Potassium Hydride–Alkyllithium as a Catalyst System for a Carbanionic Cyclization Reaction Involving Alkylarenes and Olefins

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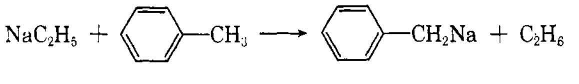
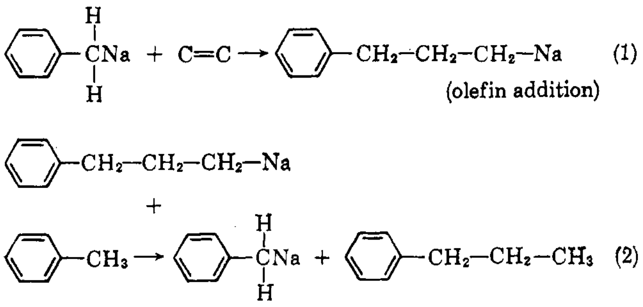
Potassium hydride–butyllithium or potassium metal–butyllithium were found to be active catalysts for the carbanionic side-chain alkylation and cyclization of aromatic hydrocarbons having an available α-hydrogen. Alkylindanes and tetrahydroacenaphthene were obtained in high yields and fast rates from the corresponding alkylbenzenes or tetralin. The relative amount of cyclization products depends mainly on the K–Li ratio of the catalyst system. The coordinative power of the lithium ion is proposed to facilitate the concerted abstraction of a hydride ion and the formation of cyclization products.

It is known that sodium or potassium alkyls have the ability to transmetalate to more "acidic" hydrocarbons by proton abstraction. This reaction occurs readily



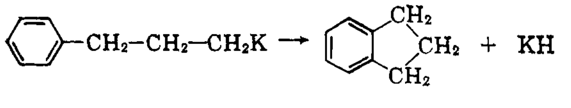
even at room temperature. Alkali metal organic compounds also show the capability to add to an olefinic double bond.

Pines, Ipatieff, and co-workers[1] have shown that these reaction principles can be applied for a fully catalytic side-chain alkylation of benzylic hydrocarbons.



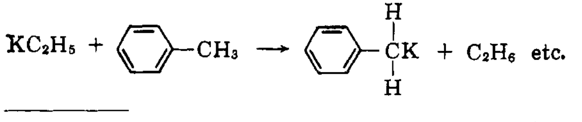
Since the rate of 2 is much faster than that of 1, no "growth" reaction is observed. The alkylation stops when all the benzylic hydrogen is alkylated. Ethylene is the preferred olefin since the reaction rates decrease sharply with the higher olefins. The reaction temperatures are in the range of 150–250°. A promoter, *e.g.*, anthracene, is used besides the alkali metal (Na, K) to initiate the formation of the active catalytic, metal organic intermediate.

Pines and co-workers[2] also found that, if potassium is used instead of sodium, a ring closure reaction occurs to some extent leading to the formation of alkylindanes as side products. The following mechanism was proposed.



(1)

$KH + C{=}C \rightarrow K{-}C_2H_5$ (2)



(3)

One mole of ethane is formed per mole of ring-closed product. Ethylene is the hydrogen acceptor for the cyclodehydrogenation.

The present work is concerned with a more active catalyst system that favors the cyclization reaction over the side-chain alkylation. Thus, there is a possibility of converting aromatic hydrocarbons with a benzylic hydrogen into the corresponding cyclized products in a catalytic manner and with considerably improved yields. The catalyst system developed for this reaction is a potassium–lithium organohydride complex. Its preparation and its catalytic properties are described in the following section.

The Catalyst.—A suspension of finely divided potassium hydride in a 0.2 *M* solution of butyllithium in hexane was ball-milled for several hours at room temperature and incremental samples were taken from the supernatent liquid and titrated for their content of butyllithium. It was found that butyllithium disappears gradually from the solution (see Fig. 1).

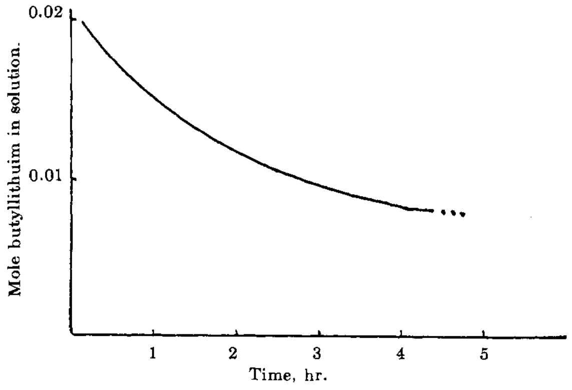
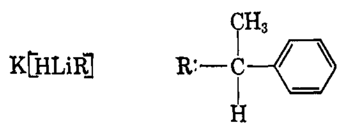


Fig. 1.—KH (0.01 *M*) and LiC_4H_9 (0.02 *M*) ball-milled in 100 cc. of hexane. Curve shows disappearance of butyllithium from the solution.

Potassium hydride or butyllithium do not metalate benzylic hydrocarbons at room temperature in hexane solvent. However, if the solid reaction product of potassium hydride and butyllithium is contacted with ethylbenzene, a bright red solid forms immediately and *n*-butane is evolved. Its analysis is approximately the following.



Its formation can be described by equation A:

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(1) H. Pines, J. Veseley, and V. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

(2) L. Schaap and H. Pines, *ibid.*, **79**, 4965 (1957).

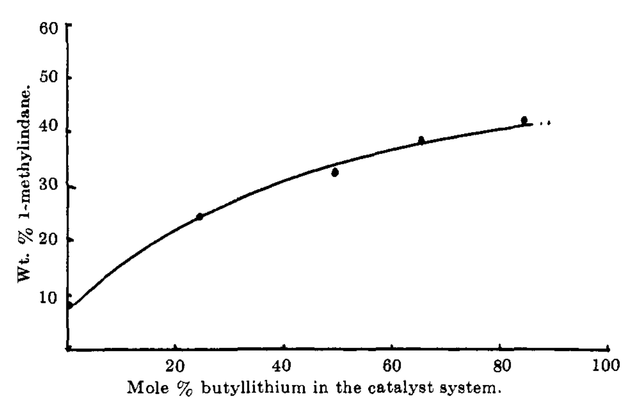


Fig. 2.—The 1-methylindane proportion in the C_{10} fraction (other component, *sec*-butylbenzene) obtained from ethylbenzene and ethylene with $KH—LiC_4H_9$ catalyst system as a function of the K–Li ratio.

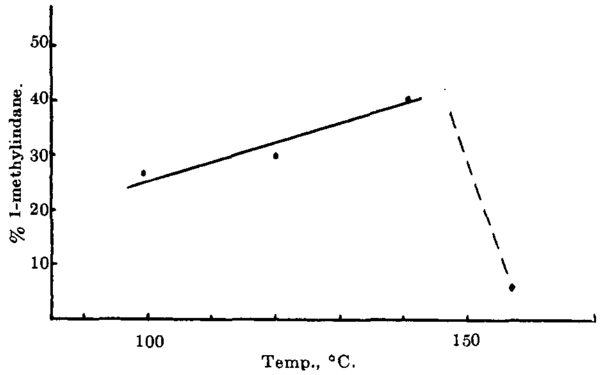
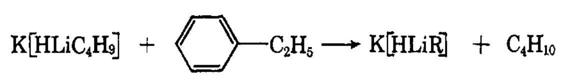


Fig. 3.—The 1-methylindane content of the C_{10} fraction derived from ethylbenzene and ethylene with a $KH\text{-}LiC_4H_9$ catalyst (molar ratio 1:2) as a function of temperature.



$K[HLiC_4H_9] + C_6H_5C_2H_5 \longrightarrow K[HLiR] + C_4H_{10}$ (A)

The complex is an active catalyst for the alkylation and cyclization reaction of benzylic hydrocarbons. After use, the catalyst was essentially unchanged; only the benzylic component reflected the distribution of the benzylic hydrocarbons produced.

Potassium hydride can be replaced by potassium metal which gives in conjunction with butyllithium a catalyst system of equivalent properties. Its formation probably occurs *via* the following steps.

$$K + LiC_4H_9 \longrightarrow KC_4H_9 + Li \quad (B)$$

$$KC_4H_9 + LiC_4H_9 \longrightarrow K[Li(C_4H_9)_2] \quad (C)$$

The exchange of the alkyl groups by benzylic residues or a hydride finally leads to a catalyst of equivalent composition.

The complex formation of organolithium compounds with other alkali metal organic compounds was observed earlier by Wittig and co-workers,[3] who describe complexes such as $Na[Li(C_6H_5)_2]\cdot OR_2$. Bryce-Smith and Turner[4] have obtained phenylpotassium by treating potassium metal with alkyl lithium in benzene.

Discussion

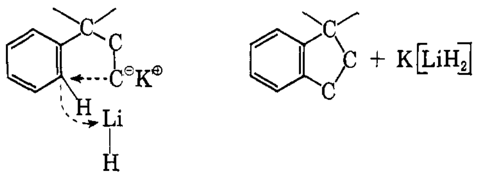
The catalyst system described above is active in the side-chain alkylation and cyclization of benzylic hydrocarbons. The type of reaction products obtained are identical with those derived from a potassium metal-promoter catalyst described by Pines,[2] *et al.* However, the distribution of products is shifted in favor of the cyclized derivatives, *e.g.*, alkylindanes from alkylbenzenes which appear as the major products of the catalytic reaction.

Further, it was found that the catalytic ring closure reaction is favorably influenced by a decreasing K–Li ratio (Fig. 2).

The activity of the catalyst is based on the presence of potassium hydride since alkyllithium itself is inactive under these conditions. The catalyst shows activity from about 80° on, and the cyclization reaction is somewhat favored up to ~150° (Fig. 3).

At temperatures above 150° the 1-methylindane yield drops abruptly, indicating a structural change in the catalyst which also changes its color from orange-red to dark purple-black.

Table I (p. 643) shows, however, that under certain conditions the carbanionic cyclization reaction remains the preferred path of catalytic conversion with a variety of aromatic hydrocarbons. The role of lithium in this catalyst complex could be visualized.



The primary carbanion derived from the addition of ethylene to the benzylic anion is stabilized by lithium hydride forming a coordination complex. This coordinative ability of the lithium ion may assist in the concerted reaction of the hydride abstraction from the aromatic nucleus and the indane ring closure. In the next step $K[LiH_2]$ adds to ethylene and the resulting alkyl hydride complex transmetalates to a benzylic carbon continuing the catalytic cycle and liberating ethane.

Results

Table I shows the distribution of the cyclized *vs.* the side-chain alkylated compounds in the successive product fractions derived from alkyl aromatics and olefins with the $KH\text{-}LiC_4H_9$ catalyst. The reaction conditions were not optimum in regard to the formation of cyclization products. Potassium metal itself with anthracene as a promoter gave, under these conditions, a C_{10} fraction containing only 7% 1-methylindane from ethylbenzene and ethylene. Further details are found in the Experimental section.

The reaction rates are quite fast, and due to the heterogeneous nature of the catalyst they depend on the degree of the catalyst dispersion. The reaction of ethylbenzene and ethylene with $KH\text{-}LiC_4H_9$ catalyst (1:2) at 135° proceeds under the conditions described below with an uptake of *ca.* 1 mole of ethylene/g. catalyst/hr. and 800-lb. ethylene pressure.

Experimental

Potassium hydride was prepared from the elements at 370° and 500-p.s.i.g. hydrogen pressure in dodecane solvent with cumene

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[3] G. Wittig, *et al.*, *Ber.*, **88**, 294 (1955); **91**, 865 (1958).

[4] D. Bryce-Smith and E. Turner, *J. Chem. Soc.*, 861 (1953).

TABLE I

CATALYTIC REACTION OF VARIOUS ALKYL AROMATICS WITH OLEFINS USING THE CATALYST SYSTEM POTASSIUM HYDRIDE–BUTYLLITHIUM (MOLAR RATIO, 1:2) AT 135°

Reactants		Reaction products	
Alkyl aromatic (1 mole)	Olefin (1 mole)		
(1) Toluene	Ethylene	C_9 fraction:	15% indane
		(70% of product)	84% propylbenzene
		C_{11} fraction:	70% 1-ethylindane
		(20% of product)	30% 3-phenylpentane
(2) Ethylbenzene	Ethylene	C_{10} fraction:	41% 1-methylindane
		(72% of product)	59% *sec*-butylbenzene
		C_{12} fraction:	90% alkylindane
		(15% of product)	10% alkylbenzene
(3) Ethylbenzene	Propylene	C_{11} fraction:	50% dimethylindane
		(80% of product)	50% 1-phenyl-1,2-dimethylpropane
		20% liquid residue:	Not analyzed
(4) Cumene	Ethylene	C_{11} fraction:	62% 1,1-dimethylindane
		(65% of product)	38% *t*-amylbenzene
		35% liquid residue:	Not analyzed
(5) Tetralin	Ethylene	C_{12} fraction:	40% tetrahydroacenaphthene[a]
		(70% of product)	60% 1-ethyltetralin
		30% liquid residue:	Not analyzed

[a] Analyzed as acenaphthene.

present as a promoter. The potassium hydride was handled under dry nitrogen.

The Catalyst.—Very finely divided potassium hydride (0.4 g.) 0.01 mole, was suspended in 30 cc. of ethylbenzene containing butyllithium (0.02 mole) in a sealed 50-cc. centrifuge glass. The gas space was swept with helium. The glass container was shaken for *ca.* 2 hr. at room temperature. The white potassium hydride was soon replaced by a bright red solid. The red precipitate was centrifuged and the supernatent liquid was decanted (nitrogen gas blanket). It was found to contain 0.01 mole of residual butyllithium. The red solid was dried *in vacuo* and weighed 1.5 g.

On alcoholysis of this compound with isopropyl alcohol 0.01 mole of a gas was obtained which was identified as hydrogen. One gram of a hydrocarbon was found in the alcoholic solution and identified as ethylbenzene by v.p.c.

In the following experiments the catalyst was not preformed, but formed *in situ* from the components during the heat-up period of the reaction vessel.

Potassium Hydride–Butyllithium as Catalyst System for the Reaction of Ethylbenzene and Ethylene.—All reactions were carried out in a 300-cc. rocking-type steel autoclave and agitation was provided by a set of steel balls. The autoclave was charged with the liquid reactant and the catalyst in a drybox under purified nitrogen.

The general procedure is illustrated by the following experiment. The autoclave was charged with 1 mole of ethylbenzene, potassium hydride (0.4 g., 0.01 mole), and butyllithium (1.3 g., 0.02 mole as 10% solution in hexane). The autoclave was assembled and the nitrogen in the autoclave was replaced by ethylene. After charging 1 mole of ethylene the autoclave was rocked while heating to 135°; at this temperature a pressure of *ca.* 1000 p.s.i.g. was observed. The pressure dropped to about half of its value within 1 hr. at which time the autoclave was rapidly cooled to room temperature. The residual gases (mainly ethane and some residual ethylene) were vented and after deactivation of the catalyst with isopropyl alcohol the liquid reaction products were washed with water, separated, and dried over anhydrous calcium chloride. The distillation of the product in a Todd column (30 plates) yielded 56 g. of ethyl benzene and a product consisting of 45 g. of a C_{10} fraction (n_D 1.5051) and 18 g. of a liquid residue (n_D 1.5123). The C_{10} fraction was fractionated into *sec*-butylbenzene and 1-methylindane which were identified by the refractive index and the boiling point (n_D 1.4902, b.p. 173°, and n_D 1.5266, b.p. 190°, respectively). The ratios of these two hydrocarbons in the C_{10} fraction were determined by gas chromatography (12 ft. × 0.25. in. PES column). The residual fraction (C_{12} and higher hydrocarbons) was analyzed by mass spectroscopy for the alkylbenzene–alkylindane ratio.

The results described in Fig. 1 and 2 were obtained from the above, as well as analogous experiments in which the K–Li ratio of the catalyst or the temperature was varied as indicated.

The Catalytic Reaction of Other Alkylarenes or Tetralin with Ethylene or Propylene.—The results described in Table I were obtained from experiments in which ethylbenzene was replaced by an alkylarene as indicated. The known hydrocarbons of the various product fractions (given in Table I) were identified by their boiling points, refractive indices, and their retention times. The C_{12} fraction obtained from tetralin and ethylene was dehydrogenated over a supported platinum catalyst and the products in the catalysate were identified as acenaphthene and 1-ethylnaphthalene.

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