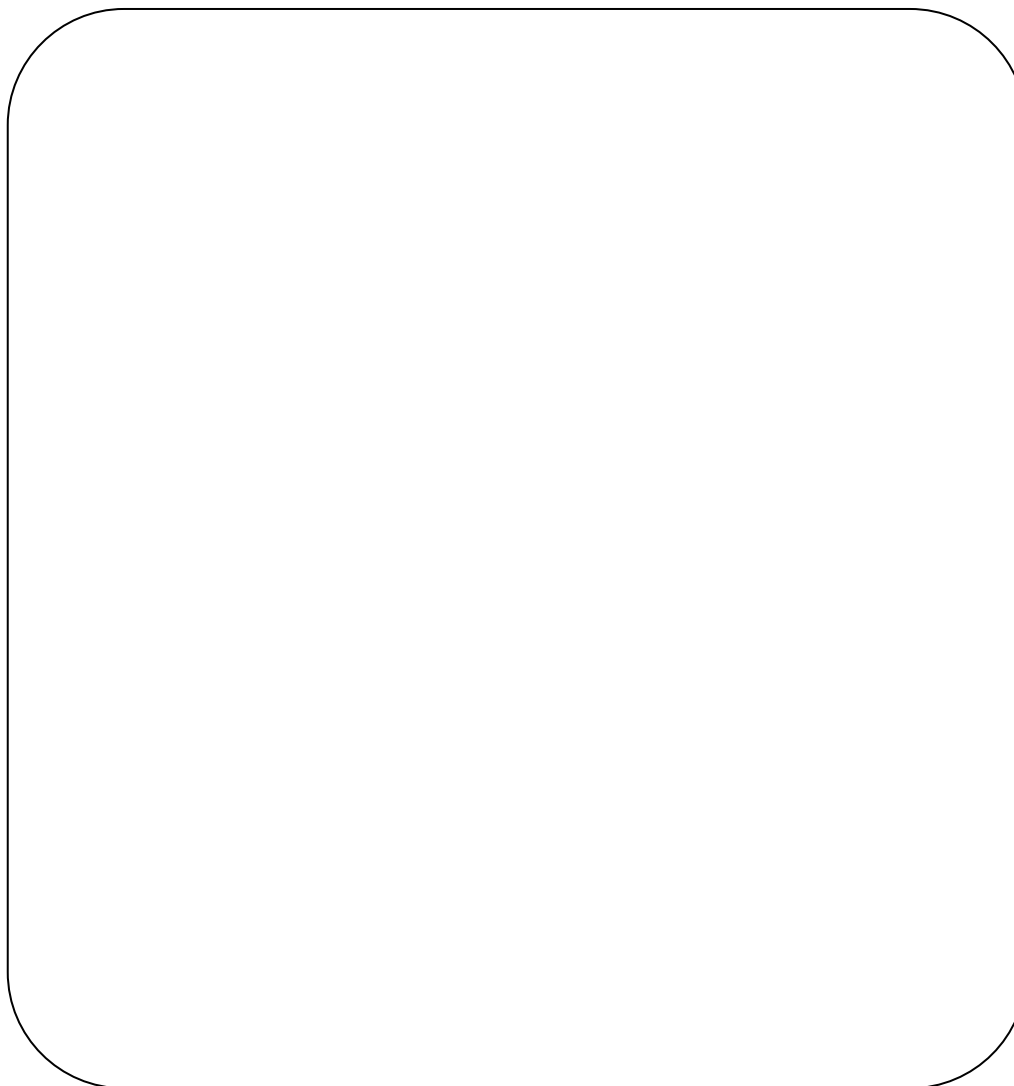


Fig. 1: Scheme of the laboratory device.

(1-reactor, 2-mixer, 3-monometer, 4-1-octene cup, 5-difmonometer, 6-heater, 7-thermocouple channel).

EXPERIMENT

Alkylation of biphenyl with 1-octene was carried out in a laboratory reactor (Figure 1). It consists of a reactor of 1.5 l (1) and a difmonometer (5) connecting liquid monomers with the reactor. Reactor is equipped with a mixer (2), a heater (6), monometer (3), thermocouple channel (7) and inlet and outlet valves. Difmonometers and reactor are made of stainless steel.

For the experiment, catalyst and biphenyl at certain amounts were added to reactor. Air in the reactor was discharged by nitrogen. Then reactor was heated and, started to be mixed when biphenyl was liquefied. After that, nitrogen application was continued and by the time reaction conditions was reached, 1-octene at sufficient amounts was added to reactor by difmonometer (5) under nitrogen pressure. Alkylation was carried out by continuous mixing. At this time reaction heat was removed from the system by water bath. After the reaction was completed, reactor was cooled by water bath to room temperature and opened. Finally samples were taken and prepared for alkyl biphenyl analyses.

RESULTS AND DISCUSSION

In this study alkylation of biphenyl with 1-octene and the effects of some parameters on the alkylation process were investigated. Results show that temperature is one of the main factors affecting the reaction rate. Its effect on the alkylation was observed between 20-80°C. The experiments show that the conversion of biphenyl and the amounts of obtained octyl biphenyls increases by the increasing the temperature. By increasing temperature from 20°C to 80°C the biphenyl conversion increases from 56% to 80%. In this case, the amounts of obtained monoethyl biphenyls and polyethyl biphenyls increase from 42% to 53% and from 33% to 37% respectively. The results of the experiment are shown in Fig. 2.

The influence of molar ratios of 1-octene to biphenyl was investigated at the different cases. The experimental results are shown in Fig. 3.

It was observed that molar ratios of monomers have a significant effect on alkylation process. When the molar ratio of biphenyl to 1-octene increases, conversion of biphenyl and the amounts of di- and polyethyl biphenyls decreases.

As shown in Fig. 3, maximum amounts of obtained

monoethyl biphenyls was observed at the 1:1 molar ratio of monomers. The effect of reaction time on the alkylation process was shown in Fig. 4.

According to experimental results, by increasing reaction time increases biphenyl conversion. Also, the selectivity of monoethyl biphenyl increases from 22% to 49%, while the amounts of di- and polyethyl biphenyls decrease from 55% to 36% in the dealkylation process. These results show that as the reaction time increases, the dealkylation reaction, accelerates parallel to the alkylation reaction.

The rate of alkylation reaction also depends on the catalyst concentration. The influence of catalyst was investigated at ratios 1,5% - 6,5%. The experimental results are shown in Fig. 5.

An increase in catalyst concentration causes biphenyl conversion increases from 70% to 90% and the amounts of monoethyl biphenyls increase from 49% to 59%, while amounts of di- and polyethyl biphenyls decrease from 36% to 32%. The decreasing of di- and polyethyl biphenyls is explained that the used catalyst is a catalyst of both alkylation and dealkylation. Therefore, as the catalyst concentration increases, dealkylation also increases and conversion of di- and polyethyl biphenyls to alkyl biphenyls increase. Consequently, after examining the effects of parameters on the process, the optimum conditions for the formation of mono-, di- and polyethyl biphenyls can be determined.

Optimum conditions for the formation of monoethyl biphenyls are shown in Table 1.

On the other hand, optimum conditions for the formation of di- and polyethyl biphenyls were determined and shown in Table 2.

The alkylate products under optimum conditions were separated to fractions. The experiments show that maximum separation of monoalkyl biphenyls realizes at temperatures 360-380°C, while maximum separation of di- and polyalkyl biphenyls occurs at temperatures 380-460°C. Physico-chemical properties of fractions are shown in Tables 3 and 4.

It was shown that under optimum conditions, 59% of the alkylate obtained in the fraction interval of 360-380°C was of monoalkyl biphenyl while di- and polyalkyl biphenyls formed 55% of the alkylate obtained in the fraction interval of 380-460°C.

Fig. 2: The effect of temperature on the variation of the biphenyl conversion and selectivities of alkyl biphenyls. Reaction conditions: reaction time 60 min., molar ratio of biphenyl to 1-octene 1:1, mass ratio of catalyst to biphenyl 1,5%.

Fig. 3: The effect of molar ratio of biphenyl to 1-octene on the variation of biphenyl conversion and the amounts of obtained alkyl biphenyls. Reaction conditions: reaction temperature 60°C, reaction time 60 min., ratio of catalyst to biphenyl 1,5%.

Fig. 4: The effect of reaction time on the variation of biphenyl conversion and the amounts of obtained alkyl biphenyls. Reaction conditions: reaction temperature 60°C, ratio of catalyst to biphenyl 1,5%, molar ratio of biphenyl to 1-octene 1:1.

Fig. 5: The effect of catalyst concentration on variation of the of biphenyl conversion and the amounts of obtained alkyl biphenyls. Reaction conditions: reaction temperature 60°C, reaction time 60 min., molar ratio of biphenyl to 1-octene 1:1.

Table 1: Optimum conditions for the monoalkyl biphenyl

Reaction conditions	Value
Reaction temperature (°C)	60
Reaction time (minute)	60
Molar ratio of biphenyl to 1-octene	1:1
Ratio of catalyst to biphenyl (%)	6.5

Table 2: Optimum conditions for the di- and polyalkyl biphenyls

Reaction conditions	Value
Reaction temperature (°C)	60
Reaction time (minute)	60
Molar ratio of biphenyl to 1-octene	1:1
Ratio of catalyst used to biphenyl (%)	1,5

Table 3: Physico-chemical properties of monoalkyl biphenyl fractions

Temperature of Fraction, °C	The percentage of separated Monoalkyl biphenyls, %	Physico – chemical properties of fractions		
		Index of refraction	Density g/cm ³	Molecular mass
360	5	—	—	—
360-380	59	1.5558	0.9503	310
380-460	32	1.5488	0.9344	335
Remainder	4	—	—	—

Reaction conditions: reaction temperature 60°C, reaction time 60min .,
molar ratio of biphenyl to 1-octene 1:1, ratio of catalyst to biphenyl 6,5%.

Table 4: Physico-chemical properties of di- and polyalkyl biphenyl fractions

Temperature of Fraction, °C	The percentage of separated Di- and Polyalkyl biphenyls, %	Physico – chemical properties of fractions		
		Index of refraction	Density g/cm ³	Molecular mass
360	20	—	—	—
360-380	22	1.5558	0.9503	300
380-460	55	1.5488	0.9344	385
Remainder	3	—	—	—

Reaction conditions: reaction temperature 60°C, reaction time 20min .,
molar ratio of biphenyl to 1-octene 1:1, ratio of catalyst to biphenyl 1,5%.

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