Journal of Organometallic Chemistry, 382 (1990) 333–343
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20511

Potassium hydroxide as a promoter for the potassium-metal catalyzed side-chain alkylation of toluene

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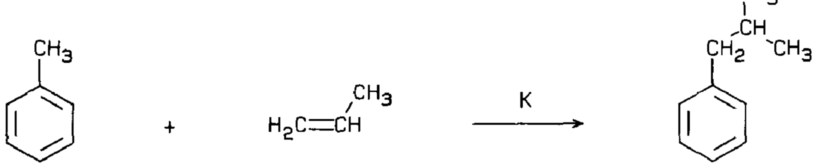
(Received May 9th, 1989)

Abstract

Potassium hydroxide acts synergistically with catalyst supports such as alumina, diatomaceous earth, or potassium carbonate to promote the potassium-metal catalyzed side-chain alkylation of toluene with propene. Carrying out the reaction with wet toluene to generate KOH in situ is a particularly effective method for promoting the reaction. The catalyst supports are not inert in the absence of the promoter, because they alter alkylation regiochemistry and increase the formation of methylindan by-products. As a mechanistic probe, the amounts of benzylpotassium that form are compared with propylation reaction rates. This is the first report concerning the amount of benzylpotassium that forms under side-chain alkylation conditions. From this and other data, a previously unrecognized mechanism for the promotion of side-chain alkylation is identified.

Introduction

Alkali metals catalyze the reaction (see eq. 1) of olefins with the benzylic carbon of alkyl-substituted aromatic compounds [1]. When the alkyl group is methyl, reaction with ethylene or propene is a simple, economical, high-yield, one-step method for the preparation of n-propyl or isobutyl substituted aromatic compounds.



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The history of this chemistry is rich with reports of catalyst promoters such as dienes [2], polynuclear aromatic compounds [3,4], organic halides [4], graphite [5], titanium metal [6], and alcohols [7]. The function of these promoters is not always clear, but most of them are believed to assist [8] in formation of benzylmetallic compounds which are the active intermediates responsible for olefin alkylation. Despite numerous reports of this type of promotion, there is no report of benzylmetallic compound yields under side-chain alkylation reaction conditions.

These alkylations are carried out either neat or with paraffin solvents at temperatures between 100–200 °C. Under these conditions, the organoalkali intermediates are insoluble, and there have been reports on the use of supports such as K_2CO_3 [9], Na_2CO_3 [5], alumina [10] and silica [10]. The role of supports in conjunction with promoters has not been investigated. In fact, it often seemed that a support is used as a substitute for the promoter.

We now report our study of potassium-metal catalyzed toluene propylation that shows a previously unrecognized type of catalyst promotion for side-chain alkylations. This involves a synergism between KOH and a catalyst support which affects the reaction via control of competitive product formation steps. An important consequence of this type of promotion is the positive effect exerted on the reaction when "wet" toluene is substituted for dry toluene, unintentionally or otherwise. We have also discovered that in the absence of KOH the support affects product distributions and alkylation regiochemistry. As a mechanistic probe we have measured the yield of benzylpotassium formed under various side-chain alkylation conditions. To our knowledge, this is the first report concerning the yield of a reaction intermediate for any side-chain alkylation.

Results and discussion

Effect of catalyst supports on toluene propylation

Reaction 1 in Table 1 shows toluene conversion and mono-alkylation product yields are poor when toluene propylation is carried out under anhydrous conditions without a catalyst support (240 min, 185 °C, 400 psig propene pressure, and moderate stir rate, 750 rpm) [11*]. In order to avoid long induction periods

Table 1

Effect of catalyst supports on the potassium catalyzed reaction of toluene with propene [a,b]

Reaction	Support	Toluene conversion (%)	Monoalkylated products [c], yield (%)
1	none	34	76
2	diatomaceous earth [d]	55	83
3	alumina [e]	46	95
4	K_2CO_3 [e]	32	96

[a] 185 °C, 92 g (1 mol) toluene, 400 psig propene pressure, 1.1 g (28 mmol) K, 240 min reaction time. [b] 60 min pre-reaction period at 185 °C prior to addition of propene. [c] Isobutylbenzene, n-butylbenzene, methylindans. The remaining converted toluene was present as numerous isomers of heptylbenzenes and propylmethylindans. [d] 4.9 g. [e] 10 g.

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* Reference numbers with an asterisk indicate a note in the list of references

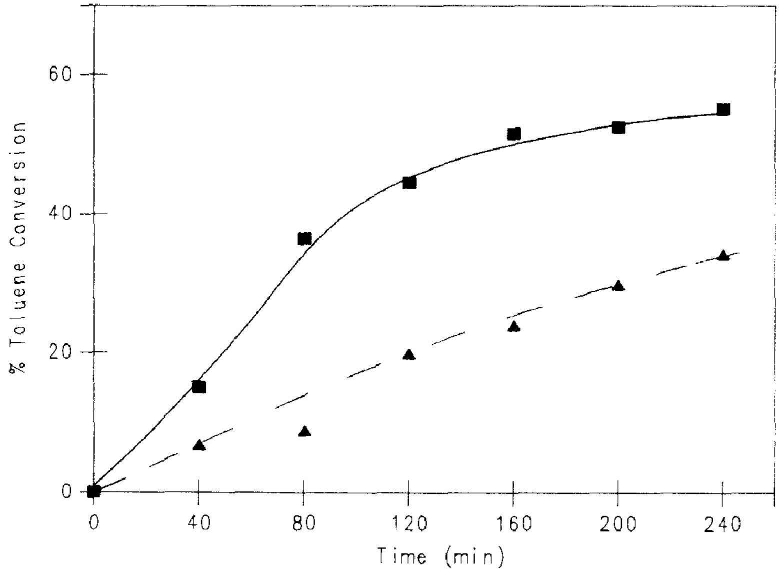


Fig. 1. Time dependence of toluene conversion with and without diatomaceous earth support (K (1.1 g, 28 mmol); toluene (92 g, 1 mol), 400 psig propene pressure). ■ 4.9 g diatomaceous earth; ▲ no support.

common to these reactions, the toluene and K are stirred 60 min at 185 °C before propene is added. Presumably, some benzylpotassium is formed during the pre-reaction period to initiate the reaction. When calcined diatomaceous earth (1.3 m^2/g surface area) or calcined alumina (4 M^2/g surface area) are added in reactions 2 and 3, respectively, there is marked improvement in toluene conversions and yields of mono-alkylation products [12*]. The addition of 150 mesh K_2CO_3 powder (0.5 m^2/g surface area) as a catalyst support to reaction 4 did not affect the toluene conversion, but it did improve the yields of mono-alkylation products. It would appear that K_2CO_3 is a poor catalyst support for this reaction, despite claims to the contrary in the patent literature [9]

The time dependences of toluene conversions for reactions 1 and 2 are compared in Fig. 1. As expected, the improved results obtained with diatomaceous earth are due to an increase in reaction rate, which we believe occurs because of an increase in total benzylpotassium surface-area by one of the following ways. The surface area per unit weight of benzylpotassium could increase, the amount of benzylpotassium could increase at a constant surface area per unit weight, or a combination of these two could occur.

In order to distinguish among these possibilities, we measured the amount of benzylpotassium formed under the conditions for reactions 1 and 2, except that no propene was added [13*]. The benzylpotassium was analyzed by first converting it to benzyltrimethylsilane via reaction with chlorotrimethylsilane as described in the experimental section. The results are shown in the first six entries of Table 2, and they can be compared with the rate data in Fig. 1 if 60 min is added to the x-axis, to account for the pre-reaction period at 185 °C prior to the addition of propene. There appears to be a close correlation between the increase in benzylpotassium yield and the increase in reaction rate when the support is present. This seems to indicate an increase in total benzylpotassium surface area, which is due mostly to an

Table 2

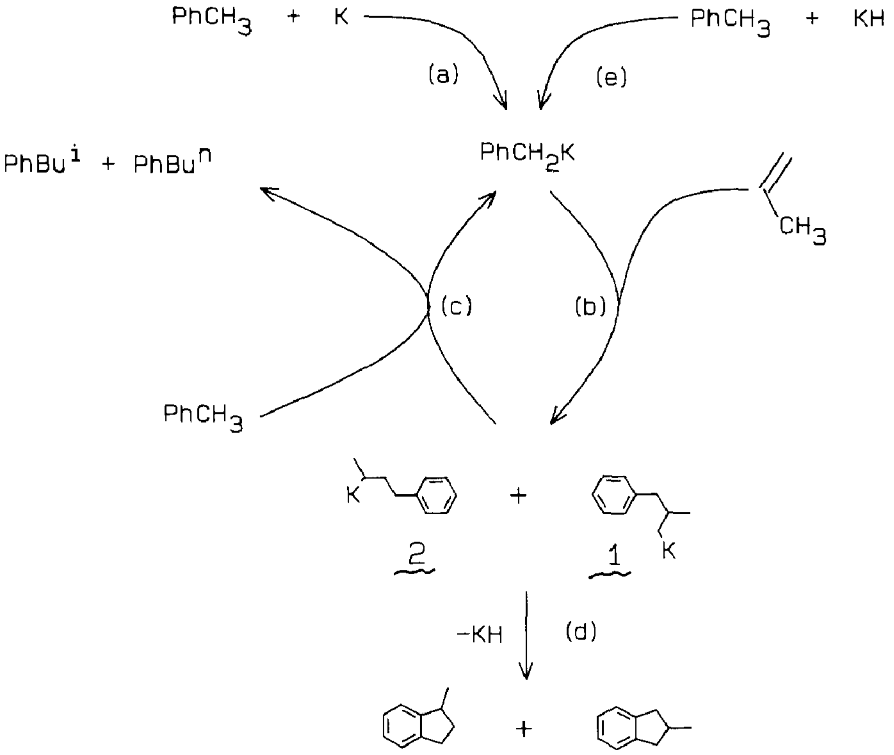
Formation of benzylpotassium under side-chain alkylation conditions [a]

Diatomaceous earth (g)	KOH [b] (mmol)	Time (min)	$PhCH_2K$ (mmol)	$PhCH_2K$, yield (%) based on K
0	0	60	1.4	5.0
0	0	120	3.2	11.4
0	0	180	4.3	15.4
5	0	60	1.3	4.6
5	0	120	5.6	20.0
5	0	180	7.5	26.7
5	2.9	180	< 0.1	< 0.3
5	2.9	240	7.0	25.0

[a] 185 °C, 92 g (1 mol) toluene, 1.1 g (28 mmol) K. [b] deposited onto diatomaceous earth.

increase in the amount of benzylpotassium at a constant surface area per unit weight.

Table 3 shows the distribution of mono-alkylation products and the ratios of attack by benzylpotassium at the two double-bond carbons of propene for the reactions in Table 1. Surprisingly, all three supports increase the formation of methylindans. Methylindans and butylbenzenes are believed to form competitively from common intermediates as shown in steps (c) and (d) of Scheme 1. The propylation regiochemistry is also changed by the supports to favor more alkylation



Scheme 1.

Table 3

Product distributions and propene regiochemistry for reactions of Table 1 [a]

Reaction	Support	Distribution (%) of mono-alkylation products [b]			Propene regio-selectivity [c]
		IBB	NBB	MeInd	
1	none	89	8	3	8/1
2	diatomaceous earth	81	3	16	11/1
3	alumina	84	4	12	11/1
4	K_2CO_3	88	7	5	10/1

[a] see footnotes of Table 1 for reaction conditions and the amounts of supports used. [b] IBB = isobutylbenzene, NBB = n-butylbenzene, MeInd = mixture of 1- and 2-methylindans. [c] Ratio for attack of benzylpotassium at the internal vs. terminal double-bond carbons.

at the internal double-bond carbon, which gives the intermediate with potassium at the more thermodynamically favored least-substituted carbon.

Effect of water on toluene propylation

The use of water to promote a side-chain alkylation has been previously reported for the sodium-metal catalyzed reaction of cumene with styrene [7]. However, no catalyst support was used, and the effect of in situ generated NaOH on the reaction appeared to be minor. We have investigated the effect of in situ generated KOH on toluene propylation by replacing the dry toluene of reaction 1 (Table 1) with "wet" toluene (565 ppm H_2O concentration) in reaction 5 of Table 4. Except for a minor improvement in the amount of mono-alkylation products, the results of reactions 1 and 5 are the same. An additional amount of potassium metal, compared to that used in reaction 1, was added to compensate for the formation of KOH.

Effect due to the combination of water and a support

When diatomaceous earth (reaction 6) or alumina (reaction 7) are added along with the "wet" toluene, toluene conversion and yields of mono-alkylation products, shown in Table 4, improve substantially compared to those in Table 1. Even small amounts of water have a profound effect when these supports are used. Figure 2 shows a plot of the toluene conversion averaged over the first 200 min as a function of the H_2O/K molar ratio. The greatest effect of water is between 0 and 4 mol%

Table 4

Effect of KOH on toluene propylation [a]

Reaction	Support	Toluene conversion (%)	Monoalkylated products, yield (%)
5	none	31	88
6	diatomaceous earth	83	92
7	alumina	71	97
8	K_2CO_3	37	95
9[b]	diatomaceous earth	70	89

[a] see footnotes of Table 1 for experimental conditions except that for reactions 5–8 1.2 g (31 mmol) K is used, and 2.9 mmol H_2O is added as a 565 ppm solution in toluene. [b] 2.9 mmol KOH supported on diatomaceous earth is substituted for the H_2O and 1.1 g K is used.

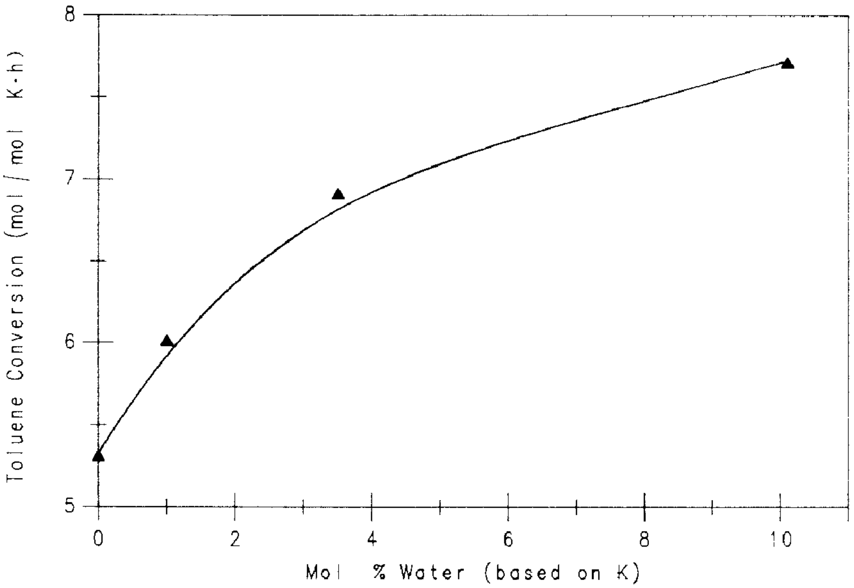


Fig. 2. Effect of water on the propylation of toluene averaged over 200 min reaction time (185 °C, toluene (92 g, 1 mol), diatomaceous earth (4.9 g), 400 psig propene pressure).

based on potassium, but even as little as 1 mol% H_2O (60 ppm concentration in toluene) affects catalyst activity. Reaction 8 shows the effect of water on the propylation with 150 mesh K_2CO_3 powder as a support. The toluene conversion shown in Table 4 increases only slightly when compared with the result of reaction 4 in Table 1. Again, K_2CO_3 appears to be a poor catalyst support.

In order to determine if there is anything special about KOH generated in situ, reaction 9 was run under anhydrous conditions with KOH that had been deposited on diatomaceous earth. A comparison of the results for reactions 6 and 9 in Table 4, shows in situ generated KOH is slightly, but not significantly, more active than the pre-supported KOH.

Table 5 shows the distribution of mono-alkylation products and the ratio of attack by benzylpotassium at the two double-bond carbons of propene for the reactions in Table 4. The product distributions and regiochemistries have changed

Table 5

Product distributions and propene regiochemistry for reactions of Table 4 [a]

Reaction	Support	Distribution (%) of mono-alkylation products			Propene regio-selectivity
		IBB	NBB	MeInd	
5	none	90	8	2	8/1
6	diatomaceous earth earth	91	8	1	9/1
7	alumina	90	10	<1	9/1
8	K_2CO_3	89	11	<1	8/1
9	diatomaceous earth	89	7	4	9/1

[a] See footnotes of Table 1.

again, but now they are similar to that for reaction 1 (Table 1), where neither support nor KOH is used. The yields of methylindans are even somewhat lower than in reaction 1.

Mechanism for support effect

Side-chain alkylations are thought to occur by the chain mechanism shown in Scheme 1 [1]. Step (a) is a chain initiation via toluene metallation to form benzylpotassium, step (b) is a chain propagation, step (c) is a chain transfer, and step (d) is one of many possible chain terminations. In order for the chain reaction to be kinetically sustained, the rate of chain termination can not exceed the rate of initiation.

When supports such as diatomaceous earth or alumina are added, two apparently opposing things occur. There is an increase in the chain initiation rate via increased benzylpotassium formation, discussed above, and the chain termination rate increases via methylindan formation. Apparently, the chain termination rate increases more than the chain initiation rate, because, as shown in Fig. 1, the propylation rate slows as the reaction proceeds and propylation stops. In contrast, without a support, methylindan formation is slow, and propylation rate does not slow as the reaction progresses. In the presence of a support, the chain-reaction survives as long as it does because potassium hydride, which forms as a co-product of methylindan formation, step (d) of Scheme 1, participates in chain initiation via step (e). This is apparent, since 73 mmol of methylindan forms from only 28 mmol of starting potassium metal in reaction 2 (see Tables 4 and 5), which would be impossible without initiation of the reaction-chain by KH. Apparently, activity of the KH for toluene metallation is slowly lost (probably due to the high reaction temperature), and the propylation reaction-chain slows to a stop.

Because steps (c) and (d) compete for the same phenylbutylpotassium intermediates (see Scheme 1), a decrease in the rate of (c) would give the same result as an increase in the rate of (d). We believe it is possible by an analysis of the regiochemistries for benzylpotassium attack on propene to determination which rate actually changes when a support is added. The presence of the supports changes the regiochemistry to give more intermediate with potassium attached to the least substituted carbon (structure **1** in Scheme 1). This intermediate forms preferentially because it is the most thermodynamically stable from both steric and electronic considerations. If a change in regiochemistry occurs due to the support's influence on electronic factors, then the most likely way this could occur is by complexation of the potassium counterion in the intermediates with surface oxygen atoms of the supports. This would give more carbanionic character to the intermediates, and this in turn would provide driving force for preferential formation of the more stable, least substituted carbonion. However, despite the obvious changes in complexation surface properties among silica, alumina, and carbonate, the regiochemistry is nearly the same in the presence of each.

Alternatively, a change in steric requirements for organopotassium intermediates adsorbed on the support seems a more likely explanation for a change in regiochemistry. Organopotassium compounds would be expected to adsorb onto a high-energy surface (such as found with the supports in this study) via electrostatic interactions between the surface and the ionic potassium–carbon bond. This would give an oriented ensemble on the surface with the potassium ion near the surface,

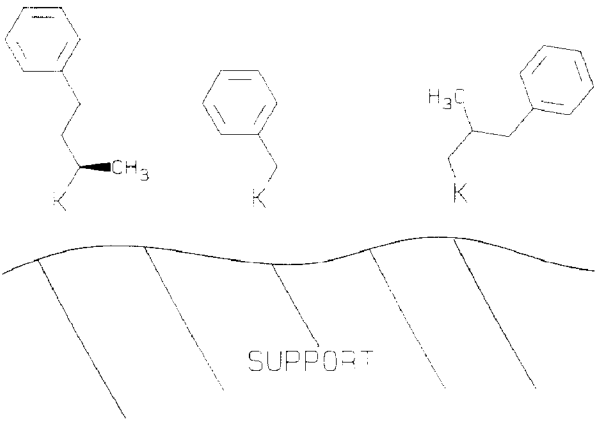


Fig. 3. Orientation of organopotassium compounds on a support.

and hydrocarbon tails sticking out perpendicular as shown in Fig. 3. This kind of orientation would cause an increase in steric requirement for the formation of the intermediate with potassium connected to the more substituted carbon (structure **2** in Scheme 1) relative to formation of the intermediate with potassium connected to the less substituted carbon (structure **1** in Scheme 1). Since all the supports have about the same surface areas, the variation in regiochemistry from one support to another due to steric requirements should be small.

Now that we have identified the importance of steric effects it is plain to see, that for subsequent reactions of the phenylbutylpotassium intermediates, the rate of intermolecular reactions such as (c) would be reduced. The approach of toluene to the potassium–carbon bonds necessary for chain transfer is hindered by the hydrocarbon tails of the ensemble. But, an intramolecular reaction such as (d) would be affected little, if at all by the oriented adsorbtion.

Mechanism for KOH-support synergism

When water or KOH are added along with the support, the yield of methylindans declines dramatically. Step (c) in Scheme 1 now appears to proceed at a faster rate relative to step (d). As a consequence, the ratio of initiation rate to termination rate is expected to be greater, and the propylation reaction rate should be maintained longer. Figure 4 compares the rates of toluene conversion for reaction 2, diatomaceous earth only, and reaction 4, diatomaceous earth with water added. As expected, the rate of toluene conversion in reaction 4 did not slow as did that for reaction 2. Figure 4 also shows that the initial rates for the two reactions are similar, if the small induction period of reaction 4 is ignored. This appears to imply that the total surface-area of benzylpotassium is not changed by the addition of KOH.

We measured the amount of benzylpotassium formed under the reaction conditions with KOH supported by diatomaceous earth, and the results were quite unexpected. As shown in Table 2, less than 0.1 mmol of benzylpotassium forms in the first 180 min, despite the considerable rate of propylation that occurs by 120 min (see Fig. 4 and remember to add 60 min to the x-axis for the pre-reaction period). It would appear that the surface-area per unit weight benzylpotassium increases tremendously in the presence of supported KOH, but for some unknown reason there is a long induction period before significant quantities of benzylpotas-

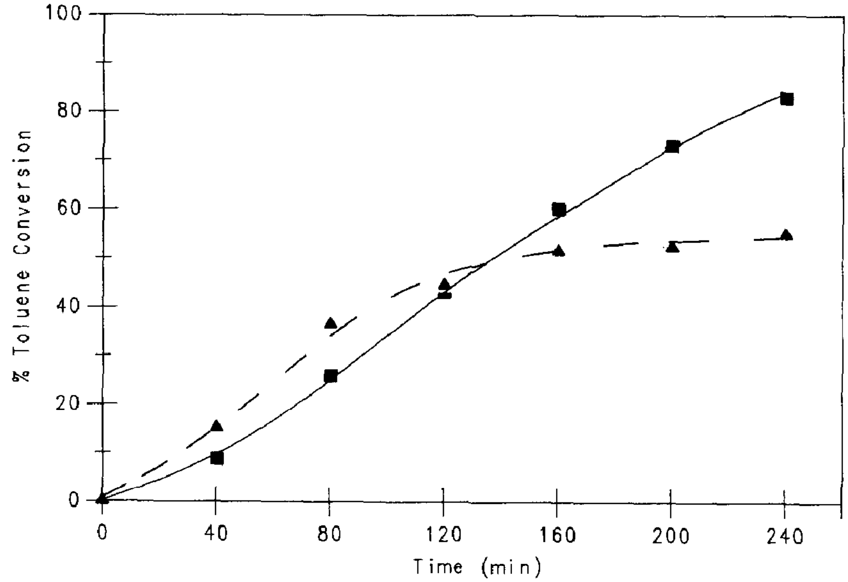


Fig. 4. Time dependence of toluene conversion with and without KOH (K (1.1 g, 28 mmol), toluene (92 g, 1 mol), diatomaceous earth (4.9 g), 400 psig propene pressure). ■ 2.9 mmol in situ generated KOH; ▲ anhydrous.

sium form. Once the benzylpotassium starts to form rapidly between 180 and 240 min (see last entry of Table 2), the surface area per unit weight may decrease, but we believe the total benzylpotassium surface-area probably increases. This would explain how the reaction rate remains fairly constant in the later stages of the reaction despite the high level of toluene conversion.

We speculate that the apparent increase in surface-area per weight of benzylpotassium due to KOH results in a greatly reduced steric environment for the potassium–carbon bond of the reaction intermediates, which are still supported in an oriented manner as shown in Fig. 3. Now there is unhindered approach of toluene to the potassium–carbon bonds of phenylbutylpotassium intermediates required for chain transfer, (c) of Scheme 1. This results in an increase in rate of (c) relative to (d), and less methylindans are observed. Also, a decrease in steric hindrance removes some of the driving force that favors formation of intermediate **1** in Scheme 1 relative to intermediate **2** in Scheme 1, and this explains the change in regiochemistry when KOH is added.

Summary

We have identified a new mechanism for the promotion of potassium-metal catalyzed side-chain alkylations that occurs only when a catalyst support is used in conjunction with KOH. The promotion seems to be general for a variety of support types, but not all supports work as well. The mechanism involves the competition between two reactions for the intermediates that result from addition of benzylpotassium to the olefin. The relative rates of the competing reactions appear to be controlled by the steric requirement about the potassium–carbon bonds of the supported intermediates, and this can be controlled in turn by the addition of KOH.

This kind of steric control exerted by a support on a solid organoalkali reagent has not been previously documented.

Experimental

Materials

All catalyst supports were dried under high vacuum for 3 h at 165 °C. Support surface areas were determined by a N_2 BET * method. KOH supported by diatomaceous earth was prepared by mixing 25 g diatomaceous earth (surface area 1.3 m^2/g) with 100 ml 0.85 wt% aqueous KOH, and then stripping off the water. The resulting solid was dried under high vacuum at 160 °C for 3 h. The water content of toluene was controlled by mixing dry toluene (distilled from Na) with water-saturated toluene (565 ppm concentration) in different proportions. Chlorotrimethylsilane (Aldrich) was stored over CaH_2 and handled under N_2.

Propylation reactions

Reactions were run in a carefully dried 300 ml Parr reactor equipped with a pitched-four-blade turbine turned at 750 rpm. A typical reaction procedure is described as follows. Toluene, n-C_{11} paraffin as an analytical standard, and freshly cut potassium metal were charged to the reactor inside a N_2 glove box. If a support was used, it was also charged at this time. The reactor was sealed, stirred, and heated to 185 °C for 1 h. Then propene (dried by 3A mol sieves) was fed by a pump to 400 psig pressure at 185 °C, and this pressure was maintained. Samples were drawn at intervals through a dip-leg into a metal side-arm.

Benzylpotassium determination

In a typical procedure 92 g toluene, 1.1 g freshly cut potassium metal, 0.5 g n-C_{13} paraffin, and in some instances, 5 g support, were charged to the reactor inside an N_2 dry-box. The reactor was sealed, stirred, and heated to 185 °C. When the desired time was reached, the reaction was quickly cooled to 75 °C by circulating cold water through the reactor cooling coils. Then 4 ml (32 mmol) chlorotrimethylsilane was injected into the reactor via a side arm. Control reactions established that benzyltrimethylsilane resulted only from the reaction of benzylpotassium with chlorotrimethylsilane, and not from a reaction of toluene, potassium, and chlorotrimethylsilane at 75 °C.

Product analyses

All product analyses were made by GC using n-C_{11} paraffin as an internal standard. Authentic samples of 1-methylindan and 2-methylindan were prepared by reaction of either 1-indanone or 2-indanone with trimethylaluminum, followed by dehydration of the tertiary alcohol and hydrogenation. Authentic samples of isobutylbenzene and n-butylbenzene used as reference standards were purchased from Aldrich. An authentic sample of benzyltrimethylsilane was obtained from Lancaster Synthesis Ltd.

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* BET = Brunauer, Emmett, Teller.

The regioselectivity for the two olefinic positions on propene were determined on samples pulled at 80 min reaction time. The yields of mono-alkylation products were nearly quantitative at this time based on toluene converted. The sum of isobutylbenzene and 2-methylindan were attributed to attack at the internal double-bond carbon, and the sum of n-butylbenzene and 1-methylindan were attributed to attack at the terminal double-bond carbon. The ratio of isobutylbenzene to n-butylbenzene was always greater than the ratio of 2-methylindan to 1-methylindan due to differences in the rates of cyclization of the organopotassium intermediates.

References and notes

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11 Bis-alkylation was responsible for the other toluene derived products of which there were a number of isomers, and they were not quantitatively determined. In addition, propene dimers were also formed in these reactions. All product yields were determined by GC analysis.

12 Fusion of supported catalyst is a serious problem when 5 g of alumina or K_2CO_3 are used, but not when 10 g is used. This is not a problem when 5 g diatomaceous earth is used. The catalyst fusion is an indication that the support has been overloaded.

13 Under these conditions toluene is metallated only at the benzylic carbon. A detailed account concerning the metallation of toluene by potassium under side-chain alkylation conditions was presented at the 198th ACS National Meeting, September 10–15, 1989, Miami, FL.