### [CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

# **Catalytic Side-Chain Alkylation of Aromatic Compounds**

# STERLING E. VOLTZ

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The side-chain ethylation of toluene and cumene occurs readily in the presence of organo-alkali metal catalysts about 200°. The ethylation of benzene requires more severe conditions. Alkali metal hydrides are active catalysts for the ethylation of toluene and polymerization of ethylene at 300°. The alkaline earth metal hydrides are inactive at this temperature. Several other hydrides have also been tested. Aniline reacts with ethylene at 200° to form N-ethyl aniline. At higher temperatures higher amines are formed. Propylene reacts with toluene to a much lesser extent than ethylene. Butenes did not react under the conditions used in this study.

Numerous studies of ring alkylation of aromatic compounds in the presence of acid catalysts have been made. Such catalysts do not cause side-chain alkylation. Several recent studies have demonstrated that side-chain alkylation takes place in the presence of alkali metals and organo-alkali compounds. Whitman<sup>1</sup> has shown that toluene reacts with ethylene at  $225^{\circ}$  in the presence of sodium to form *n*-propylbenzene and 3-phenylpentane. The reaction is probably initiated by the formation of benzyl sodium formed by the metalation of toluene. Little<sup>2</sup> and Pines and coworkers<sup>3,4,5</sup> have shown that this type of reaction takes place more readily in the presence of organo-alkali metal compounds. Pines and coworkers<sup>6</sup> have also shown that organoalkali metal compounds are catalysts for double bond isomerization.

Whitman<sup>7</sup> has alkylated amines with olefins in the presence of alkali metals or alkali metal hydrides. Closson and coworkers have also alkylated amines as well as other types of compounds.<sup>8</sup>

A mechanism for side-chain alkylation has been given by Pines and coworkers.<sup>4</sup> A more detailed study of the mechanism has recently been made by Hart.<sup>9</sup>

The work reported in this paper is concerned with the use of organo-metallic compounds, hydride catalysts, and other catalysts for the ethylation of aromatic compounds. Alkylations with propylene and butenes have also been investigated.

- 1954); 2,688,044<sup>(Aug. 31, 1954)</sup>; 2,721,885 (Oct. 25, 1955); 2,721,886 (Oct. 25, 1955); and 2,721,887 (Oct. 25, 1955).
- (4) Pines, Vesely, and Ipatieff, J. Am. Chem. Soc., 77, 554 (1955).

(5) Pines and Mark, Paper No. 33, Division of Organic Chemistry, 127th ACS Meeting, Cincinnati, Ohio, April 1955.

- (6) Pines, Vesely, and Ipatieff, J. Am. Chem. Soc., 77, 347 (1955).
  - (7) Whitman, U. S. Patent 2,501,556 (March 21, 1950).
     (8) Closson, Ligett, and Kolka, U. S. Patents 2,728,802

(Dec. 27, 1955); 2,750,384 (June 12, 1956); 2,750,417 (June 12, 1956); 2,75

#### EXPERIMENTAL

A rocking autoclave with a capacity of 200 cc. was used to carry out most of the reactions in this work. In the experiments employing organo-alkali metal catalysts, 2.0 g. of the alkali metal and 0.8 g. anthracene were used. In the experiment with chlorobenzene, 1.0 g. of this compound was used. Four g. of catalyst were used in all the experiments with the alkali metal hydrides, alkaline earth metal hydrides, and the various commercial catalysts tested.

Most of the organic chemicals used in this work were purified by distillation or recrystallization. The hydrides were supplied by Metal Hydrides, Inc.

The gaseous products were analyzed by mass spectrometry. In most instances the liquid products were decanted or filtered off and the residue washed with pentane. The pentane washings were combined with the liquid products and the mixture was distilled and analyzed by infrared spectroscopy.

In most experiments no attempt was made to analyze the solid residues. These materials were often unstable in air when dry. The autoclave was generally emptied under a blanket of nitrogen and the solid residues were promptly disposed of.

## RESULTS AND DISCUSSION

Ethylation of alkyl-aromatic compounds with organo-alkali metal catalysts. Initial work in this study was concerned with the alkylation of toluene and cumene with ethylene in the presence of organo-alkali metal compounds. High yields of *n*-propylbenzene and 3-phenylpentane are obtained in the ethylation of toluene with sodium anthracene catalysts at 200°. The yield of alkylated products increases as the ethylene concentration increases. Lithium anthracene is less active for the ethylation of toluene than sodium anthracene. This is an agreement with the activities of other lithium and sodium organo-compounds used as catalysts in other types of reactions.

Sodium reacts at room temperature with chlorobenzene in toluene to form sodium phenyl, which in turn metalates toluene to give sodium benzyl at higher temperatures.<sup>10,11</sup> Sodium chlorobenzene is not so effective as sodium anthracene for the ethylation of toluene, but reasonable yields of ethylated products were obtained with this catalyst.

Cumene is also ethylated in the presence of sodium anthracene to give t-amylbenzene. These results with toluene and cumene are comparable to those obtained by Pines, Vesely, and Ipatieff.<sup>4</sup>

Small amounts of ethane and other hydrocarbons ( $C_4$ - $C_4$ ) and traces of hydrogen and methane are formed in these

(11) Bryce-Smith and Turner, J. Chem. Soc., 1975 (1950).

(12) Morton, Brown, Holden, Letsinger, and Magat, J. Am. Chem. Soc., 67, 2224 (1945).

<sup>(1)</sup> Whitman, U. S. Patent 2,448,461 (Sept. 7, 1948).

<sup>(2)</sup> Little, Jr., U. S. Patent 2,548,803 (April 10, 1951).

<sup>(3)</sup> Pines and Ipatieff, U. S. Patents 2,670,390 (Feb. 23,

<sup>12, 1956);</sup> and 2,751,426 (June 19, 1956).

<sup>(9)</sup> Hart, J. Am. Chem. Soc., 78, 2619 (1956).

<sup>(10)</sup> Gilman, Pacevitz, and Blaine, J. Am. Chem. Soc., 62, 1514 (1940).

ethylations. With lithium anthracene appreciable quantities of gaseous C<sub>4</sub> compounds are obtained; olefins are also present in the liquid product in this case. Pines and coworkers<sup>4</sup> report the formation of ethane and hydrogen in their work.

The ethylation of benzene to ethylbenzene in the presence of an alkyl-sodium compound has been reported.<sup>6</sup> The ethylation of benzene does not take place in the presence of sodium anthracene at 200°. At 300°, appreciable quantities of ethylbenzene, s-butylbenzene, and 3-methyl-3-phenylpentane are formed. Considerable amounts of liquid olefins and gaseous  $C_4$  compounds also are formed. Neither toluene nor benzene are thermally alkylated under these conditions.

Alkali metal hydride catalysts. The ethylation of toluene over lithium and sodium hydrides (unsupported) has been investigated. At 200° lithium hydride is completely inactive, and only a trace of *n*-propylbenzene is obtained with sodium hydride. Both hydrides are active for ethylation and polymerization at 300°; typical data are given in Table I. In the presence of toluene, both alkylation and polymerization take place over lithium hydride. With sodium hydride alkylation is the predominant reaction, and only a very small amount of polymerization occurs. In the absence of toluene both hydrides are active for polymerization. ethylation of toluene and polymerization of ethylene. All three hydrides are inactive for the ethylation of toluene at 300°. A small amount of ethylene polymerization occurred in the ethylation experiment with barium hydride and traces may have also occurred in the ethylation runs with the other two hydrides. In the absence of toluene, however, calcium hydride was the only active catalyst for the polymerization of ethylene.

Samples of Hydrimix (calcium hydride supported on inert salts) were also examined as catalysts for the ethylation of toluene at 300°. The areas of these preparations are generally 2-4 m.<sup>2</sup>/g.; the supports are nonporous and the surface area depends on the particle size. Appreciable quantities of liquid olefins and some *n*-propylbenzene are formed. Ethylene polymerization is the predominant reaction.

Hydrides of titanium, zirconium, and tantalum. Titanium and tantalum hydrides are inactive for the ethylation of toluene at 300°. With both catalysts, however, liquid olefins are formed. In the absence of toluene these catalysts are inactive even for ethylene polymerization. Zirconium hydride is active both for the ethylation of toluene and ethylene polymerization at 300°. Large quantities of liquid olefins are formed in the ethylation of toluene together with

TABLE I

ETHYLATION AND POLYMERIZATION WITH ALKALI M	ETAL HYDRIDES AT 300°
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	Expt.	xpt. Hydro-			Gaseous Products (Mole)			
	No.	carbon	$Catalyst^b$	Liquid Products	$C_2H_4$	$C_2H_6$	Other	
-	1	Toluene <sup>4</sup>	LiH	0.098 mole toluene + 6 cc. liquid (b.p. 111-287°) con- sisting mostly of <i>n</i> -propyl- benzene and olefins with small amounts of 3-phenyl- pentane and unidentified products	0.068	0.083	0.027	
	2	None	${ m LiH}$	0.5 g. olefins	0.050	0.15	0.052	
	3	Toluene <sup>d</sup>	NaH	0.034 mole toluene 0.045 mole <i>n</i> -propylbenzene 0.039 mole 3-phenylpentane Small amount of olefins	0.009	0.12	0.004	
	4	None	$\operatorname{NaH}$	1.1 g. olefins	0.15	0.14	0.014	

<sup>a</sup> 0.4 mole of ethylene charged in each experiment at 800-900 p.s.i.g. at room temperature. <sup>b</sup> 4.0 g. hydride used in each experiment. <sup>e</sup> Primarily C<sub>4</sub> with small amounts of H<sub>2</sub>, CH<sub>4</sub>, C<sub>5</sub>, C<sub>5</sub>, and C<sub>6</sub>. <sup>d</sup> 0.2 mole toluene charged.

The quantities of ethane formed in all these runs are greater by a factor of 10 than those obtained with organoalkali catalysts. Pines, Vesely, and Ipatieff<sup>4</sup> explain the formation of ethane in the presence of organo-sodium catalysts by assuming some of the sodium alkyl-aromatic hydrocarbons decompose to form sodium hydride. The sodium hydride can then react with ethylene to form sodium ethyl: the latter through the metalation of alkyl-aromatic hydrocarbons then forms ethane and sodium alkyl-aromatic compounds. In the experiments described in Table I. appreciable quantities of lithium ethyl and sodium ethyl were probably formed by the interaction of ethylene with the hydrides. Metalation of toluene by the alkali ethyl compounds would lead to the formation of ethane. However, this mechanism cannot be applied to the experiments made without toluene. Metalation of some of the polymeric olefin products could account for the formation of ethane in these runs. This picture is consistent with the results reported by Morton, Brown, Holden, Letsinger, and Magat.<sup>12</sup> .They found that butenes and other olefins are readily metalated by sodium amyl; in many instances the metalations occur by substitution.

Relatively large amounts of butenes were present in the gas phase of the runs with lithium hydride.

Alkaline earth metal hydrides. The hydrides (unsupported) of calcium, strontium, and barium were examined both for appreciable quantities of n-propylbenzene. The predominant reaction is ethylene polymerization. Zirconium hydride is even active for polymerization in the absence of toluene.

In many instances in this study, more polymerization of ethylene occurs in the presence of toluene than when it is absent. In several cases, catalysts which appear to be inactive for ethylene polymerization give appreciable yields of liquid olefins in the presence of toluene. When toluene is present, there is a competitive reaction (ethylation of toluene) that can take place. The reason for this activating effect of toluene has not yet been determined. It would be interesting to determine whether other substances have the same effect.

Miscellaneous catalysts. Four commercial petroleum processing catalysts were tested for the ethylation of toluene at  $300^{\circ}$ . Trace amounts of *n*-propylbenzene and 3-phenylpentane were formed over chromia-alumina. With molybdenaalumina and cobalt molybdate-alumina, trace amounts of methyl-ethyl-benzenes were formed. Both types of ethylation occurred to a small extent over platinum-alumina catalyst. Small amounts of ethylene polymerization were observed in most cases.

Ethylation of amines. A short investigation has been made of the ethylation of aniline and its derivatives in the presence of sodium and sodium anthracene. The experiments reported by Whitman<sup>7</sup> were carried out at higher pressures

	Propylene		Temp.	Liquid Product (Mole)		Gaseous Products $(Vol.\%)$		
Expt. No.	(Mole)	$Catalyst^{b}$	(°C)	Toluene	Isobutylben- zene	$C_3H_6$	$C_3H_8$	Other
1	0.2	NaH	300	0.11	Trace	87.4	12.1	0.5
<b>2</b>	0.4	NaH	300	0.12	0.032	68.5	27.3	4.2
3	0.2	Na-anthracene	200	0.16	None	96.6	3.4	
4	0.4	Na-anthracene	200	0.15	None	95.9	2.0	<b>2.1</b>
5	0.4	Na-anteachrne	300	0.14	0.020	85.1	13.6	1.3

TABLE II

<sup>a</sup> 0.20 mole toluene charged in each experiment. <sup>b</sup> 4 g. NaH or 2 g. Na-anthracene. <sup>c</sup> Includes H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>, C<sub>4</sub>-C<sub>6</sub>.

than employed in this work and it was desirable to determine whether aromatic amines could be alkylated under conditions under which toluene reacts.

The ethylation of aniline at  $200^{\circ}$  was studied with both sodium and sodium anthracene. Similar results were obtained in both cases. The liquid product from the experiment with sodium present consisted of 0.024 mole of unreacted aniline and 0.022 mole N-ethyl aniline; 0.024 mole unreacted aniline and 0.021 mole N-ethyl aniline were obtained with sodium anthracene. In these experiments, 0.2 mole toluene and 0.4 mole of ethylene were initially charged. No ethylene polymerization occurred in these experiments; the ethylene used up in both instances corresponds almost exactly to the amounts of N-ethyl aniline formed. The amounts of hydrogen produced in these runs are greater than in corresponding ones in the ethylation of toluene.

The considerable amounts of solid materials obtained from these experiments were not analyzed. They probably contained condensation products of aniline, sodium anilide, and other organo-sodium compounds.

At higher pressures Whitman<sup>7</sup> obtained N,N-diethyl aniline as well as N-ethyl aniline at 200° in the presence of sodium. N-ethyl aniline does not react with ethylene at 200° in the presence of sodium anthracene under the conditions used in this work. o-Ethyl aniline likewise does not react under these conditions. The *ortho*-ethyl group could deactivate aniline in the following ways: (1) it may exert a steric effect or (2) the electron-repelling effect of this group could decrease the acidity of the amino hydrogen atoms.

At 300° aniline reacts with ethylene in the presence of sodium or sodium anthracene to give large amounts of N-ethyl aniline; N,N-diethyl aniline; N-n-butyl aniline; and higher amines.

Alkylation of toluene with propylene and butenes. In view of the activity of sodium hydride and sodium-anthracene for the alkylation of toluene with ethylene, the alkylations of toluene with propylene and butenes over these catalysts have been investigated.

Typical data for propylene are given in Table II. Propylene reacts with toluene in the presence of either sodium hydride or sodium-anthracene at 300° to give isobutylbenzene. The yields of alkylated products are much lower than those obtained with ethylene under the same conditions. No alkylation occurs with propylene over sodiumanthracene at 200°, whereas large amounts of alkylated products are obtained with ethylene at this temperature. Neither isobutylene nor butene-2 reacts with toluene at  $300^{\circ}$  in the presence of sodium hydride or sodium anthracene under the above conditions. Appreciable quantities of butene-1 were formed in the experiments with butene-2. This result means that butene-1 is also inactive for the alkylation of toluene under these conditions. Pines, Vesely, and Ipatieff<sup>4</sup> have shown that butene-1 is isomerized to butene-2 at about  $100^{\circ}$  in the presence of organo-alkali metal compounds. Under certain conditions isobutylene reacts with toluene to form neopentylbenzene.<sup>5</sup>

# SUMMARY

1. Both toluene and cumene are readily ethylated in the side chain in the presence of organo-alkali metal catalysts at about 200°. The ethylation of benzene requires more severe conditions.

2. Lithium and sodium hydrides (unsupported) are active catalysts for the side-chain ethylation of toluene and polymerization of ethylene at  $300^{\circ}$ . Both hydrides are inactive at  $200^{\circ}$ .

3. The alkaline earth metal hydrides (unsupported) are inactive for the ethylation of toluene or polymerization of ethylene at  $300^{\circ}$ .

4. Hydrimix catalysts (calcium hydride supported on inert salts) are active for the polymerization of ethylene at 300°, and some ethylation of toluene occurs at this temperature.

5. Zirconium hydride is active for the ethylation of toluene and polymerization of ethylene at 300°. Titanium and tantalum hydrides are inactive for the ethylation of toluene at 300°.

6. Chromia-alumina, molybdena-alumina, cobalt molybdate-alumina, and platinum-alumina are inactive for the ethylation of toluene at 300°.

7. Aniline is ethylated at  $200^{\circ}$  to give N-ethyl aniline. At  $300^{\circ}$  the products include N-ethyl aniline, N,N-diethyl aniline, N-n-butyl aniline, and other ethylated products.

8. Propylene reacts with toluene in the presence of sodium hydride or sodium anthracene to form isobutylbenzene. The yields of alkylated products are much less than obtained with ethylene under the same conditions. Neither isobutylene nor butene-2 reacts with toluene under these conditions.

MARCUS HOOK, PA.