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High Pressure Thermal Alkylation of Monoalkylbenzenes by Butenes[1]

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The thermal reactions of toluene, ethylbenzene and cumene with 1-butene were studied in a flow-type system at 410 atm. pressure and at a temperature of 450°. Selectivity in the addition of aralkyl radicals to 1-butene was found to parallel the order of greater stability of secondary over the primary free radical. The selectivity of the addition of the arenes to 1-butene was compared with that of addition to propylene. In the case of ethylbenzene and cumene the selectivity in the addition to 1-butene is much greater than that to propylene. The thermal alkylation reactions were accompanied by 1,2-phenyl migration. The thermal reaction of toluene with 2-butene was much slower than that with 1-butene. Part of the 2-butene isomerized to 1-butene which reacted with toluene to form *n*-pentylbenzene. Under the conditions of thermal alkylation 1-butene isomerizes to 2-butene and undergoes polymerization to form alkenes and alkylcyclopentanes.

The thermal alkylation of monoalkylbenzenes by simple olefins at elevated temperatures and pressures has been reported.[1,4] It was found that the selectivity of addition of aralkyl radicals to unsymmetrical olefins paralleled the stability of the intermediate free radical formed, *viz.*, III, II, I in decreasing order of stability. It also was found that arene reactivity decreased in the order toluene, ethylbenzene, cumene, indicating the importance of steric factors in these reactions. Evidences for cyclization or 1,2-phenyl migration also were observed in certain cases. These studies were continued with a view to (1) compare the side chain alkylation by 1-butene with that by propene and (2) to compare the reactivities of aralkyl radicals toward 1- and 2-butenes. For the latter purpose the reaction of toluene toward 1-butene was compared with that toward 2-butene. Reactions of 1-butene with toluene, ethylbenzene and cumene were studied. To understand the primary processes involved the thermal reactions of toluene, ethylbenzene, cumene and isobutylbenzene at the temperature and pressure of the alkylations also were studied.

The reactions were carried out in a stainless steel reactor with or without copper linings. The contact medium for the reaction mixture was a zone of copper punchings in the copper-lined reactor while a zone of stainless steel shot was used in the unlined reactor. The experiments were carried out at 410 atmospheres and an hourly liquid space velocity (H.L.S.V.) of 2, unless otherwise stated, and at a temperature of 454°. In the case of toluene the effect of temperature, namely, 433 and 494°, upon the reaction was investigated.

TABLE I

TOLUENE-BUTENE EXPERIMENTS AT 410 ATM.

Experiment	1	2	3[b]	4	5
Temperature, °C.	433	454	454	454	492
Reactants, moles					
Toluene	4.54	1.82	2.86	3.28	3.67
Butene[a]	1.16	0.45	0.67	0.91	0.94
Butene reacted, mole%	78.4	96.0	89.1	68.0	99.0
Yields based on butene reacted					
Saturation	5.5	2.8	4.5	2.5	7.2
Isomerization[c]	9.0	5.4	11.7	5.6	1.6
Polymerization	52.7	41.8	51.2	23.5	60.0
Monoadducts	20.0	23.2	24.6	7.3	16.3
Toluene reacted, mole %	5.96	7.1	6.1	2.2	5.07
Yields based on toluene reacted, mole %					
Benzene	17	14	10.9	50	7.5
Ethylbenzene	0.3	6.2	14.9	10.5	43.0
Isopropylbenzene	0.1	0.3	0.6	....	6.5
n-Propylbenzene	1.3	6.3	5.1	2.2	16.1
Isobutylbenzene	0.5	0.4	0.6	0.4	2.8
n-Butylbenzene	2.4	4.8	4.02	2.6	5.1
2-Methyl-1-phenylbutane	10.3	14.0	13.2	18.0	3.9
n-Pentylbenzene	50.6	45.7	46.0	6.6	5.8

[a] 2-Butene for run 4, and 1-butene for all the other runs. [b] Stainless steel reactor; all other runs in copper reactor. [c] To *cis*- and *trans*-2-butenes in the 1-butene runs and to 1-butene in the 2-butene runs.

Discussion

Tables I–III give the reaction conditions and products of the alkylation reactions. A comparison of runs 2 and 3 indicates that stainless steel has no appreciable catalytic effect under the conditions used.

Reactivity of Arenes.—Table IV gives the percentage conversion of alkylbenzenes to monoadducts. The order of decreasing reactivity, toluene, ethylbenzene, cumene, is in agreement with previous findings on the reaction of these arenes with propylene and isobutylene.[1] The present work is also in agreement with reported data in that the decrease in going from toluene to ethylbenzene is slight whereas the reactivity of cumene is markedly less than that of ethylbenzene.[1] This fact indicates that the effect is probably predominantly steric in nature. The stability of the primary benzylic free radical formed is also in line with the observed reactivity of the arenes. The effect of temperature on the toluene–1-butene experiments is also in agreement with that on the toluene–propylene experiments previously reported.[1] The percentage of arene reacted drops off at the higher temperature indicating the increased importance of side reactions.

Rearrangements.—Several instances of molecular rearrangements involving the migration of a phenyl

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[1] Paper II of the series Thermal Alkylation Reactions. For paper I see H. Pines and J. T. Arrigo, THIS JOURNAL, **79**, 4958 (1957).

[2] Universal Oil Products Co., Predoctoral Fellow, 1957–1958.

[3] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[4] V. N. Ipatieff, H. Pines and B. Kvetinskas, U. S. Patent 2,758,140 (1956).

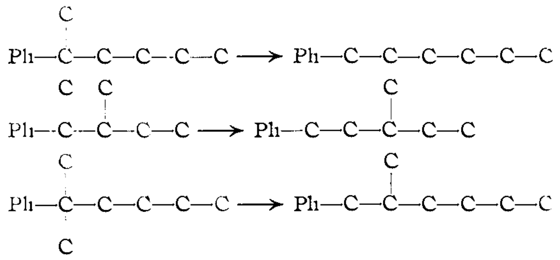
TABLE II

ETHYLBENZENE–1-BUTENE EXPERIMENTS AT 410 ATM.

Experiment	7	8[a]
Temperature, °C.	454	454
Reactants, moles		
Ethylbenzene	2.23	3.58
1-Butene	0.57	1.26
1-Butene reacted, mole %	87.2	88.3
Yields based on 1-butene reacted, mole %		
Saturation	7.0	7.1
Isomerization	15.8	15.3
Polymerization	26.0(?)	52.3
Monoadduct	20.0	20.5
Ethylbenzene reacted, %	7.8	7.6
Yields based on ethylbenzene reacted, mole %		
Benzene	10.9	2.4
Toluene	20.7	12.7
Isopropylbenzene	10.9	9.2
n-Propylbenzene	7.5	6.5
sec-Butylbenzene	2.3	5.1
n-Butylbenzene	1.7	1.7
2-Phenylpentane	4.6	4.4
1-Phenyl-3-methylbutane	1.1	1.0
n-Pentylbenzene	2.9	4.8
2-Phenylhexane	27.0	32.5
1-Phenyl-3-methylpentane[b]	1.7	2.4
n-Hexylbenzene	5.7	9.9

[a] Run 8 in stainless steel reactor; run 7 in copper reactor. [b] The expected alternate monoadduct, 2-phenyl-3-methylpentane, could not be detected.

radical have been observed.[5] In the present study three instances of rearrangement have been observed



Thermal isomerization of cumene, *p*-cymene and *sec*-butylbenzene at 480–530° and 12,000 p.s.i. pressure have been reported previously.[6]

Table V shows the behavior of cumene under the conditions of temperature and pressure employed in the alkylation studies. At 450° conversion of cumene to the lower alkylbenzenes is not appreciable. Isomerization to *n*-propylbenzene takes place to the extent of 0.7%. However the addition of a small amount of bibenzyl, which acts as a free radical chain initiator, increases the extent of isomerization to 1.4%, even though this reaction was carried out at an HLSV of 3.6 as compared to 2 for the non-initiated reaction. This confirms the assumption that the isomerization is radical in nature. Among the examples observed during the course of the present study the rearrangement always seems to involve the shifting of a phenyl radical to an adjacent primary carbon atom. No instance of a phenyl migration to a non-terminal carbon atom has been observed. The question of rearrangements is being pursued further.

TABLE III

CUMENE–1-BUTENE EXPERIMENT AT 410 ATM.

Experiment	10[a]
Temperature, °C.	454
Reactants, moles	
Cumene	3.13
1-Butene	0.73
1-Butene reacted, mole %	82.2
Yields based on butene reacted, mole %	
Saturation	6.7
Isomerization	20.0
Polymerization	50.3
Monoadduct	11.7
Cumene reacted, mole %	5.0
Yields based on cumene reacted, mole %[b]	
Benzene	2.6
Toluene	9.0
n-Propylbenzene	5.8
Isobutylbenzene	7.1
n-Butylbenzene	3.2
t-Amylbenzene + 2-methyl-1-phenylbutane	5.8
n-Pentylbenzene	4.5
2-Methyl-2-phenylpentane + 2-methyl-1-phenylpentane	3.9
2-Methyl-2-phenylhexane	10.4
2-Methyl-1-phenylhexane	9.0

[a] Stainless steel reactor. [b] No product corresponding to alternate addition could be detected in this experiment.

TABLE IV

MONOADDUCT YIELDS

	Based on arene charged[a]			Based on olefin charged[a]		
Temperature, °C.	430	450	490	430	450	490
Reactants						
Toluene–1-butene	4.8	5.5	4.4	15.7	22.1	15.8
		5.1			22.3	
Toluene–2-butene		0.7			5.0	
Toluene–propylene	3.7	5.2	0.9	17.3	23.8	1.6
Ethylbenzene–1-butene		5.1			17.4	
Ethylbenzene–propylene	3.2	2.9		15.8	14.8	
Cumene–1-butene		2.2			9.6	
Cumene–propylene	0.7	1.6		3.5	7.8	

[a] Data pertaining to propylene are taken from ref. 1 and included for comparison.

TABLE V

CUMENE AND CUMENE–DIBENZYL EXPERIMENTS AT 410 ATM.

Experiment	11	12
Temperature, °C.	454	454
HLSV	2.0	3.6
Initiator	None	Dibenzyl
Mole % of initiator	None	1.0
Cumene reacted, mole %	1.7	3.4
Isomerization to *n*-propylbenzene based on cumene charged, mole %	0.70	1.4
Yields based on cumene reacted, mole %		
Ethylbenzene	32	15
n-Propylbenzene	43	41
α-Methylstyrene	14	6

Reactivity of the Olefin.—Table IV summarizes the yields of monoadduct formed based on olefin

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(5) For a short review see ref. 1.

(6) V. N. Ipatieff, B. Kvetinskas, E. E. Meisinger and H. Pines, THIS JOURNAL, **75**, 3323 (1953).

TABLE VI

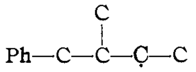
SELECTIVITY RATIOS

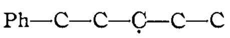
(Secondary *vs.* primary intermediate radical)

Temperature, °C.	430	450	490
Reactants			
Toluene–propylene[a]	5.1	4.1	2.3
Toluene–1-butene	4.9	3.3, 3.5	1.0
Ethylbenzene–propylene[a]	6.6	4.2	
Ethylbenzene–1-butene		19.1, 17.7	
Cumene–propylene[a]	7	9	
Cumene–1-butene		All secondary	

[a] From ref. 1.

charged. The results on propylene reported previously[1] are also included for comparison. There is no significant difference in the reactivity of 1-butene and propylene. However with 2-butene the conversion is considerably less. This is significant since the intermediate free radical formed in this case, I, should be comparable in stability to that formed from 1-butene, II.

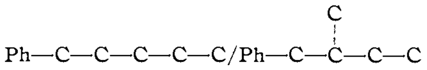

I


II

Addition of free radical to non-terminal double-bonds is usually more difficult than to a terminal double bond.[7–11] The low methyl affinity of the 2-butenes compared to ethylene or isobutylene may also be recalled.[12,13] The effect seems to be essentially steric in nature.

There is appreciable interconversion of 1- and 2-butene at the temperature of the reactions. In the 2-butene–toluene experiments, *n*-pentylbenzene is formed by the addition of the benzyl radical to the 1-butene formed as a result of the initial isomerization of the 2-butene. Knowing the selectivity ratio for 1-butene at 454° the monoadduct formation by 2-butene alone is calculated. This value is 4.5 mole % based on 2-butene charged as compared to the apparent conversion of 5.0 mole % shown in Table IV. It is seen that at 450° the reactivity of benzyl radical toward 2-butene is only about one-fifth that toward 1-butene.

Selectivity.—Selectivity is defined as the ratio of the extent of normal addition to that of alternate addition. In the toluene 1-butene experiments this is the ratio



$$\text{Ph—C—C—C—C—C/Ph—C—}\overset{\text{C}}{\overset{|}{\text{C}}}\text{—C—C}$$

Table VII represents the normal and alternate monoadducts which can be produced from the addition of the alkylbenzenes to butenes. Table VI gives the selectivity ratios for toluene, ethylbenzene and cumene toward the olefins propylene and 1-butene.

TABLE VII

MONOADDUCT PRODUCTS

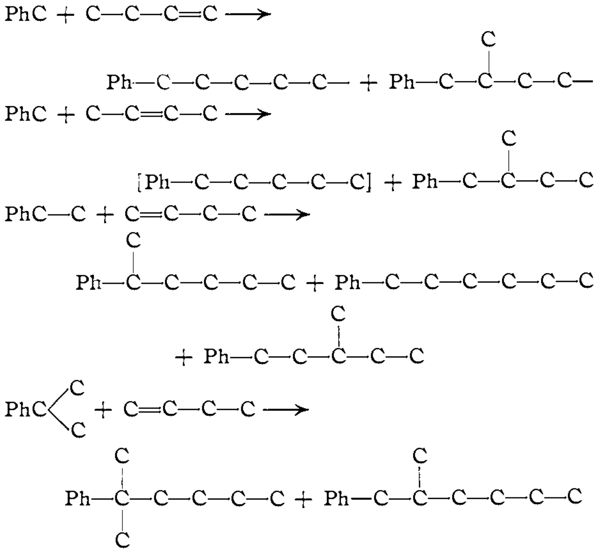


TABLE VIII

PERCENTAGE DISTRIBUTION OF *cis*- AND *trans*-2-BUTENE

Run	1	2	3	4	5	7	8	10
Temp., °C.	430	450	450	450	490	450	450	450
cis-2-Butene	39	43	40	45	43	41	47	44
trans-2-Butene	61	57	60	55	57	59	53	56

THERMODYNAMIC EQUILIBRIUM MIXTURE OF 2-BUTENES[18]

	450°	490°
cis-	43	45
trans-	57	55

Selectivity of the addition of benzyl radical is very nearly the same for the two olefins. The selectivity of methylbenzyl radical from ethylbenzene is greater than that of benzyl in both cases. Also the selectivity is appreciably larger with 1-butene than with propylene. The effect is even more pronounced with the dimethylbenzyl radical (from cumene). The increased selectivity with increase in substitution on the α-carbon atom of the arene may be due to the steric factor involved and also due to the lesser reactivity of the more substituted radical. In the series methyl, ethyl, isopropyl and *t*-butyl radicals each added methyl group contributes about 5 kcal. to the hyperconjugative stabilization energy of the radical.[14,15] The increase in selectivity seems to be much larger than that to be expected from the increase in stability of the aralkyl radical. The steric effect may be the major contributing factor.

There is greater selectivity in the reactions of ethylbenzene and cumene with 1-butene than with propylene. In the case of toluene the selectivity is about the same. The latter phenomenon is not clear since in a straight chain alkyl free radical the stability seems to be increased by increase in chain length. Indeed the primary C–H bond dissociation energy in the series ethane, propane and butane decreases in that order.[16]

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(7) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

(8) M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949).

(9) M. S. Kharasch, W. Nudenberg and E. Simon, *ibid.*, **18**, 328 (1953).

(10) M. S. Kharasch, O. Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947).

(11) J. I. G. Cadogan and D. H. Hey, *Quart. Revs.*, **8**, 3089 (1954).

(12) R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **78**, 5557 (1956).

(13) R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1956).

(14) J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **20**, 745 (1952).

(15) N. Miller and R. S. Mulliken, THIS JOURNAL, **80**, 3489 (1958).

(16) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1954.

The question of selectivity is somewhat complicated by the probable decomposition of monoadducts to lower alkylbenzenes and benzene itself. In all the experiments alkylbenzenes of lower molecular weight than the monoadduct were isolated. These might have been formed primarily by the decomposition of the monoadducts, and only to a small extent by the alkylation of the arene by the lower radicals (methyl, ethyl, *n*-propyl, isopropyl, etc.) formed by the pyrolysis of the butene. Toluene, ethylbenzene, cumene and isobutylbenzene when independently passed through the reactor at 450° and 410 atm. did not decompose appreciably to lower alkylbenzenes or to benzene.

Other Side Reactions.—No evidence of cyclization or nuclear alkylation could be detected in the present study. Cyclization to form indan derivatives has been observed in the case of cumene and propylene.[1] The reason for the apparent absence of cyclization in the cumene–1-butene experiment is not evident.

Isomerization of 1-Butene.—Table VIII gives the per cent. distribution of *cis*- and *trans*-2-butene in the recovered hydrocarbon gases. The ratios in all cases are close to the thermodynamic equilibrium ratios for the two isomers.[17,18]

That little or no isomerization of 1-butene to 2-butene occurs below 500° in the absence of catalysts[19] shows that the formation of the butenyl radical as a primary step does not take place below 500°. This is in support of the assumption made previously that the primary step in the thermal alkylation is the formation of a benzylic radical from the arene rather than the formation of an allylic radical from the olefin.[1]

Percentage isomerization of 1- to 2-butene increases as the arene reactant is varied from toluene to ethylbenzene to cumene. This may be expressed as

$$\mathrm{Ar\cdot + CH_2{=}CH{-}CH_2{-}CH_3 \longrightarrow Ar{-}CH_2{-}\underset{\cdot}{C}H{-}CH_2{-}CH_3} \quad (1)$$

$$\begin{aligned}\mathrm{Ar\cdot + CH_2{=}CH{-}CH_2CH_3} &\longrightarrow \mathrm{ArH + CH_2{=}CH{-}\dot{C}H{-}CH_3}\\ &\qquad\qquad\updownarrow\\ &\qquad\mathrm{\cdot CH_2{-}CH{=}CH{-}CH_3} \quad (2)\end{aligned}$$

$$\mathrm{ArH + \cdot CH_2{-}CH{=}CH{-}CH_3 \longrightarrow Ar\cdot + CH_3{-}CH{=}CH{-}CH_3} \quad (3)$$

With the increased substitution of the α-H of the benzyl radical, Ar, reaction 3 may become more favored than 1. This will result in an increase in isomerization.

Polymerization of 1-Butene.—In all the experiments where 1-butene was used about 50% of the reacted 1-butene was accounted for as polymers. A representative portion of the non-aromatic mixture obtained from experiments 1, 2 and 3 was hydrogenated and distilled on a Podbielniak Whirling Band column.[20] The data on the fractions collected are given in Table IX. Infrared spectrum of the dimer fraction indicated the presence of 3-methylheptane.[21] A band at 937 cm.$^{-1}$ indicated also the presence of 1-methyl-3-ethylcyclopentane. Vapor-phase chromatographic analysis using Podbielniak Chromacon series 9475 apparatus and a tricresyl phosphate column showed three closely placed peaks, of which 3-methylheptane constitutes about 30% of the total dimer. 3-Methylheptane and 1-methyl-3-ethylcyclopentane might have been formed by the dimerization of 1-butene according to the mechanism suggested previously.[22]

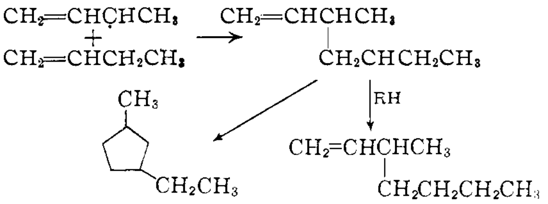
TABLE IX

POLYMERIZATION PRODUCTS OF 1-BUTENE (AFTER SELECTIVE HYDROGENATION)

B.p., °C.	Nature of polymer	Weight, %	$n^{20}D$	Analyses C, %	Analyses H, %
80–117	....	9	1.4000		
117–125	Dimer	35	1.4100[a]	84.93	14.78
125–187	....	5	1.4421[b]		
187–195	Trimer	18	1.4367[c]	85.86	14.54
Above 195 (Residue)	....	34			

[a] Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Calcd. for C_8H_{16}: C, 85.71; H, 14.29. [b] Contaminated by traces of aromatics. [c] Calcd. for $C_{12}H_{26}$: C, 84.71; H, 15.29. Calcd. for $C_{12}H_{24}$: C, 85.71; H, 14.29.

$$\mathrm{CH_2{=}CHCH_2CH_3 + R\cdot \longrightarrow CH_2{=}CH\underset{\cdot}{C}HCH_3}$$



Elementary analysis and refractive index of the trimer fraction indicate that it is composed mainly of cyclanes.

Experimental

Apparatus and Procedure.—The high pressure flow-type apparatus in which the experiments were carried out has been described previously.[1,23] Experiments 1, 2, 4, 5 and 6 were carried out in a copper lined reactor[1] with copper spacer and preheater and $^1/_8$ by $^1/_8''$ copper punchings as contact medium. The remaining experiments were carried out in a stainless steel reactor without the copper lining, using stainless steel spacer and preheater and $^1/_8''$ stainless steel balls as contact medium. The experimental procedure was similar to the one described previously.[1]

These gases were analyzed by vapor-phase chromatography[20] using a tricresyl phosphate-on-Celite column of 12-ft. length. The analyses were done at room temperature with helium as the carrier gas.

Four fractions were collected by distillation on the Vigreux column. The first fraction, boiling between room temperature and the boiling point of the arene charged, was composed mainly of olefins, non-aromatic cyclic products and aromatic hydrocarbons of lower boiling point than the arene. Percentage of unsaturation in this fraction was determined by amperometric titration using a microbromination apparatus.[24] This fraction was then selectively hydrogenated using copper–chromium oxide catalyst and the non-aromatic components were separated by displacement chromatography over silica gel using absolute alcohol as the displacing agent. The aromatic fraction was analyzed by vapor-phase chromatography using a 6-ft. tricresyl phosphate column at a suitable temperature.

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(17) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Stand.*, **36**, 554 (1946).

(18) H. H. Voge and N. C. May, THIS JOURNAL, **68**, 550 (1946).

(19) C. D. Hurd and A. R. Goldsby, *ibid.*, **56**, 1812 (1934).

(20) Podbielniak, Inc., Chicago, Ill.

(21) API Research Project, Catalogue of Selected Infrared Absorption Spectrograms, spectrum number 603.

(22) V. Mark and H. Pines, THIS JOURNAL, **78**, 5946 (1956).

(23) V. N. Ipatieff, G. S. Monroe and L. E. Fischer, *Ind. Eng. Chem.*, **40**, 2054 (1948).

(24) F. A. Leisey and J. F. Grutsch, *Anal. Chem.*, **28**, 1553 (1956)

The second fraction collected was the one in the boiling range of the starting arene. The percentage unsaturation in this fraction was determined. Non-aromatic components were separated over silica gel after selective hydrogenation.

The third and fourth fractions having components in the boiling range of the monoalkylated arenes also were treated in a similar manner, either combined or separately, depending on the complexity of the mixture. Final vapor-phase chromatographic analysis of the arene mixture in this case was done on a column made of silicone "550"[25] deposited on Celite. Residual materials having a boiling point higher than the highest possible monoadduct were not analyzed. In all the experiments the monoadduct fraction was further distilled over a spinning band column[20] and identifications were confirmed by comparison of the infrared spectra with those of authentic samples.

Method of Vapor-phase Analysis and Accuracy of Data.—Identifications of the components in the vapor-phase were done by comparison of retention times with known specimens. Quantitative analysis was done in all cases by assuming that the areas of the individual peaks are proportional to the weight percentage. This assumption was checked in a number of cases with mixtures of known composition and was found to be reasonably valid. In certain cases where separation was not very good, quantitative analysis was done by comparison of peak heights with those produced by mixtures of known composition. In the case of the lower alkylbenzenes which had to be separated and analyzed from a large bulk of unchanged starting material the error in analysis may be somewhat larger. In the cumene–1-butene experiment where the separation was not satisfactory the error may be somewhat larger than in the other runs.

Toluene–1-Butene (Expt. 1–5).—In these and the subsequent experiments where butenes were used, the gaseous hydrocarbons which were condensable in the Dry-Ice trap were found to consist of ethylene, propane, propene, *n*-butane, 1-butene and *cis*- and *trans*-2-butenes. These were identified by their retention times on tricresyl phosphate columns and estimated by peak area measurements. The alkylbenzenes of Table I were identified by comparison of retention times with authentic samples. *n*-Pentylbenzene, b.p. 205.0° at 746.0 mm., n^{20}D 1.4872, was further identified by its infrared spectrum.

Ethylbenzene–1-Butene (Expt. 7 and 8).—The fraction boiling at 25–85° was hydrogenated over palladium–charcoal catalyst and analyzed over tricresyl phosphate column at room temperature. Butane, isopentane, *n*-pentane, isohexane, 3-methylpentane, *n*-hexane and methylcyclopentane were identified in this fraction. Non-aromatics in the higher boiling fractions, n^{20}D 1.4400, were not analyzed. The alkylbenzenes were identified by vapor-phase chromatography. 1-Phenyl-3-methylpentane was further identified by its infrared spectrum in a cut, b.p. 75–76.3° (4.5 mm.), n^{20}D 1.4950. 2,3-Diphenylbutane was isolated from a cut, b.p. 95° (1.5 mm.) and was crystallized from pentane, m.p. 124.5–125° (lit.[26] m.p. 126–127°).

Cumene–1-Butene (Expt. 10).—Non-aromatic components which seemed to be of the same nature as in the previous runs were not analyzed. The alkylbenzenes were identified by vapor-phase chromatography of monoadduct distillation cuts. 2-Methyl-1-phenylpentane, 1,1-dimethyl-1-phenylpentane and 2-methyl-1-phenylhexane were synthesized for purposes of comparison of retention times and spectra. The infrared spectra of fractions boiling in the range 220–235° (760 mm.) did not show bands corresponding to 1,1-dimethyl-3-ethylindan, b.p. 227° (760 mm.).[27]

Toluene, Ethylbenzene and Isobutylbenzene (Expt. 6, 9 and 13).—These compounds were passed independently through the reactor at 410 atm. and 454° (the last mentioned one as a 10% solution in toluene). In all three cases the starting materials were recovered quantitatively unchanged.

Cumene and Cumene–Dibenzyl (Expt. 11 and 12).—Toluene, ethylbenzene, *n*-propylbenzene and α-methylstyrene were identified in the cumene–dibenzyl experiment and the last mentioned three in the cumene experiment. They were quantitatively estimated by comparison of the chromatograms with those produced by mixtures of known composition,

Synthesis of Hydrocarbons. 2-Methyl-1-phenylhexane.—(a) 2-Methyl-1-phenyl-2-hexanol was prepared from phenylacetone and *n*-butyl Grignard; yield 57%, b.p. 120° (8 mm.), n^{20}D 1.5058.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.18; H, 10.49. Found: C, 81.57; H, 9.95.

(b) 2-Methyl-1-phenylhexane was prepared from 2-methyl-1-phenyl-2-hexanol by dehydration with potassium hydrogen sulfate and then selective hydrogenation in the presence of palladium-charcoal catalyst; yield 56%, b.p. 98° (10 mm.), n^{20}D 1.4922.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 89.18; H, 11.39.

2-Methyl-1-phenylpentane.—2-Methyl-1-phenyl-2-pentanol, b.p. 113–114° at 9 mm., n^{20}D 1.5104, was prepared in 87% yield from methyl propyl ketone and benzyl Grignard. Without further purification this was dehydrated with potassium hydrogen sulfate and hydrogenated over 10% palladium-on-charcoal catalyst; yield based on the carbinol 72%, b.p. 83° (9 mm.), n^{20}D 1.4932 (lit.[28] b.p. 219°) (740 mm.).

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.69; H, 10.93.

2-Methyl-2-phenylhexene-5.—To a 2-methyl-2-phenylpropylmagnesium chloride prepared from 16.8 g. (0.1 mole) of 2-methyl-2-phenylpropyl chloride and 25 g. of magnesium, was added 7.6 g. of allyl chloride and the solution was refluxed for 4 hours. The mixture which was worked out as usual yielded 7.0 g. of 1-methyl-1-phenylhexene-5, b.p. 82° (7 mm.), n^{20}D 1.5102.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.81; H, 10.44.

t-Butylbenzene, 6.65 g. (50% yield), b.p. 55–57° (14 mm.), also was isolated.

2-Methyl-2-phenylhexane.—2-Methyl-2-phenylhexene-5, 2.3 g., was hydrogenated over 10% palladium–charcoal catalyst to yield 2.3 g. of 2-methyl-2-phenylhexane, n^{20}D 1.5010.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.72; H, 11.05.

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(25) Dow–Corning Corporation, Midland, Mich.

(26) E. Ellingboe and R. C. Fuson, THIS JOURNAL, **55**, 2960 (1933).

(27) L. Schaap, Ph.D. Dissertation, Northwestern University, 1957.

(28) H. Stenzl and F. Fichter, *Helv. Chim. Acta*, **20**, 846 (1937).