distilled 3-diethylaminopropylamine in 25.5 g. (0.25 mole) of 3-chloro-3-methyl-1-butyne. The two-layer mixture was allowed to stand at room temperature for 6 days and then was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was worked up as described above. Distillation gave 27 g. (55% yield), b.p. 99–135° at 30 mm. Redistillation yielded 20 g. (41%), b.p. 83–86° at 4.5 mm., n^{25}D 1.4275.

Preparation of 3-Piperidino-3-methyl-1-butyne (Method C).[9]—A mixture of 127.5 g. (1.5 moles) of piperidine, 100 ml. of ether, 50 ml. of water, 0.3 g. of cuprous chloride and 0.3 g. of copper bronze powder was prepared under nitrogen in a three-neck flask equipped with mechanical stirrer. 3-Chloro-3-methyl-1-butyne (51 g., 0.5 mole) dissolved in 50 ml. of ether was then added dropwise with stirring (1.5 hours) under nitrogen while maintaining an inside temperature of 17-20°. After stirring for an additional 2 hours at room temperature, the mixture was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was washed with cold water, dried for 15 minutes with anhydrous potassium carbonate, filtered, redried with potassium hydroxide pellets overnight and then distilled. Two distillations gave 51.5 g. (68% yield), b.p. 83° at 35 mm., m.p. 56–57°.

Preparation of 3-Phenylamino-3-methyl-1-butyne (Method D).[9]—A mixture of 27.9 g. (0.3 mole) of aniline, 40.5 g. (0.4 mole) of triethylamine, 100 ml. of ether, 25 ml. of water, 0.3 g. of cuprous chloride and 0.3 g. of copper bronze powder was prepared under nitrogen in a three-neck flask equipped with mechanical stirrer. 3-Chloro-3-methyl-1-butyne (25.5 g., 0.25 mole) dissolved in 25 ml. of ether was added dropwise with stirring (1 hour) while maintaining an inside temperature of 16–20°. After stirring for an additional 2 hours at room temperature, the mixture was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was treated as described immediately above. Two distillations yielded 23.5 g. (59% yield), b.p. 76–78° at 0.2 mm., m.p. 49–50°. The analytical sample was purified by sublimation.

Hydrogenation of Acetylenic Amines.—Three procedures (methods E, F and G) were employed. Typical applications are recited below.

Semi-hydrogenation of 3-Isopropylamino-3-methyl-1-butyne (Method E).—A solution of 12.8 g. (0.1 mole) of 3-isopropylamino-3-methyl-1-butyne in 50 ml. of petroleum ether (Skellysolve B) containing 0.010 g. 10% palladium-on-activated charcoal was subjected to hydrogenation at room temperature under an initial pressure of 41 p.s.i.g. The pressure dropped by 6.8 p.s.i.g. within 1.5 hours and by 8.8 p.s.i.g. after 5.5 hours, corresponding to hydrogen uptake for semi-hydrogenation. After removal of the catalyst by filtration, two distillations gave 9.2 g. (71% yield) of 3-isopropylamino-3-methyl-1-butene, b.p. 121–122°, n^{25}D 1.4172.

Semi-hydrogenation of 3-*t*-Butylamino-3-methyl-1-pentyne (Method F).—A solution of 15.3 g. (0.1 mole) of 3-*t*-butylamino-3-methyl-1-pentyne in 50 ml. of petroleum ether containing 0.075 g. of 5% palladium-on-barium carbonate was hydrogenated at room temperature under an initial pressure of 44 p.s.i.g. as described above. The theoretical amount of hydrogen was absorbed in less than 2 hours. Two distillations gave 10 g. (64% yield) of 3-*t*-butylamino-3-methyl-1-pentene, b.p. 66° at 25 mm., n^{25}D 1.4372.

Hydrogenation of 3-Ethylamino-3-methyl-1-butyne (Method G).—A solution of 11.1 g. (0.1 mole) of 3-ethylamino-3-methyl-1-butyne in 50 ml. of 95% ethanol containing 2 g. (wet with alcohol) of Raney nickel[6] was hydrogenated at room temperature under an initial pressure of 40 p.s.i.g. The pressure dropped by 22.5 p.s.i.g. within 2 hours and 10 minutes. The catalyst was removed by filtration and the alcoholic solution was acidified (cold) by dropwise addition of concentrated hydrochloric acid. The alcohol was then distilled, the last portion *in vacuo*. The pasty residue was dissolved in 100 ml. of water and the aqueous solution was extracted with two 100-ml. portions of ether (discarded). The amine was then released from the aqueous solution by slow addition of cold 40% sodium hydroxide solution. The amine layer was removed and the aqueous solution was extracted twice with 75-ml. portions of ether. The amine and ether extracts were combined, dried and distilled. Two distillations gave 9.0 g. (78% yield) of 2-ethylamino-2-methylbutane, b.p. 112–115°, n^{25}D 1.4055–1.4051.

Amine hydrochlorides were precipitated in substantially quantitative yields by addition of dry ethereal hydrogen chloride to solutions of the amines in anhydrous ether and were purified by crystallization from a mixture of anhydrous ethanol and ethyl acetate. Melting points listed in Tables I, II, III and IV, were determined in sealed capillaries and are uncorrected.

Acknowledgments.—The authors express their sincere thanks to Dr. C. O. Herman, Air Reduction Chemical Co., New York, for generous samples of acetylenic alcohols. Special thanks are due W. L. Brown, G. M. Maciak, H. L. Hunter and R. M. Hughes of the Lilly Research Laboratories, Indianapolis, Ind., for a large number of analytical determinations; also Dr. Harold Boaz of the Lilly Laboratories for pK_a determinations and to Eli Lilly and Co. for the support of this work.

Notre Dame, Ind.

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[9] Caution must be exercised during the first distillation of product when this method is used. In several instances vigorous decomposition of still residue occurred while distillation was in progress. Redistillations were not troublesome.

[Contribution from the California Research Corp., Richmond, Calif.]

The Alkali Metal Catalyzed Alkylation of Toluene with Propylene

By R. M. Schramm and G. E. Langlois

Received February 17, 1960

The alkylation of toluene with propylene in the presence of lithium, sodium and potassium catalysts was studied over a range of temperatures from 100 to 300°. The principal product is isobutylbenzene, but abnormal addition to form *n*-butylbenzene is an important side reaction. At the higher temperatures hydrogen transfer reactions to form propane and "coke" are also important. Catalyst activity increases in the order lithium < sodium < potassium. Product composition also varies with the alkali metal used. Reaction mechanisms consistent with the observed kinetics and product distribution are presented. With the active potassium catalyst at low temperatures the reaction is suitable for the preparation of butylbenzenes in high yield.

The alkylation of alkylaromatics with olefins employing an alkali metal catalyst has been previously reported.[1–8] Aromatic alkylation with acid-type catalysts results in alkylation of the benzene ring. The alkali metal catalyzed reaction usually results in alkylation of the side chain, although

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[1] Herman Pines, J. A. Vesely and V. N. Ipatieff, This Journal, **77**, 554 (1955).

[2] Herman Pines and Victor Mark, *ibid.*, **78**, 4316 (1956).

[3] Luke Schaap and Herman Pines, *ibid.*, **79**, 4967 (1957).

[4] Herman Pines and Luke Schaap, *ibid.*, **80**, 3076 (1958).

[5] Herman Pines and Dieter Wunderlich, *ibid.*, **80**, 6001 (1958).

[6] R. D. Closson, A. J. Kolka and W. B. Liggett, U. S. Patent 2,769,850 (1956).

[7] E. Field and M. Feller, U. S. Patent 2,780,660 (1957).

[8] C. E. Frank and J. S. Swinehart, U. S. Patent 2,761 886 (1954).

TABLE I

REACTION OF TOLUENE AND PROPYLENE WITH SODIUM CATALYST

Run number	1	2	3	4	5	6	7	8	9	10	11[a]	12
Temp., °C.	397							232				204
Time, hours	4							20				
Catalyst,	Sodium											
mole	0.1											
Activator,	Anthracene	Fluorene	Indene	Cyclopentadiene	α-Methylpyridine	None	None	Anthracene	Fluorene	None	None	Anthracene
mole	0.003	0.003	0.003	0.003	0.003	....	....	0.003	0.003	.....	.....	0.003
Feed, mole												
Toluene	0.50	0.50	0.50	0.50	0.50	0.50	1.00	1.00	1.00	1.00	1.00	1.00
Propene	0.485											
Propane	0.015											
Product, mole												
Methane	0.008	0.002	0.004	0.015	0.014	0.006	0.004	0.003	0.003	0.001	0.001	0.001
Propene	.072	.271	.287	.074	.110	.133	.086	.059	.051	.109	.129	.287
Propane	.150	.072	.077	.146	.133	.114	.107	.091	.069	.053	.071	.037
Hexenes	.031	.027	.023	.040	.032	.029	.033	.058	.038	.048	.047	.032
Toluene	.374	.413	.450	.361	.380	.397	.898	.782	.803	.807	.798	.910
Isobutylbenzene	.113	.057	.056	.122	.103	.096	.119	.215	.197	.185	.196	.092
n-Butylbenzene	.011	.004	.004	.010	.008	.010	.009	.013	.010	.010	.013	.004
Methylindane	.....	.....	.....	.....	.....	.002	....	.002	.....	.....	.....	......
Insolubles, g.	4.4	2.7	1.7	4.0	4.0	2.6	2.5	2.3	2.6	1.1	1.1	......
Yields, mole % propene reacting												
Propane	31	27	31	32	31	28	23	18	12	10	16	11
Hexenes	15	25	23	20	17	17	17	27	18	26	26	32
Alkylate	30	29	27	32	30	31	32	54	48	52	59	49
Isobutyl/*n*-butylbenzene	10.0	14.2	12.5	12.2	12.9	9.6	13.2	16.5	19.7	18.5	16.3	23.0
Half-time, min.	55	170	180	47	69	94	50	430	530	520	460	1200

[a] Specially purified toluene used.

Table II

Reaction of Toluene and Propylene with Potassium and Lithium Catalysts

Run number	$13^{a,b}$	14	15	16^{a}	$17^{a,c}$	18	19	20^{a}	21	22^{a}	23	24	25
Temp., °C.	204					149				107	232	273	307
Time, hours	2	3	1	2	2	12	12	6	9	29	20	18	20
Catalyst,	Potassium										Lithium		
mole	0.06								0.26	0.06	0.36	0.36	0.36
Activator,	Anthracene	Cyclopentadiene	None			Cyclopentadiene	None				Anthracene	None	None
mole	0.003	0.003	....	....	....	0.003	.....	....	.....	......	0.003		
Feed, mole													
Toluene	1.00								4.00	1.00	1.00	1.00	1.00
Propene	0.485	0.485	0.534	0.485					2.14	0.493	0.485	0.493	0.485
Propane	0.015	0.015	0.016	0.015					0.02	0.007	0.015	0.007	0.015
Product, mole													
Methane	0.001	0.003	0.000	0.001	0.002	0.001	0.003	0.000	.....	......	0.002	0.002	0.032
Propene	.093	.020	.057	.010	.020	.211	.194	.007	0.10	0.205	.429	.278	.107
Propane	.071	.059	.089	.047	.054	.030	.033	.023	.021	.024	.022	.045	.170
Hexenes	.021	.021	.031	.018	.017	.024	.027	.025	.17	.015	.012	.024	.018
Toluene	.743	.680	.656	.649	.653	.806	.806	.621	2.48	.885	.994	.900	.964
Isobutylbenzene	.230	.288	.290	.308	.292	.172	.176	.334	1.27	.101	.019	.062	.039
n-Butylbenzene	.021	.028	.035	.034	.032	.017	.022	.012	0.17	.011	.0007	.006	.906
Methylindane	....	....	.002	....	....	.....	....	....	.....	......	.002	.006	.008
Insolubles, g.	1.9	2.5	.5	1.4	2.6	0	0	0	0.3	0	0	1.0	1.1
Yields, mole % propene reacting													
Propane	13	9	15	7	8	5	6	2	4	5	12	18	41
Hexenes	10	9	13	8	7	18	19	10	18	10	42	22	10
Alkylate	61	68	69	72	70	69	68	79	75	39	39	34	14
Isobutyl/*n*-butylbenzene	11.0	10.3	8.3	9.1	9.1	10.0	8.0	7.9	7.5	9.2	27	10.3	6.6
Induction period, min.	....	....	....	....	....	330	480	0	210	0	......	....	.....
Half-time, min.	30	34	23	8	9	290	220	65	140	1500	3900	....	700

[a] Toluene and potassium heated together for one hour at 204° before adding propene. [b] Anthracene present during prereaction of toluene and potassium. [c] Specially dried and purified toluene used.

nuclear alkylation has also been reported.[2,9] Pines and his co-workers have studied a variety of aromatic hydrocarbons and olefins to determine the effects of molecular structure on rate of reaction and product distribution.[1-5] In this research a single reaction, the alkylation of toluene with propylene, was studied more extensively in order to evaluate the effects of some of the reaction variables, particularly temperature and type of alkali metal.

Experimental

All runs were made in a 250-ml. Magnedash autoclave. The catalyst and reactants were charged to the reactor and heated and stirred for the desired time. The reactor was then cooled to 40° and depressured. The gas removed was metered and analyzed by mass spectrometer. The reactor was then cooled to room temperature, opened, and the liquid and solid product removed and filtered under nitrogen. The liquid product was analyzed by gas chromatography. The solid residue was treated with methanol to dissolve any remaining metal and to decompose metal organic compounds. If any insoluble material remained after this treatment, it was weighed and reported in the tables as "insolubles."

The toluene and alkali metals used were J. T. Baker C.P. chemicals. The propylene was Phillips technical grade. The reactants were used without further purification except in two runs in which the toluene was purified by distillation. An 80% center cut was taken and dried over silica gel prior to use.

Pure compound standards were used to determine the retention times in the gas chromatograph under the conditions used for the analysis of the liquid product. The reaction products were then identified by their retention times. In order to be certain of the identification of the two major alkylation products—isobutylbenzene and *n*-butylbenzene—the product from run 21 was fractionated in a Podbielniak Hypercal column to separate the iso- and *n*-butylbenzene fractions. Physical properties measured were:

Benzene	B.p., °C.		$n^{20}D$		d., 60°F.	
	Lit. 10	Exptl.	Lit. 10	Exptl.	Lit. 10	Exptl.
Isobutyl-	174	175	1.4864	1.4863	0.8577	0.858
n-Butyl-	183	183	1.4898	1.4898	0.8646	0.863

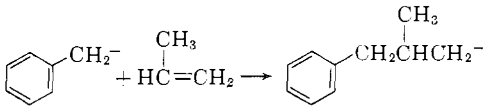
Infrared spectra of the two fractions confirmed their identification. All products reported, with the exception of *n*-butylbenzene, had been previously found by Pines and his co-workers.

A rough indication of the reaction rates in the runs is given in the tables as the half-time. To obtain this figure, it was assumed that the pressure drop in the run was proportional to the amount of reaction. Typically, the pressure drop was gradual at first, accelerated to an essentially constant rate for the major part of the reaction and then slowed down again near the end of the reaction. From the conversion and the total pressure drop a theoretical pressure drop for complete reaction was calculated. The half-time was defined as the time required at the maximum rate to give half this theoretical pressure drop.

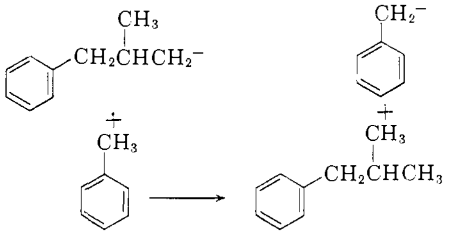
The experimental data are given in Tables I and II.

Discussion of Results

The principal product from the reaction of toluene with propylene in the presence of an alkali metal catalyst is isobutylbenzene, although significant quantities of other products including normal butylbenzene, hexene, propane, methane, and "coke" are formed. Pines and Mark[2] postulated that the formation of isobutylbenzene occurs by the addition of a benzyl anion to propylene. The addition normally occurs at the two position to form a new carbanion with the charge on a terminal carbon, which is the most stable configuration

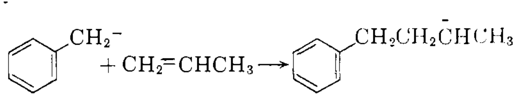


(1)

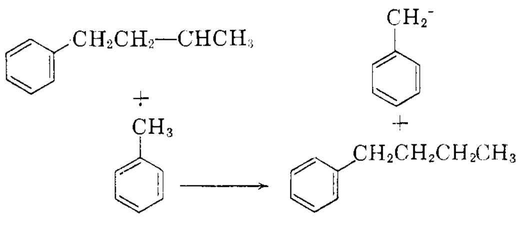


(2)

Normal butylbenzene would result from abnormal addition of the benzyl anion to the one position of the propylene resulting in the formation of a secondary carbanion intermediate



(3)



(4)

The occurrence of this abnormal addition was not noted by previous investigators, although in the alkylation of cumene with propylene some evidence for abnormal addition was given.[3]

Some polymerization of the propylene to hexenes also occurs. A mechanism for this reaction has been proposed by Pines and co-workers.[2,11]

A major side reaction, particularly at the higher temperatures, is a hydrogen transfer reaction to form propane and an uncharacterized hydrogen deficient carbonaceous solid. A possible mechanism for this reaction is

$$RCH_2\bar{C}HCH{=}CH_2 + CH_3CH{=}CH_2 \longrightarrow RCH{=}CHCH{=}CH_2 + CH_3CH_2CH_2^- \quad (5)$$

$$CH_3CH_2CH_2^- + RH \longrightarrow CH_3CH_2CH_3 + R^- \quad (6)$$

Polyolefins formed in this way presumably condense and transfer more hydrogen to form the solid carbonaceous residue. Although the data are not conclusive, the material balances suggest that most of the solid was formed from the propylene rather than from the toluene.

The mechanism of initiation of the reaction chain is still obscure. Pines and his co-workers[1,2] reported that an activator is necessary in order to obtain a significant rate of reaction. A number of compounds including anthracene, fluorene and *o*-chlorotoluene were said to be effective as activators. Our data indicate that the reaction will proceed readily in the absence of activators. The addition of such substances as anthracene, fluorene, indene, cyclopentadiene and α-methylpyridine to serve as

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(9) D. L. Esmay, P. Fotis, Jr., and C. E. Johnson, U. S. Patent 2,836,633 (1958).

(10) Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, October 31, 1957.

(11) Victor Mark and Herman Pines, THIS JOURNAL, **78**, 5946 (1956).

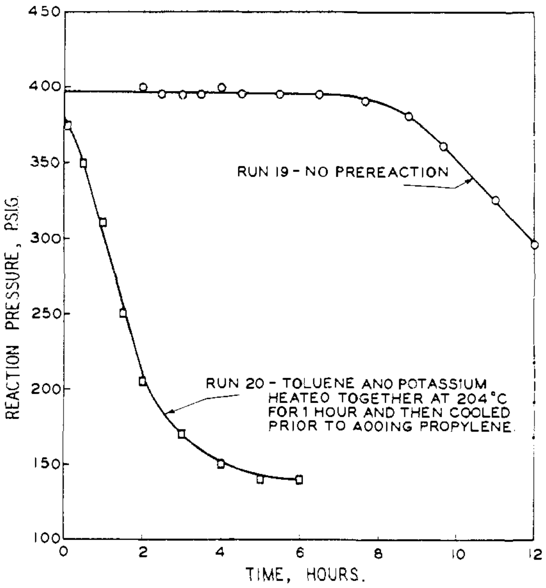


Fig. 1.—Effect of prereaction of toluene and potassium on induction period.

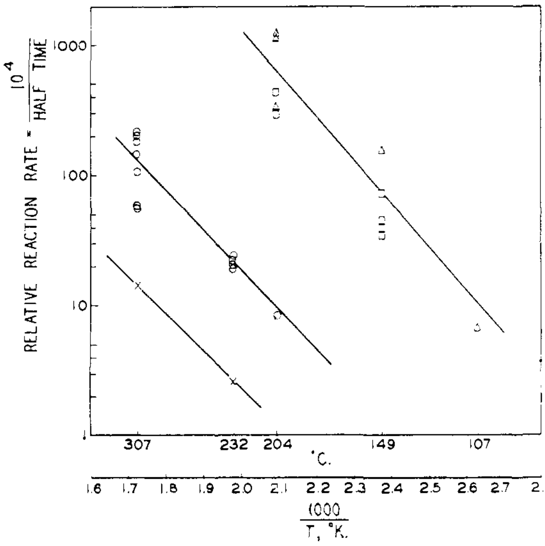


Fig. 2.—Alkylation of toluene with propylene; effect of temperature on reaction rate: ×, lithium catalyst; O, sodium catalyst; □, potassium catalyst, no prereaction; Δ, potassium catalyst, toluene and potassium heated for 1 hour at 204°F. prior to adding propylene.

activators had no large effect on the rate of reaction. With a potassium catalyst the activators appeared to slow the reaction slightly. With a sodium catalyst, experiments with activators had both higher and lower rates of reaction than those without activators. It may be that some impurity in the reactants used was serving as an activator. However, specially purified toluene was used in two of the experiments without a significant change in the rate of reaction.

Plots of reaction pressure *versus* time show that the rate of pressure drop is initially slow, increases to an essentially constant rate for the major part of the reaction, and then slows down again near the end of the reaction. At temperatures below 200°, a well-defined induction period is observed. This is shown in Fig. 1 which gives the pressure–time curve for a reaction catalyzed by potassium at 149°. A prereaction between the toluene and potassium for one hour at 204° prior to addition of the propylene eliminates the induction period, as shown in Fig. 1.

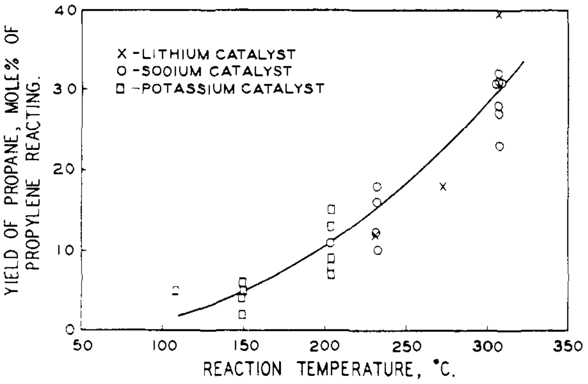


Fig. 3.—Effect of temperature on yield of propane.

Presumably, reaction of the toluene and potassium to form benzylpotassium is necessary before the alkylation reaction can proceed. At temperatures below about 200°, the rate of formation of the benzyl salt is quite slow. At temperatures of 200° and above, the formation of the benzyl salt occurs sufficiently rapidly with all three of the alkali metals so that no well-defined induction period is observed although, as stated above, the initial rate of pressure drop is slow.

Figure 1 shows that after the initial phase, the rate of pressure drop is constant for most of the reaction. This means that over a considerable range of propylene concentrations, the reaction rate remains constant; and, hence, that the rate is independent of propylene concentration. The data also suggest that the rate is independent of the toluene concentration. This conclusion is not firm, however, because changes in toluene concentration in the course of a reaction were relatively small.

Effect of Type of Metal and Temperature on Rate of Reaction.—There are large differences in the catalytic activity of the three alkali metals tested. The activity increased in the order: lithium < sodium < potassium. As shown in Fig. 2, the over-all rate of reaction with a sodium catalyst is about 10 times as rapid as that with the lithium catalyst. The potassium gives a rate of about 50 times greater than that of the sodium catalyst. The effect of temperature on the over-all rate of reaction was about the same with all three metals, corresponding to an energy of activation of 13 to 15 kcal./mole.

Effect of Type of Metal and Temperature on Product Distribution.—The yield of propane appears to be independent of the metal employed and dependent only on the reaction temperature as shown in Fig. 3. The hydrogen transfer reaction which leads to propane formation is a major reaction at 300° but decreases rapidly with temperature and is almost completely eliminated at 149°. The production of coke decreases similarly with temperature, and at 149° no measurable quantity of insoluble solid was produced.

Figure 4 shows the effect of temperature and type of metal on the ratio of isobutylbenzene to *n*-butylbenzene. In general, the amount of abnormal addition to form *n*-butylbenzene increases in the order of increasing catalyst activity from lithium to potassium. In the case of lithium and sodium the amount of abnormal addition also increases with increasing reaction temperature. With the potassium catalyst, however, the ratio of isobutyl to *n*-butylbenzene is independent of temperature over the range studied. Formation of *n*-butylbenzene cannot be attributed to isomerization of isobutylbenzene because no isomerization was observed when pure isobutylbenzene was contacted with potassium at 200° for several hours.

If it is assumed that the rate laws for the formation of *n*- and isobutylbenzene are the same, *i.e.*, that the molecules combining to form the transition state are the same, then the ratio of isobutyl- to *n*-butylbenzene in the product is equal to the ratio of the specific reaction rate constants for formation of the isobutyl and *n*-butyl species

$$\frac{I}{N} = \frac{k_I}{k_N} = \frac{(kT/h)e^{\Delta S_I^*/R}\, e^{-\Delta H_I^*/RT}}{(kT/h)e^{\Delta S_N^*/R} e^{-\Delta H_N^*/RT}} \qquad (7)$$

$$\log \frac{I}{N} = \frac{\Delta S_I^* - \Delta S_N^*}{2.3R} + \frac{\Delta H_N^* - \Delta H_I^*}{2.3RT} \qquad (8)$$

where

I = amt. of isobutylbenzene formed
N = amt. of *n*-butylbenzene formed
k_I, k_N = specific reacn. rate constants for formation of isobutyl- and *n*-butylbenzene, resp.
ΔH_I^*, ΔH_N^* = energies of activation for formation of isobutyl- and *n*-butylbenzene, resp.
ΔS_I^*, ΔS_N^* = entropies of activation for formation of isobutyl- and *n*-butylbenzene, resp.
T = absolute temperature
R = gas constant
k = Boltzmann's constant
h = Planck's constant

A plot of log I/N *vs.* $1/T$ should be a straight line with a slope of $\Delta H_N^* - \Delta H_I^*/2.3R$ and an intercept of $\Delta S_I^* - \Delta S_N^*/R$. Such a plot is shown in Fig. 4. The quantities $\Delta H_N^* - \Delta H_I^*$ and $\Delta S_I^* - S_N^*$ have been evaluated for each of the three metals as catalysts and are

Metal	($\Delta H_N^* - \Delta H_I^*$), cal.	($\Delta S_I^* - \Delta S_N^*$)
Lithium	8200	−10.4
Sodium	3150	− 0.5
Potassium	0	4.3

With the potassium catalyst, the activation energies for formation of the isobutyl- and *n*-butylbenzenes are the same. However, the entropies of activation favor the formation of isobutylbenzene. With the lithium catalyst, on the other hand, the activation energy is much lower for the formation of isobutylbenzene. The entropy, however, favors formation of *n*-butylbenzene.

Discussion of the Alkylation Mechanism.—The reaction mechanism formulated in eq. 1 and 3, *i.e.*, the addition of a completely ionized benzyl anion to propylene, cannot be strictly correct because the ratio of isobutyl to *n*-butylbenzene should then be independent of the type of metal used which is not consistent with the experimental data. A transition state including the alkali metal must be involved in the product-determining step. Furthermore, because the rate of reaction is independent of the propylene concentration, the rate-determining step cannot involve the propylene molecule. A possible reaction mechanism is

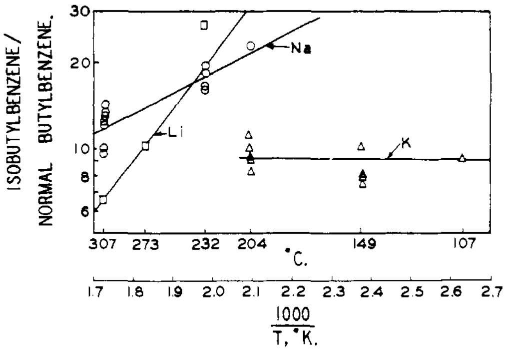
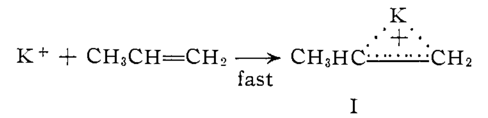
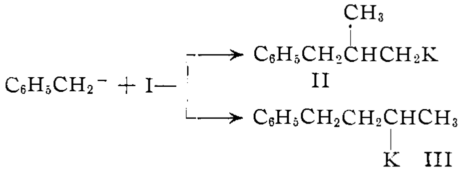


Fig. 4.—Effect of temperature and type of metal on the ratio of isobutyl benzene to *n*-butylbenzene in product: □, lithium catalyst; O, sodium catalyst; △, potassium catalyst.

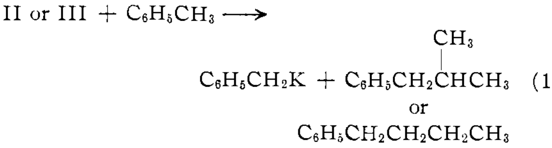
$$C_6H_5CH_2K \xrightarrow[\text{slow}]{} C_6H_5CH_2^- + K^+ \qquad (9)$$



$$K^+ + CH_3CH{=}CH_2 \xrightarrow[\text{fast}]{} \underset{\text{I}}{CH_3HC\overset{\overset{K}{+}}{\cdots\cdots}CH_2} \qquad (10)$$



$$C_6H_5CH_2^- + \text{I} \begin{cases} \longrightarrow \underset{\text{II}}{C_6H_5CH_2\overset{\overset{CH_3}{|}}{C}HCH_2K} & (11) \\ \longrightarrow C_6H_5CH_2CH_2\underset{\underset{K}{|}}{C}HCH_3 \quad \text{III} & (12) \end{cases}$$



$$\text{II or III} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2K + C_6H_5CH_2\overset{\overset{CH_3}{|}}{C}HCH_3 \text{ or } C_6H_5CH_2CH_2CH_2CH_3 \qquad (13)$$

The slow, rate-determining step is the ionization of benzylpotassium (reaction 9). The rate of this reaction would be independent of both the propylene and toluene concentrations. The highly acidic metal ion would react rapidly with the propylene to form a positively charged intermediate to which the negative benzyl anion would subsequently add.

In a complex formed by propylene and potassium ion the positive charge would probably be fairly uniformly distributed between the central and terminal carbon atoms of the propylene because the large size of the potassium ion would reduce the tendency to form a localized bond with a specific carbon atom. If so, the energy of activation would be about the same for addition of the benzyl ion to either the central or terminal position. This is consistent with experimental observation that the energies of activation for formation of isobutyl- and *n*-butylbenzene are the same for a potassium catalyst. The entropies of the two species would not be the same, however. The bulky potassium atom in the 2-position would interfere much more with the free rotation of the methyl group than would a benzyl group. Consequently, entropy considerations would favor addition of the benzyl group to the 2-position, and this is consistent with the experimental data.

With the lithium atom, on the other hand, its relatively small size would permit the formation of a more localized bond in the propylene–lithium ion complex. The positive charge should be concentrated on the secondary carbon atom of such a complex since secondary carbonium ions are much more stable than primary carbonium ions. The addition of a benzyl anion to the 2-position would consequently have a much lower activation energy than addition to the 1-position, again consistent with the experimental data. The entropy factors should be just opposite to those for a potassium atom and should favor addition of the benzyl group to the 1-position, as the data indicate. The sodium atom, which is intermediate in size, is also intermediate with respect to energy and entropy of activation.

An alternative explanation for the increase in *n*-butylbenzene formation at higher temperatures with the sodium and lithium catalysts could be the occurrence of some side chain alkylation through a free radical intermediate. The present data do not provide the basis for a definite choice between these two possibilities.

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Pyrolysis of β-Hydroxyolefins. III. A Novel Method for Extending Carbon Chains

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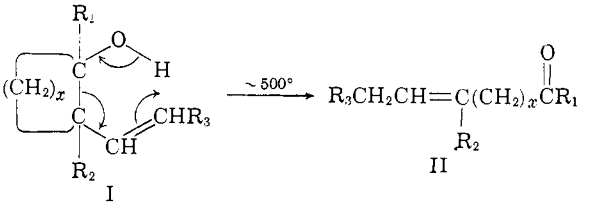
A new method is described for extending carbon chains. It is based upon the synthesis of 2-(1′-alkenyl)-cycloalkanols which, when pyrolyzed at temperatures near 500°, yield long open-chain, unsaturated, carbonyl compounds.

In two earlier publications[4,5] from this Laboratory, it has been demonstrated that the pyrolysis of β-hydroxyolefins to give olefinic substances and carbonyl compounds is a general reaction, and the evidence[5] strongly supports the view that this transformation proceeds *via* a cyclic transition state.

As previously employed, the thermal decomposition of β-hydroxyolefins is a degradation reaction leading to the formation of two distinct molecular species. It occurred to us, however, that if the carbon–carbon bond undergoing fission were made an appropriate element of a cyclic structure, the reaction could be employed as a new and general method for extending carbon chains as indicated.

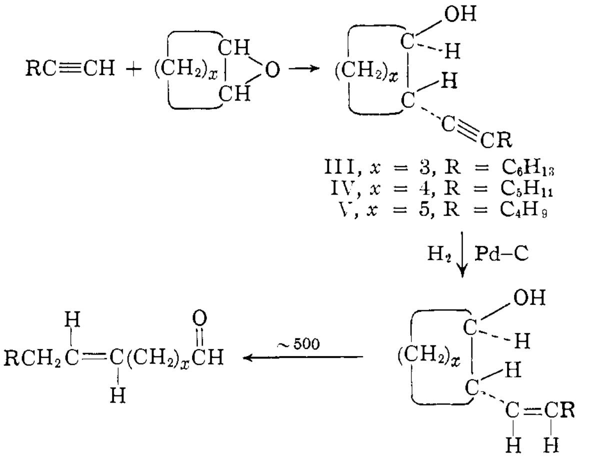


I

II

If the proposed mechanism[5] is valid, one should be able to predetermine the exact location of the carbon–carbon double bond with respect to the carbonyl group by merely selecting a proper value for "*x*" in I, since it has been established that[4] the newly formed olefinic bond is not prone to rearrange under the experimental conditions employed.

The above expectations have now been fully realized. In this preliminary paper, we wish to report on three specific examples in which carbon chains have been extended by five, six and seven carbon atoms to yield isomeric unsaturated aldehydes containing thirteen carbon atoms. The major reaction sequence is outlined.



III, $x = 3$, $R = C_6H_{13}$
IV, $x = 4$, $R = C_5H_{11}$
V, $x = 5$, $R = C_4H_9$

VI, $x = 3$, $R = C_6H_{13}$
VII, $x = 4$, $R = C_5H_{11}$
VIII, $x = 5$, $R = C_4H_9$

IX, $x = 3$, $R = C_6H_{13}$
X, $x = 4$, $R = C_5H_{11}$
XI, $x = 5$, $R = C_4H_9$

Although monosubstituted or asymmetrically disubstituted ethylene oxides react readily with lithium acetylides to form open-chain acetylenic alcohols,[4,6] we have found the oxides of cyclic olefins to be relatively inert toward these reagents. In fact, when ether was used as solvent, no appreciable amount of product was formed. Even when boiling dioxane was employed as a solvent, we were able to

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[4] R. T. Anrold and G. Smolinsky, THIS JOURNAL, **81**, 6443 (1959).

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[6] W. J. Gensler and C. B. Abrahams, THIS JOURNAL, **80**, 4593 (1958).