lized from benzene, it formed almost black needles with bluish lustre (m.p. 214°). The red benzene solution showed a green fluorescence.

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.20; H, 5.28; N, 15.33.

2. **Condensation with *p*-Diethylaminobenzaldehyde.**—The dinitrile (1.42 g., 0.01 mole) was heated with an excess of aldehyde and 15 drops of piperidine for 4 hr. at 155°. After preliminary purification with ethanol and one crystallization from benzene–ethanol, 1.11 g. (37%) of 4-(*p*-diethylaminostyryl)-isophthalonitrile was obtained. Further purification over alumina and recrystallization from benzene–ethanol brought it to the form of orange prisms melting at 190°.

Anal. Calcd. for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.80; H, 6.33; N, 14.12.

VI. **2,4-Bis-(benzenesulfonyl)-toluene. Condensation with *p*-Dimethylaminobenzaldehyde.**—The sulfone (3.7 g., 0.01 mole) was heated 4 hr. at 145° with 2 g. of aldehyde and 10 drops of piperidine. Even at this temperature a solid crystalline mass formed, which after a washing with ethanol and crystallization from dioxane formed a brick-red powder (2.4 g., 48%). Recrystallized twice from pyridine, it formed wine-red prisms of 2,4-bis-(benzenesulfonyl)-4′-dimethylaminostilbene (m.p. 265°).

Anal. Calcd. for $C_{28}H_{25}O_4NS_2$: C, 66.77; H, 5.00; S, 12.73. Found: C, 66.68; H, 5.30; S, 12.52.

Absorption spectra were determined on a Beckman model DU spectrophotometer with 10-mm. quartz cells. All solutions were made up of 1 mg. of solute in 100 ml. of methanol.

FRIBOURG, SWITZERLAND
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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

High Pressure Thermal Alkylation of Monoalkylbenzenes by Simple Olefins[1]

BY HERMAN PINES AND JOSEPH T. ARRIGO[2]

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The thermal reactions of monoalkylbenzenes with simple olefins were studied in a flow-type system at 420 atm. pressure and in the temperature range of 400–485°. With respect to the formation of 1:1 adducts with the arenes, it was observed that the olefin reactivity decreased in the order propylene > isobutylene > 2-methyl-2-butene. Arene reactivity decreased in the sequence toluene > ethylbenzene > cumene. Selectivity in the addition of aralkyl radicals to unsymmetrical olefins was found to parallel the order of stability of free radicals, III > II > I. Intermediate radicals were found to undergo cyclization or 1,2-phenyl migration in certain cases. Free radical mechanisms for the various reactions are discussed.

The side-chain alkylation of alkylbenzenes by simple olefins at elevated temperatures and pressures has been reported recently.[3] Results of the reaction of toluene with propylene indicated that there was about a sevenfold predominance of *n*- to isobutylbenzene formed. In view of these data, the purpose of the present work was to make a

TABLE I

TOLUENE–PROPYLENE EXPERIMENTS

Experiment	1	2	3	4	5
Temperature, °C.	409	430	456	475	485
Reactants, moles					
Toluene	4.31	4.31	4.14	4.11	2.46
Propylene	0.85	0.85	0.82	0.85	0.50
Results: Propylene reacted, mole %	34	51	54	42	35
Yields based on propylene reacted, mole %					
Propylene dimers	24	21	19	19	16
Propylene trimers	10	11	7.4	3.8	4.1
Monoadducts	28	34	44	37	13
Toluene reacted, mole %	3.4	6.4	10.4	10.4	13.7
Yields based on toluene reacted, mole %[a]					
Benzene	0.7	0.2	0.8	1.3	4
Ethylbenzene	5	3	8	13.2	22.5
Cumene	0.3	0.1	0.3	0.6	0.5
n-Propylbenzene	....	....	1.8	4.2	3
Cymenes(*o*-, *m*-, and *p*-)	....	....	....	1	0.8
Isobutylbenzene	11	9.4	9.8	9.3	2.0
n-Butylbenzene	47	47.6	40.3	24	4.6
Diadduct[b]	36	27.2	12	8	3.6
Diarylalkanes	....	12.5	27	38.4	59[c]
Unsatn. of monoadducts, mole %	2	5.3	4.6	6.8	14

[a] Arenes boiling above the reactant and through the monoadduct range were analyzed after selective hydrogenation (see Experimental). [b] 1:2 arene–olefin products. [c] There was also isolated 0.04 g. of anthracene from expt. 5.

TABLE II

TOLUENE–ISOBUTYLENE EXPERIMENTS

Experiment	6	7	8
Temperature, °C.	411	432	456
Reactants, moles			
Toluene	4.40	4.88	4.72
Isobutylene	0.92	1.03	1.00
Results			
Isobutylene reacted, mole %	28	41	54
Yields based on isobutylene reacted, mole %			
Isobutylene dimers	40	48	47
Isobutylene trimers	10	9.7	7.3
Monoadducts	31	31	24
Toluene reacted, mole %	2.5	4.6	7.5
Yields based on toluene reacted, mole %			
Benzene	1.8	0.4	1.1
Ethylbenzene	5	5	8.1
Unident. butylbenzene (?)	....	....	3.7
Neopentylbenzene	1.6	1.6	1.7
Isopentylbenzene	71.8	56.3	35.4
Diadduct	19.8	9.4	11
Diarylalkanes	....	27.3	39
Unsatn. of monoadducts, mole %	5.5	5.7	10

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(1) Taken in part from a dissertation submitted by J. T. Arrigo to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, October, 1956.

(2) Universal Oil Products Co. Predoctoral Fellow, 1953–1956.

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

TABLE III

TOLUENE–2-METHYL-2-BUTENE EXPERIMENTS

Experiment	9	10	11
Temperature, °C.	403	432	456
Reactants, moles			
Toluene	5.40	5.37	4.92
2-Methyl-2-butene	1.08	1.08	0.99
Results			
2-Methyl-2-butene reacted, mole %	4.1	12	24
Ratio of 2-methyl-2-butene/2-methyl-1-butene recovd.	4.3	2.3	2.0
3-Methyl-1-butene	....	[a]	[a]
Yields based on 2-methyl-2-butene reacted, mole %			
Methylbutene dimers	66	71	71
Monoadducts	18	20	21
Toluene reacted, mole %	0.25	0.67	1.94
Yields[b] based on toluene reacted, mole %			
Benzene	7	6	3
Unident. pentylbenzene (?)	13	13	7
2,3-Dimethyl-1-phenylbutane	36	38	25
3-Methyl-1-phenylpentane	25	34	28
Diadduct	19	9	6
Diarylalkanes	....	....	31
Unsatn. of monoadducts, mole %	38	37	34

[a] Only a negligible and small amount of 3-methyl-1-butene was detected in expts. 10 and 11, respectively. [b] The presence of 2,2-dimethyl-1-phenylbutane (VI) was excluded by comparison of its infrared spectrum with those of the hexylbenzene cuts from expts. 9–11.

TABLE IV

ETHYLBENZENE–PROPYLENE EXPERIMENTS

Experiment	12	13	14
Temperature, °C.	402	434	456
Reactants, moles			
Ethylbenzene	4.69	4.22	4.46
Propylene	0.93	0.85	0.89
Results			
Propylene reacted, mole %	23	35	41
Yields based on propylene reacted, mole %			
Propylene dimers	25	23	18
Propylene trimers	6.5	4.2	....
Monoadducts	34	45	36
Ethylbenzene reacted, mole %	2.8	5.5	8.1
Yields based on ethylbenzene reacted, mole %			
Benzene	1.3	1	1
Toluene	5.1	1	1
Cumene	14	6	12
n-Propylbenzene	0.3	1	5
Unident. butylbenzene (?)	....	....	2
2-Methyl-3-phenylbutane	7.6	8	7
2-Phenylpentane	49	51	29
Diadduct	21.3	15	13
2,3-Diphenylbutane[a]	1.4	2	1
Diarylalkanes	....	15	29
Unsatn. of monoadducts, mole %	21	13	13

[a] This represents only the material which crystallized out of the higher boiling cuts.

systematic study of the direction and extent of addition of representative monoalkylbenzenes to unsymmetrical olefins at various temperatures. Toluene, ethylbenzene and cumene were chosen to illustrate a phenyl-activated primary, secondary and tertiary radical, respectively. The competition between primary *vs.* secondary, primary *vs.* tertiary and secondary *vs.* tertiary intermediate monoadduct (1:1 arene–olefin adduct) radical formation was represented by propylene, isobutylene and 2-methyl-2-butene, respectively.

The reactions were carried out in a flow-type system having a copper-lined reaction tube with a zone of copper punchings as contacting medium for the arene–olefin mixtures. Extensive studies have shown that copper has no catalytic effect upon the thermal reactions of hydrocarbons (ref. 3 and unpublished results). The conditions and results are summarized in Tables I–VII and the skeletal structures of the monoadducts isolated (after selective hydrogenation) from experiments 1–19 are given in Table VIII.

TABLE V

ETHYLBENZENE–ISOBUTYLENE EXPERIMENT

Experiment	15
Temperature, °C.	455
Reactants, moles	
Ethylbenzene	4.53
Isobutylene	1.00
Results	
Isobutylene reacted, mole %	37
Yields based on isobutylene reacted, mole %	
Isobutylene dimers	54
Isobutylene trimers	6.8
Monoadducts	24
Ethylbenzene reacted, mole %	5.2
Yields[a] based on ethylbenzene reacted, mole %	
Benzene	1
Toluene	8
Cumene	9
n-Propylbenzene	3
Unident. pentylbenzene (?)	2
2-Methyl-4-phenylpentane	18
Isohexylbenzene	20
Diadduct	5
2,3-Diphenylbutane[b]	2
Diarylalkanes	32
Unsatn. of monoadducts, mole %	31

[a] 2,2-Dimethyl-3-phenylbutane, the expected "alternate" monoadduct, was not detected in the product cuts. The infrared spectrum of an authentic sample (b.p. 205°, $n^{20}\mathrm{D}$ 1.4954) had a characteristic band at 12.95 μ. The presence of this arene's possible rearrangement product, 3,3-dimethyl-1-phenylbutane (lit.[48] b.p. 211.6–212° at 750 mm., $n^{20}\mathrm{D}$ 1.4826) was not indicated by the properties of the monoadduct cuts from expt. 15. [b] This represents only the material which crystallized out of the higher boiling cuts.

The experiments were carried out at 420 ± 15 atm. and at an hourly liquid space velocity (H.L.S.V.) of 2.0 except in experiment 5 which was performed at H.L.S.V. 1.0. The amount of noncondensable (−78°) gases was negligible, in most cases being less than 0.5 liter.

TABLE VI

CUMENE-PROPYLENE EXPERIMENTS

Experiment	16	17	18
Temperature, °C.	404	433	454
Reactants, moles			
Cumene	4.17	4.02	4.31
Propylene	0.83	0.80	0.86
Results			
Propylene reacted, mole %	8.6	16	39
Yields based on propylene reacted, mole %			
Propylene dimers	37	50	42
Propylene trimers	37	16	20
Monoadducts	14	22	20
Cumene reacted, mole %	0.63	1.34	5.92
Yields[a] based on cumene reacted, mole %			
Benzene	1	1	1
Toluene	35	2	5
n-Propylbenzene[b]	0.02	0.21	2.8
Isobutylbenzene	....	2	3
Unident. pentylbenzene (?)	10	4	8
2-Methyl-2-phenylpentane	20	26	15
2-Methyl-1-phenylpentane[c]	4	9	15
1,1,3-Trimethylindan	14	19	14
1,1,2-Trimethylindan	3	8	5
Diadduct	13	14	17
Diarylalkanes	....	15	17
Unsatn. of monoadducts, mole %	29	41	37

[a] The expected "alternate" monoadduct, 2,3-dimethyl-2-phenylbutane, could not be detected in the product cuts by comparison of their infrared spectra with that of an authentic sample (b.p. 210°, $n^{20}D$ 1.4995). [b] Yields based on cumene charged. [c] This compound could not be isolated in a pure form; its infrared spectrum contained two bands not present in that of an authentic sample.

TABLE VII

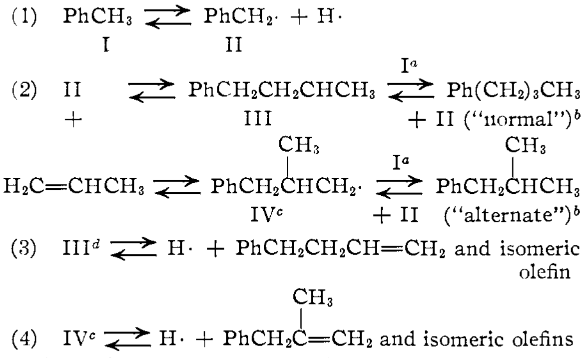
CUMENE-ISOBUTYLENE EXPERIMENT

Experiment	19
Temperature, °C.	454
Reactants, moles	
Cumene	4.31
Isobutylene	0.89
Results	
Isobutylene reacted, mole %	31
Yields based on isobutylene reacted, mole %	
Isobutylene dimers	65
Isobutylene trimers	9.7
Monoadducts	9.5
Cumene reacted, mole %	4.36
Yields[a] based on cumene reacted, mole %	
Benzene	2
Toluene	6
n-Propylbenzene[b]	2.8
Isobutylbenzene	11
Unident. heptylbenzene (?)	14
2,4-Dimethyl-1-phenylpentane	23
1,1,3,3-Tetramethylindan	3
Diadduct	28
Diarylalkanes	13
Unsatn. of monoadducts, mole %	43

[a] The expected monoadducts could not be detected in the product cuts of expt. 19. 2,3,3-Trimethyl-2-phenylbutane[53] (b.p. 219-233° cor. to 760 mm., $n^{20}D$ 1.5055) exhibited a sharp infrared band at 12.91 μ not present in the spectra of the product cuts. 2,4-Dimethyl-2-phenylpentane[53] (b.p. 215° cor. to 760 mm., $n^{20}D$ 1.4932) has a characteristic infrared band at 13.04 μ which was not detected in the spectra of the product cuts. [b] Yields based on cumene charged.

Discussion

The products of the thermal reactions are clearly the result of free radical processes. The following mechanism of monoadduct formation is suggested, similar to that proposed for the thermal alkylation of alkanes.[4]



$$(1)\quad \underset{\text{I}}{PhCH_3} \rightleftarrows \underset{\text{II}}{PhCH_2\cdot} + H\cdot$$

$$(2)\quad \text{II} + H_2C{=}CHCH_3 \rightleftarrows \underset{\text{III}}{PhCH_2CH_2CHCH_3} \overset{\text{I}^a}{\rightleftarrows} Ph(CH_2)_3CH_3 + \text{II}\ (\text{“normal”})^b$$

$$H_2C{=}CHCH_3 \rightleftarrows \underset{\text{IV}^c}{PhCH_2\overset{\overset{CH_3}{|}}{C}HCH_2\cdot} \overset{\text{I}^a}{\rightleftarrows} PhCH_2\overset{\overset{CH_3}{|}}{C}HCH_3 + \text{II}\ (\text{“alternate”})^b$$

$$(3)\quad \text{III}^d \rightleftarrows H\cdot + PhCH_2CH_2CH{=}CH_2 \text{ and isomeric olefin}$$

$$(4)\quad \text{IV}^c \rightleftarrows H\cdot + PhCH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2 \text{ and isomeric olefins}$$

[a] The olefin may also serve as hydrogen donor, yielding allyl radicals in this case. [b] For convenience, addition leading to the more stable intermediate radical is termed "normal" and to the least stable radical "alternate." [c] IV may also eliminate a methyl radical to yield allylbenzene. [d] Although the concentrations of radicals III and IV are probably low, the formation of alkenylbenzenes by the disproportionation of these radicals should not be excluded.

It is assumed that the main source of benzylic free radicals was the direct pyrolytic homolysis of benzylic C-H bonds. The relevant bond dissociation energies for toluene, ethylbenzene and cumene are 77.5, 74 and 71 kcal./mole, respectively.[5] In the latter two cases, although C-C cleavage of the side chain has a lower energy requirement, under the present conditions only negligible amounts of products which could have been formed by such cleavage were found. Benzylic radicals were probably formed in part by hydrogen abstraction from arenes by allylic radicals (generated by olefin pyrolysis), which have comparable stabilities.[5] Toluene is known to serve as an effective hydrogen-donating solvent to allyl radicals formed by the pyrolysis of allyl chloride.[6]

The formation of alkenylbenzenes by hydrogen atom elimination (equation 3 and 4) appears to be of only minor importance under the conditions used, judging from the monoadduct unsaturation data (Tables I-VII), which, although approximate, give an upper limit of alkenylbenzene concentration.

The effect of structure on reactivity is evident from the data in Table IX on the conversions of arenes to monoadducts (based on arenes charged).

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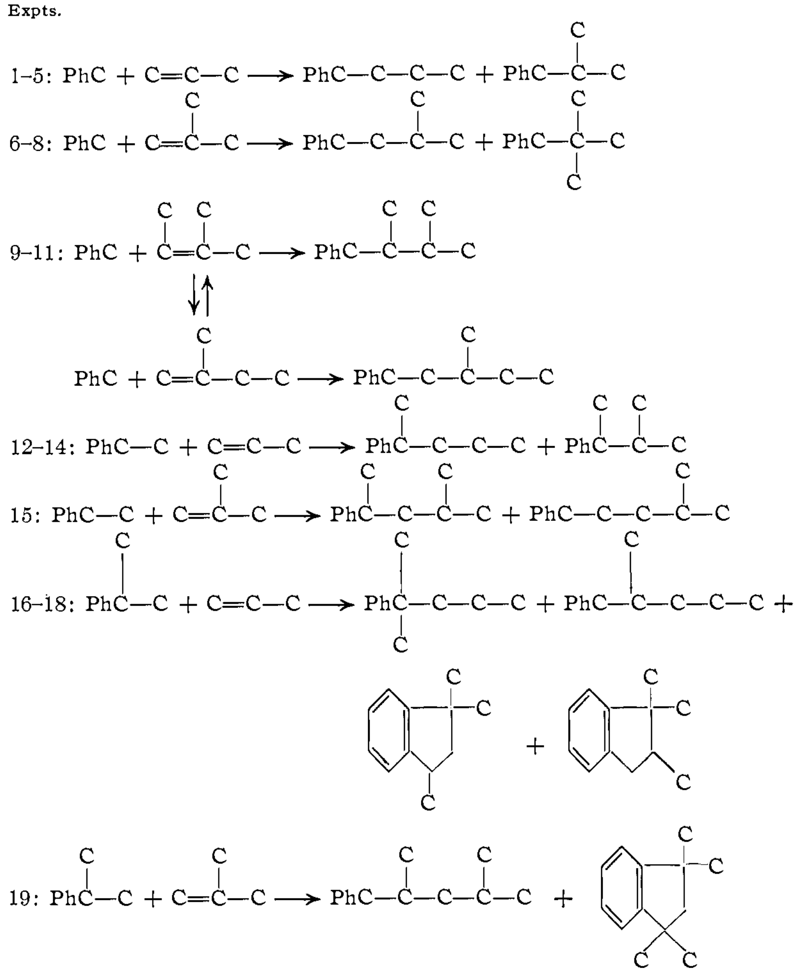
(4) F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, **28**, 1439 (1936).

(5) (a) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950); (b) for a recent tabulation of bond dissociation energy values, see E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1954.

(6) L. M. Porter and F. F. Rust, THIS JOURNAL, **78**, 5571 (1956).

TABLE VIII

MONOADDUCT PRODUCTS OF EXPERIMENTS 1–19[a]



[a] Ph = C_6H_5.

The observed olefin reactivity toward a given arene is seen to decrease in the order propylene > isobutylene > 2-methyl-2-butene. This sequence concurs with that reported in the thermal alkylation of paraffins with olefins.[7,8]

As with the olefin reactants, it was found that increasing substitution decreased the reactivity of the alkylbenzenes toward a given olefin in the sequence toluene > ethylbenzene > cumene. It is of interest to note that in both series there is a small decrease going to the second member but a sharper drop-off in reactivity with the most substituted compound. The latter decrease is less marked as the temperature increases, presumably due to increased activation of the reactant molecules. A similar effect of increasing substitution was encountered by Huisgen and co-workers[9] in the thermal additions of arenes to azodicarboxylic ester.

As the temperature increased, the conversions of arenes charged also rose, falling off, however, at 475 and 485° where secondary reactions became intensified. The yields of monoadducts based on arenes reacted (in parentheses in Table IX) decreased at the higher temperatures, further indicating the increased importance of side reactions.

Selectivity.—The selectivity of benzylic radical addition to unsymmetrical olefins may be expressed in terms of the selectivity ratio, defined as the ratio of "normal" to "alternate" addition, *e.g.*, *n*-/isobutylbenzene in the toluene–propylene reactions. The results are given in Table X.

The selectivity data support the following generalizations: 1. The order of relative ease of formation of the intermediate monoadduct radicals decreases in the series tertiary > secondary > primary. There is a tenfold increase in the selectivity of addition of toluene to isobutylene as compared to propylene at 405°, while only tertiary radical products were detected in the methylbutene reaction. Comparable selectivity has been reported in the additions of methyl radicals to propylene and isobutylene.[10] 2. The selectivity among the aralkyl radicals toward a given olefin de-

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[7] G. G. Oberfell and F. E. Frey, *Oil and Gas J.*, **38**, 70 (1939).

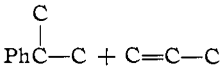
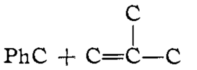
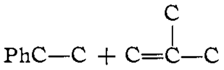
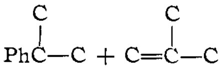
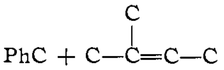
[8] A. A. O'Kelly and A. N. Sachanen, *Ind. Eng. Chem.*, **38**, 462 (1946).

[9] R. Huisgen, F. Jakob, W. Siegel and A. Cadus, *Ann.*, **590**, 1 (1954).

[10] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95 (1948).

TABLE IX

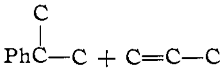
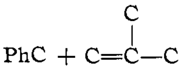
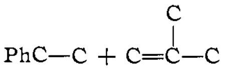
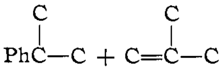
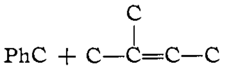
CONVERSIONS OF ALKYLBENZENES TO MONOADDUCTS[a]

Reactants	Approximate temperature 405°	430°	455°	475°	485°[b]
PhC + C=C—C	2.0 (58)	3.7 (57)	5.2 (50)	3.5 (33)	0.91 (6.6)
PhC—C + C=C—C	1.6 (57)	3.2 (59)	2.9 (36)		
 $\mathrm{Ph}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C + C{=}C{-}C}$	0.25 (41)	0.70 (62)	1.6 (49)		
 $\mathrm{PhC + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$	1.8 (73)	2.7 (58)	2.8 (37)		
 $\mathrm{PhC{-}C + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$			2.0 (38)		
 $\mathrm{Ph}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$			0.62 (40)		
 $\mathrm{PhC + C{-}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{=}C{-}C}$	0.15 (61)	0.48 (72)	1.0 (53)		

[a] Mole % yields based on arene charged; values in parentheses are yields based on arene reacted. [b] H.L.S.V. 1.0, all others H.L.S.V. 2.0.

TABLE X

SELECTIVITY RATIOS

Competing intermediate radical types	Reactants	Approximate temperature 405°	430°	455°	475°	485°[a]
Secondary *vs.* primary	PhC + C=C—C	4.4	5.1	4.1	2.6	2.3
	PhC—C + C=C—C	6.5	6.6	4.2		
	 $\mathrm{Ph}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C + C{=}C{-}C}$	13	7	9		
Tertiary *vs.* primary	 $\mathrm{PhC + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$	45	35	20		
	 $\mathrm{PhC{-}C + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$			All tertiary		
	 $\mathrm{Ph}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C + C{=}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{-}C}$			All tertiary		
Tertiary vs. secondary	 $\mathrm{PhC + C{-}}\overset{\mathrm{C}}{\overset{\vert}{\mathrm{C}}}\mathrm{{=}C{-}C}$		All tertiary			

[a] H.L.S.V. 1.0, all others H.L.S.V. 2.0. [b] Partial isomerization of the olefin to 2-methyl-1-butene occurred.

creases in the order α,α-dimethylbenzyl > α-phenylethyl > benzyl, as is evident from their additions to propylene at 405°. It is of interest to note that a selectivity of similar magnitude has been reported in the addition of *t*-butyl radicals to propylene.[8] The decrease in selectivity in the higher temperature reactions may be due to the enhanced activation of the reacting species; however, due to certain inherent complexities,[11] further data are necessary before any clear-cut relationship can be established.

Orientation in free radical additions to olefins has received much study in recent years. It is well established that moderate temperature peroxide- or light-induced additions are unidirectional, attack leading exclusively to the most stable intermediate radical.[12] In contrast, the higher temperature additions of alkyl radicals to olefins have been found to yield products of both modes of addition.[4,8,10] In the present study, the observed selectivity of benzylic radical addition was found to depend on the structure of the reactants and the reaction temperature. The order of increasing reactivity is in accord with bond dissociation energy data[5] and hydrogen abstraction results.[13,14] It has been reported that selectivity in hydrogen atom abstraction reactions paralleled the stability of the attacking species.[15] The selectivity–activity concept[16] used in correlating isomer distribution in electrophilic aromatic substitution has been applied recently in explaining the thermal polymerization of olefins.[17] In accordance with these views, the present results indicate that the most stable benzylic radicals are the most selective in the addition to unsymmetrical olefins.

Although the relative importance of polar *vs.* steric effects in determining the point of radical

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[11] Any preferential secondary reactions of either of the monoadduct radical species would affect the apparent selectivity to some extent, as would coupling of allylic and benzylic radicals which is known to proceed to a small extent in a similar reaction (ref. 6). Monoadduct unsaturation data indicate that the latter factor is only of minor importance.

[12] For a general review, see J. I. G. Cadogan and D. H. Hey, *Quart. Revs.*, **8**, 308 (1954).

[13] G. A. Russell, THIS JOURNAL, **78**, 1047 (1956).

[14] A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

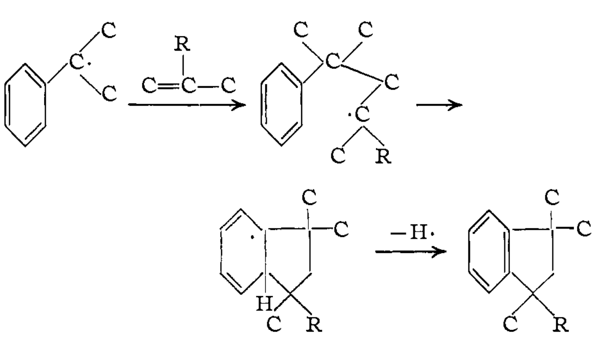
[15] G. A. Russell and H. C. Brown, *ibid.*, **77**, 4578 (1955).

[16] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

[17] V. Mark and H. Pines, *ibid.*, **78**, 5946 (1956).

attack on an unsymmetrical olefin is difficult to assess, the results of many studies appear to favor the predominance of the former.[12] The decreasing susceptibility of olefins to attack as methyl groups are substituted on the unsaturated carbons indicates that steric factors are quite important in the present study. Maximum hindrance was found in the 2-methyl-2-butene reactions. Isomerization of the olefin led to approximately an equilibrium mixture of methylbutenes.[18] If the relative ease of addition of benzyl radicals to 2-methyl-2-butene and 2-methyl-1-butene were comparable, it might be expected that roughly proportional amounts of 2,3-dimethyl-1-phenylbutane and 3-methyl-1-phenylpentane would have resulted[19] (Table VIII). By dividing the ratio of the two recovered olefins by that of the corresponding monoadducts, it was found that addition to the terminal double bond of 2-methyl-1-butene was favored by at least a factor of about 2:1 at the upper temperatures.

Nuclear Alkylation.—In the cumene–propylene and isobutylene reaction, alkylindans were identified and probably arose as

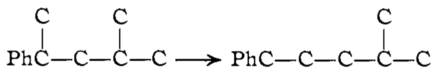


expts. 16–18 (R = H); expt. 19 (R = C)

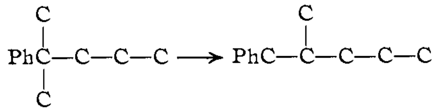
Recently, similar cyclizations of 4-phenyl-1-butyl free radicals to form tetralin have been reported.[20,21] It is possible that the presence in the intermediate radicals of *gem*-dimethyl groups, which are known to exert a marked enhancement on ring closure reactions,[22] favored cyclization in experiments 16–19.

The only other occurrence of nuclear alkylation in the present study, *viz.*, the formation of isomeric cymenes in minute amounts in experiments 4 and 5, is not explainable readily by known free radical mechanisms.

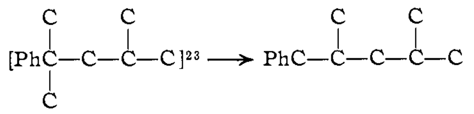
Monoadduct Rearrangement.—The following examples of 1,2-phenyl migrations were noted in the present work



$$\mathrm{Ph\overset{C}{\overset{|}{C}}{-}C{-}\overset{C}{\overset{|}{C}}{-}C \longrightarrow PhC{-}C{-}C{-}\overset{C}{\overset{|}{C}}{-}C} \quad \text{(a)}$$

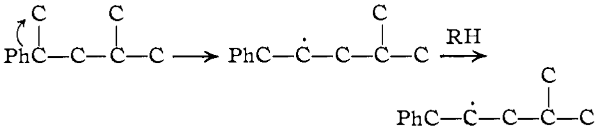


$$\mathrm{Ph\underset{C}{\underset{|}{\overset{C}{\overset{|}{C}}}}{-}C{-}C{-}C \longrightarrow PhC{-}\overset{C}{\overset{|}{C}}{-}C{-}C{-}C} \quad \text{(b)}$$



$$\mathrm{[Ph\underset{C}{\underset{|}{\overset{C}{\overset{|}{C}}}}{-}C{-}\overset{C}{\overset{|}{C}}{-}C]^{23} \longrightarrow PhC{-}\overset{C}{\overset{|}{C}}{-}C{-}\overset{C}{\overset{|}{C}}{-}C} \quad \text{(c)}$$

Cumene also was found to rearrange to *n*-propylbenzene as previously reported.[24] The mechanism may be formulated as



$$\mathrm{Ph\overset{\dot{C}}{\overset{|}{C}}{-}C{-}\overset{C}{\overset{|}{C}}{-}C \longrightarrow PhC{-}\dot{C}{-}C{-}\overset{C}{\overset{|}{C}}{-}C \xrightarrow{RH} PhC{-}\dot{C}{-}C{-}\overset{C}{\overset{|}{C}}{-}C}$$

The initial primary radicals could have been formed by direct hydrogen abstraction or hydrogen atom isomerization of related species. It is noteworthy that the rearranged products found all appeared to be due to phenyl migration to a terminal carbon.

The 1,2-phenyl migration in liquid phase free radical reactions has been investigated in detail in recent years.[25] Evidence has been reported which favors the discrete primary radical rather than a cyclic intermediate in the case of neophyl radicals.[26,27] More recently, the unique rearrangement of the 4-methyl-4-phenyl-1-pentyl radical to yield ultimately isohexylbenzene has been reported.[20] It was suggested that aryl participation led to a spiro free radical intermediate capable of forming the product. Although such a process cannot be excluded in (c), it fails to account for the products in (a) and (b).

Side-Reaction Products.—The hydrogenated propylene dimer cuts were found to contain *n*-hexane with the presence of methylcyclopentane also indicated, while isobutylene yielded mainly 1,1,3-trimethylcyclopentane. These findings concur with results observed in reactions at lower pressures.[17,28] Evidence also was found for the formation of polyalkylcyclopentanes as well as linear dimers from 2-methyl-2-butene.

Side-chain decomposition products of arene reactants and products were found in all reactions in small amounts increasing with the severity of conditions, in accordance with the report[24] that cumene and *s*-butylbenzene yielded all possible lower monoalkylbenzenes under similar conditions.

In most of the experiments, the arene reactants' next higher homolog was found, *e.g.*, toluene yielded ethylbenzene. Similar "methylation" by the combination of methyl and benzylic radicals has been shown to occur.[10,24] The detection of methane in all analyzed non-condensable gases suggests such a

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[18] R. H. Ewell and P. E. Hardy, Abstracts of the 102nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1941, p. 231.

[19] Only the two arenes formed from tertiary intermediate radicals were found; secondary radicals would have yielded 2,2-dimethyl-1-phenylbutane in each case.

[20] S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

[21] D. F. DeTar and C. Weis, THIS JOURNAL, **78**, 4296 (1956).

[22] For a discussion of the *gem*-dimethyl effect, see G. S. Hammond, "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 462–469.

[23] This expected monoadduct was not detected, only its rearrangement and cyclization products were.

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

[25] For literature references, see D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

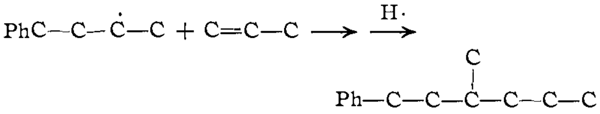
[26] W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

[27] F. H. Seubold, Jr., *ibid.*, **75**, 2532 (1953).

[28] J. B. McKinley, D. R. Stevens and W. E. Baldwin, *ibid.*, **67**, 1455 (1945).

reaction was occurring. The data also indicate that some decomposition of the normal adducts took place at higher temperatures, *e.g.*, the formation of ethylbenzene and ethylene by cleavage of *n*-butylbenzene. The complexity of secondary reactions makes any detailed conclusion beyond the scope of this work.

The diadduct products were only investigated in the simplest case, from toluene and propylene. It was reasoned *a priori* that the main component might be either *n*-heptylbenzene (from benzyl radical addition to 1-hexene, an expected olefin dimer) or 3-methyl-1-phenylhexane, formed as



$$\mathrm{PhC{-}C{-}\dot{C}{-}C + C{=}C{-}C \longrightarrow \xrightarrow{H\cdot} Ph{-}C{-}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}C{-}C}$$

The purified heptylbenzene did not correspond to either of the above compounds and was not further investigated. The infrared spectrum established that the arene had two benzylic hydrogens, thus excluding its formation by dialkylation of the methyl group of toluene.

Diarylalkane fractions probably consisted of two types of compounds: one being composed of two arene molecules, *e.g.*, anthracene from toluene and 2,3-diphenylbutane from ethylbenzene. It has been shown that the decomposition of benzoyl peroxide in ethylbenzene leads to 2,3-diphenylbutane as well as ethylbiphenyls.[29] The fact that toluene with propylene yielded three times the amount of diarylalkanes as it did with 2-methyl-2-butene at 456° suggests that such fractions arose in part by the combination of two arenes and one olefin molecule.

Experimental

Apparatus and Procedure.—The experiments were carried out in a previously described high-pressure flow-type apparatus,[24,30] using 45 ml. of $^1/_8 \times {}^1/_8''$ copper punchings as contacting agent. The vertical furnace was automatically controlled. The arene–olefin charge was accurately delivered by means of a Ruska proportioning pump[31] into the system which was initially pressurized to about 408 atm. with nitrogen. The liquid product was collected in a calibrated receiver and the effluent gases were passed through a Dry Ice–acetone-cooled trap, metered by a wet test meter and collected in a gas collecting bottle.

The liquid product was distilled initially through a Lecky-Ewell column[32] to remove the unreacted arene and lower boiling components; then the residue was distilled through a Vigreux column. The fractions boiling up to the lower diadduct range were combined, selectively hydrogenated and chromatographed to remove saturates. The aromatic portion was then carefully fractionated through a Podbielniak whirling band column[33] at atmospheric pressure and the composition of the individual cuts determined by infrared spectral analysis.[34]

Non-condensable gases were analyzed by means of a mass spectrograph.

Hydrogenation.—The selective hydrogenations were performed in a 114-ml. rotating autoclave at temperatures of 150–225° and initial hydrogen pressure of 100–130 atm., using 10 wt. % or the charge of copper chromite[35] catalyst and pentane solvent. The approximate mole % of unsaturation of the monoadduct products was calculated from the pressure drop, after correction was made for the hydrogen uptake of the catalyst[36] as determined in a blank run.

Chromatography.—The separation of arenes from saturates was done by displacement chromatography on silica gel[37,38] using absolute ethanol as the desorbing agent. Separations of arene mixtures[39] were similarly carried out using a *n*-pentane pre-pass.

Infrared Spectral Analysis.—The analyses were performed on a Baird double beam recording infrared spectrophotometer[40] by the base-line technique.[41] The wave lengths of the absorption bands used in the calculations are given in Table XI.[42]

TABLE XI

ANALYTICAL INFRARED ABSORPTION BANDS

Compound	Wave length,[a] μ
Benzene	14.86
Toluene	13.74
Ethylbenzene	13.39
Cumene	13.15
n-Propylbenzene	13.47
n-Butylbenzene	8.99
Isobutylbenzene	7.28, 8.53
p-Cymene[b]	12.28
m-Cymene[b]	12.78
o-Cymene[b]	13.21
Isopentylbenzene	9.33
Neopentylbenzene	13.87
2-Phenylpentane	7.63, 10.07
2-Methyl-3-phenylbutane	7.89, 8.53, 9.81, 10.28
2-Methyl-4-phenylpentane	13.07
Isohexylbenzene	13.35
3-Methyl-1-phenylpentane	9.65
2,3-Dimethyl-1-phenylbutane	7.28
2-Methyl-2-phenylpentane	7.28, 9.64
2-Methyl-1-phenylpentane	8.63, 9.64
1,1,3-Trimethylindan	7.58, 9.69
1,1,2-Trimethylindan	13.66
2,4-Dimethyl-1-phenylpentane	8.51
1,1,3,3-Tetramethylindan	7.60
2-Methyl-2-butene	8.98, 12.44
2-Methyl-1-butene	6.04, 11.24

[a] Wave lengths are uncorrected. [b] Approximate calculations were made based on the corrected absorptivities reported by R. B. Williams, S. H. Hastings and J. A. Anderson, Jr., *Anal. Chem.*, 24, 1911 (1952).

Mass Spectral Analyses.—Non-condensable gaseous products were formed to the extent of 0.5–2 liters in the experiments, somewhat larger volumes being produced only in the 475 and 485° reactions. Mass spectral data on a number of samples showed that the gases were composed mainly of nitrogen (from the initial pressurization) and

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(29) R. L. Dannley and B. Zaremsky, THIS JOURNAL, **77**, 1588 (1955).

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

(31) Ruska Instrument Corp., Houston, Texas.

(32) H. S. Lecky and R. H. Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

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

(34) In expts. 1-19, charged arenes were 93-98% accounted for, while the olefins were accounted for to the following extent (average): C_3H_6, 59%; C_4H_8, 72%; C_5H_{10}, 93%.

(35) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 142.

(36) H. Adkins, E. E. Burgoyne and H. J. Schneider, THIS JOURNAL, **72**, 2626 (1950).

(37) B. J. Mair and A. F. Forziatti, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

(38) B. J. Mair, *ibid.*, **34**, 435 (1945).

(39) B. J. Mair, J. W. Westhaver and F. D. Rossini, *Ind. Eng. Chem.*, **42**, 1279 (1950).

(40) Baird Associates, Inc., Cambridge, Mass.

(41) N. Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

(42) Additional details on the infrared identifications and analyses along with photographs of the spectrograms of the butylbenzenes and higher homologs used in this study are given in the Ph.D. thesis of J. T. Arrigo, Northwestern University Library.

TABLE XII

SYNTHESES OF INTERMEDIATE CARBINOLS

Reactants									Analyses, %	
Halide	Ketone	Carbinol[a]	Yield, %[b]	B.p. °C.	Mm.	n^{20}_D	d^{20}_4	MR_D Obsd.	Found C	H
(2-Bromoethyl)-benzene	2-Pentanone	3-Methyl-1-phenyl-3-hexanol[43] (Ia)	57	152–153	20	1.5080	0.9462	60.59[e]	81.58[e]	10.01[e]
Benzyl chloride	3-Methyl-2-butanone	2,3-Dimethyl-1-phenyl-2-butanol[43] (IIa)	69	124.6–126	15.5	1.5116	.9599	55.65[f]	80.89[f]	9.93[f]
(2-Bromoethyl)-benzene	2-Butanone	3-Methyl-1-phenyl-3-pentanol[c] (IIIa)	59	132–133	12	1.5114	.9552	55.93[f]	80.92[f]	10.20[f]
Isobutyl bromide	Acetophenone	4-Methyl-2-phenyl-2-pentanol[d] (IVa)	15	112–114	12	1.5062				
Benzyl chloride	4-Methyl-2-pentanone	2,4-Dimethyl-1-phenyl-2-pentanol[43] (Va)	64	120-121	10	1.5043	.9412	60.57[e]	81.27[e]	9.95[e]

[a] The Grignard reaction products were hydrolyzed with aqueous ammonium chloride and distilled from a small amount of potassium carbonate to minimize dehydration. [b] Based on ketone charged. [c] A. Klages, *Ber.*, **37**, 2301 (1904), reported b.p. 129–130° at 13 mm. [d] A. Klages, ref. *c*, reported b.p. 110–112° at 12 mm. [e] Calcd. for $C_{13}H_{20}O$: C, 81.19; H, 10.48; MR_D, 60.15. [f] Calcd. for $C_{12}H_{18}O$: C, 80.87; H, 10.16; MR_D, 55.54.

TABLE XIII

SYNTHESES OF INTERMEDIATE OLEFINS

		B.p.,				Analyses, %			
						Calcd.		Found	
Carbinol charged	Isomeric alkenylbenzenes	°C.	Mm.	n^{20}_D	Yield, %[a]	C	H	C	H
Ia	3-Methyl-1-phenyl-x-hexene (Ib)	121–124.5	20.5	1.5060–1.5075	69	89.59	10.41	89.24	10.16
IIa	2,3-Dimethyl-1-phenyl-x-butene[b] (IIb)	97–101	15	1.5120–1.5233	86	89.93	10.07	90.29	10.11
IIIa	3-Methyl-1-phenyl-x-pentene[c] (IIIb)	100–102	13.5	1.5092–1.5100	80	89.93	10.07	89.99	10.21
Va	2,4-Dimethyl-1-phenyl-x-pentene[d] (Vb)	95–101	10.5	1.5038–1.5101	80				

[a] Based on carbinol charged. [b] L. Claisen, F. Kremers, F. Roth and E. Tietze, *J. prakt. Chem.*, [2] **105**, 65 (1922), reported that 2,3-dimethyl-1-phenyl-2-butene has b.p. 220–221° at 750 mm. [c] A. Klages (Table XII, ref. *c*) reported b.p. 103–104° at 15 mm., n^{18}_D 1.5100. [d] J. M. Lamberti and P. H. Wise, THIS JOURNAL, **75**, 4787 (1953), reported the following products: 2,4-dimethyl-1-phenyl-2-pentene, b.p. 222.5–224.5°, n^{20}_D 1.4996–1.4998; 2,4-dimethyl-1-phenyl-1-pentene, b.p. 234–236.5°, 1.5192–1.5199.

TABLE XIV

SYNTHESIS OF ALKYLBENZENES

	B.p.,				MR_D		Analyses, %			
							Calcd.		Found	
Alkylbenzene[a]	°C.	Mm.	n^{20}_D	d^{20}_4	Calcd.	Obsd.	C	H	C	H
3-Methyl-1-phenylhexane[b,43] (I)	123.6–123.8	22	1.4868	0.8535	58.63	59.39	88.56	11.44	88.88	11.06
2,3-Dimethyl-1-phenylbutane[c,d] (II)	213.7–213.9	735	1.4901	0.8646	54.02	54.24	88.82	11.18	88.93	11.01
3-Methyl-1-phenylpentane[e] (III)	219.4	752	1.4872							
2-Methyl-4-phenylpentane[g] (IV)	203.0–204.8	756	1.4849							
2,4-Dimethyl-1-phenylpentane[h] (V)	223.2–223.6	747	1.4835							

[a] The products were isolated in good yield and were redistilled subsequent to use as infrared standards. [b] Acetylation (ref. 44) yielded a ketone forming a 2,4-dinitrophenylhydrazone melting at 121–122°. *Anal.* Calcd. for $C_{21}H_{26}N_4O_4$: N, 14.06. Found: N, 14.29. [c] Claisen, *et al.*, (Table XIII, ref. *b*) reported b.p. 216.5–217.5° at 755 mm. [d] The 2,4-dinitrophenylhydrazone of the acetylated arene had m.p. 153–154°. *Anal.* Calcd. for $C_{20}H_{24}N_4O_4$: N, 14.57. Found: N, 14.97. [e] A. Klages and R. Sautter, *Ber.*, **37**, 649 (1904), reported b.p. 220° at 757 mm., $n^{14.5}_D$ 1.4896. [f] Carbinol IVa was hydrogenolyzed directly (see isohexylbenzene synthesis). [g] Reported b.p. 197°, n^{15}_D 1.4876, A. Klages (Table XII, ref. *c*). [h] Lamberti and Wise (Table XIII, ref. *d*) reported b.p. 225.0°, n^{20}_D 1.4872.

minor amounts of propylene which passed through the Dry Ice trap in the propylene reactions. The remainder, 5–6% in most cases, consisted of hydrogen, methane, ethylene and ethane.

Synthesis of Infrared Reference Samples. 3-Methyl-1-phenylhexane, 2,3-dimethyl-1-phenylbutane, 3-methyl-1-phenylpentane, 2-methyl-4-phenylpentane and 2,4-dimethyl-1-phenylpentane were made from carbinols synthesized by the Grignard method. Details of the syntheses and physical properties of the alkylbenzenes and intermediate products are given in Tables XII, XIII and XIV. The Grignard reactions were performed on a 0.15–0.3-mole scale, the carbinols dehydrated with fused potassium bisulfate in refluxing toluene and the isomeric alkenylbenzenes selectively hydrogenated using copper chromite catalyst.

2,2-Dimethyl-1-phenylbutane[43] (VI) was synthesized by adding 0.50 mole of *t*-pentyl chloride to an ether solution of benzylmagnesium chloride (prepared from 0.50 mole each of magnesium and benzyl chloride) over a 2.7-hr. period at room temperature. The suspension was refluxed with stirring for an additional 3 hr. and worked up in the usual manner. The ether was removed and the residual liquid refluxed with 3 g. of sodium for 2 hr., after which it was cooled, decanted and distilled. The product cuts were combined and redistilled, yielding 36.2 g. (45%) of VI, the heart-cut of which had the following physical properties: b.p. 212.4–212.5° at 742 mm., n^{20}_D 1.4938, d^{20}_4 0.8708; MR_D calcd. 54.02, obsd. 54.19.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.89; H, 11.18.

The compound was acetylated according to the procedure of Pines and Shaw[44] and the 2,4-dinitrophenylhydrazone prepared, m.p. 181–182°.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: N, 14.57. Found: N, 14.96.

The arene has been reported[45]; however, subsequent reinvestigations,[46,47] have shown that the initially assigned structure of the $C_{12}H_{18}$ product which arose from a complex reaction was incorrect.

Isohexylbenzene (VII) was synthesized by the modified procedure of Berliner and Berliner.[48] Isocaproyl chloride was made in 81% yield from isocaproic acid and thionyl chloride; it boiled at 141.5–142°. Isocaprophenone was obtained in 71% yield by the Friedel–Crafts acylation of

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[43] No previous characterization of this compound could be found in the literature.

[44] H. Pines and A. Shaw, *J. Org. Chem.*, **20**, 373 (1955).

[45] J. Tafel and W. Jurgens, *Ber.*, **42**, 2548 (1909).

[46] J. Tafel and F. Andre, *ibid.*, **45**, 437 (1912).

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

[48] E. Berliner and F. Berliner, THIS JOURNAL, **72**, 222 (1950).

benzene with the acid chloride; it distilled at 128.5–130° at 12.5 mm., $n^{20}\text{D}$ 1.5093. The ketone, 18.1 g., was hydrogenolyzed at 215–230° with 2 g. of copper chromite in 15 ml. of pentane and initial hydrogen pressure of 125 atm. The arene was obtained in 72% yield and a heart-cut had the following physical constants: b.p. 216.9–217.0° at 743 mm., $n^{20}\text{D}$ 1.4853 (lit.[48] b.p. 219–219.1° at 767 mm., $n^{20}\text{D}$ 1.4853).

1,1,3-Trimethylindan (VIII).—A sample of 3,3-dimethyl-1-indanone (obtained through the courtesy of Dr. H. L. Dryden, Jr.) after redistillation, had b.p. 123–125° at 16 mm., $n^{20}\text{D}$ 1.5429 (lit.[49] b.p. 130–131° at 18 mm., $n^{14.3}\text{D}$ 1.5453). The ketone, 0.15 mole, was treated with methylmagnesium iodide prepared from 0.18 mole each of methyl iodide and magnesium in ether. The crude 1,3,3-trimethyl-1-indanol was obtained in 89% yield (23.5 g.); a heart-cut had b.p. 122.0–122.2 at 15 mm., $n^{20}\text{D}$ 1.5275 (lit.[50] b.p. 128° at 25 mm., m.p. 45°), and solidified on standing. The infrared spectrum exhibited characteristic bands at 8.54, 10.68 and 13.15 μ, with an O–H stretching band at about 2.9 μ. Attempts to purify the carbinol by recrystallization were unsuccessful, and the recovered liquid was found to have undergone dehydration. Hydrogenolysis of 14.9 g. of the carbinol with copper chromite yielded a product contaminated with an olefin which exhibited at 12.21 μ infrared band characteristic of a trisubstituted double bond.[51] Hydrogenation with palladium-on-charcoal catalyst afforded olefin-free 1,1,3-trimethylindan boiling at 203.9–204.8° at 748 mm., $n^{20}\text{D}$ 1.5082 (lit.[50] b.p. 90° at 21 mm., $n^{25}\text{D}$ 1.5059).

1,1,3,3-Tetramethylindan (IX) was synthesized by the method of Bogert and Davidson.[52] Cyclization of 12.1 g. of isomeric alkenylbenzenes[53] (b.p. 68.7–69.0° at 4 mm., $n^{20}\text{D}$ 1.5086) made by the dehydration of 2,4-dimethyl-4-phenyl-2-pentanol was carried out by treatment with 17 ml. of 85% sulfuric acid. The product was worked up in the usual manner, and after redistillation it boiled at 208.3–208.9° at 752 mm., $n^{20}\text{D}$ 1.5020 (lit.[52] b.p. 206–209°).

Identification of Products from Experiments 1–19.—The following alkylbenzenes were identified by the physical constants of purified cuts from the various reaction products and by comparison with infrared spectra of authentic samples[54]: benzene, toluene, ethylbenzene, cumene and *n*-propylbenzene. Identification of the isomeric cymenes was tentative, being based on the characteristic infrared bands in the 12–14 μ region (Table XI). The compounds followed by a question mark in Tables II–VII could not be positively identified by physical constants and infrared spectra due to the small amounts present but appeared to correspond to the appropriate monoadduct less one methyl group in most cases.

Experiments 1–5 (Toluene–Propylene).—Propylene dimer cuts from several experiments (their infrared spectra indicated the presence of $\text{RHC}{=}\text{CH}_2$ and *trans*-$\text{RHC}{=}\text{CHR}'$ components) were combined, and 6.4 g. was hydrogenated using platinum oxide catalyst. The main distillation cut was composed of *n*-hexane. The presence of a minor amount of methylcyclopentane was indicated by the presence of its infrared band at 10.25 μ (A.P.I. No. 255)[54] and the behavior of the saturates on chromatography, as the refractive indices of later cuts rose in accordance with the generalization that paraffins are less strongly adsorbed than cyclanes on silica gel.[37,38]

Cuts boiling in the propylene trimer range, after selective hydrogenation and chromatographic removal of aromatics, had $n^{20}\text{D}$ 1.4221–1.4253. The consistently higher indices of these cuts and those from subsequent propylene experiments over those of the less-highly branched C_9-alkanes indicated the presence of cyclanes.

Isobutylbenzene was isolated in a cut boiling at 172–173°, $n^{20}\text{D}$ 1.4873. Aside from weak bands due to the close-boiling cymenes present, the infrared spectrum was identical to that of an authentic sample.

n-Butylbenzene was found in a cut boiling at 185–186°, $n^{20}\text{D}$ 1.4886. Its infrared spectrum was identical to that of a chromatographed sample of authentic *n*-butylbenzene.

An unidentified heptylbenzene isomer was separated from the selectively hydrogenated cuts from expts. 2–5. Chromatography and refractionation yielded an arene boiling at 99.8° at 8 mm., $n^{20}\text{D}$ 1.4874, d^{20}_4 0.8515; *MR*D calcd. 58.63, obsd. 59.57. Its infrared spectrum exhibited a characteristic band at 13.43 μ indicative of a monoalkylbenzene with two α-hydrogens on the benzylic carbon,[55] while that of 3-methyl-1-phenylhexane (I, Table XIV) was at 13.37 μ. The difference in melting points of the 2,4-dinitrophenylhydrazones of the acetylated arenes confirmed the fact that the heptylbenzene was not I.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.88; H, 11.03.

The compound was acetylated and the following derivatives prepared:

The 2,4-dinitrophenylhydrazone, m.p. 111–111.5°. *Anal.* Calcd. for $C_{21}H_{26}N_4O_4$: N, 14.06. Found: N, 13.99.

The semicarbazone, m.p. 179–179.5°. *Anal.* Calcd. for $C_{16}H_{25}N_3O$: N, 15.26. Found: N, 15.51.

The *p*-nitrophenylhydrazone, m.p. 99.5–100.5°. *Anal.* Calcd. for $C_{21}H_{27}N_3O_2$: N, 11.89. Found: N, 11.76.

The reported[56] melting points of the semicarbazone and *p*-nitrophenylhydrazone of the product of the acetylation of *n*-heptylbenzene are 176 and 140°, respectively, excluding this as the possible structure of the unidentified arene. The compound was not further investigated.

Diarylalkane cuts from expt. 5, b.p. 110° at 8.5 mm. to 183° at 3 mm., $n^{20}\text{D}$ 1.5801–1.6261, were refractionated through a Piros–Glover column[57] but gave no distinct plateaus. The infrared spectra of the cuts indicated the possible presence of 5–6 components, consequently none of the diarylalkane cuts of subsequent reactions was investigated.

Anthracene was isolated in impure form from high boiling cuts of expt. 5. Treatment with Norit and recrystallization from ethanol gave a minute amount of light yellow crystals, m.p. 197–204°. The infrared spectrum (carbon disulfide solvent) exhibited characteristic bands identical to those of an authentic sample.

Experiments 6–8 (Toluene–Isobutylene).—Cuts were found corresponding to isobutylene trimers (b.p. 160–190°) and after selective hydrogenation and chromatography had $n^{20}\text{D}$ 1.4310–1.4312. No further investigation was made.

Neopentylbenzene was found in a cut boiling 180–187°, $n^{20}\text{D}$ 1.4771 (a small amount of saturates present lowered the index). The infrared spectrum had the characteristic bands at 8.02, 12.92 and 13.87 μ identical to those of an authentic sample (b.p. 185.6–187°, $n^{20}\text{D}$ 1.4878).

Isopentylbenzene was isolated in nearly pure state, b.p. 194.8–196.5°, $n^{20}\text{D}$ 1.4862. The infrared spectrum was identical to that of an authentic sample, b.p. 195–197°, $n^{20}\text{D}$ 1.4860.

Experiments 9–11 (Toluene–2-Methyl-2-butene).—2-Methyl-1-butene was found in a cut boiling at 28.7–32.0°, $n^{20}\text{D}$ 1.3747. The characteristic infrared bands at 6.04, 8.05 and 11.26 μ corresponded to those in an authentic sample. In this cut 3-methyl-1-butene was also detected by its strong band at 10.96 μ. The reported value for this band is 10.89 and 10.96 μ, as it is actually a doublet on finer resolution (A.P.I. No. 360).[54] Due to the volatility of this component, it was only qualitatively determined by liquid and gas phase infrared methods.

Methylbutene dimers were separated from cuts boiling at 150–159°. Aromatics and unsaturated dimers were removed by chromatography and the saturates, 2.91 g., were distilled yielding cuts boiling at 153–158°, $n^{20}\text{D}$ 1.4282–1.4322. On the basis of the infrared spectra and relatively high refractive indices of the cuts, it is possible that cyclanes as well as alkanes were present.

2,3-Dimethyl-1-phenylbutane was found in a cut boiling at 208–214°, $n^{20}\text{D}$ 1.4892. Its infrared spectrum was essentially identical to that of the synthetic sample II.

3-Methyl-1-phenylpentane was found in a cut boiling at 218.6–218.8, $n^{20}\text{D}$ 1.4881, the infrared spectrum of which was identical to that of the synthetic sample III.

Experiments 12–14 (Ethylbenzene–Propylene).—2-Methyl-3-phenylbutane was detected in a cut boiling at 192–194°, $n^{20}\text{D}$ 1.4900. The infrared spectrum exhibited the characteristic bands at 9.80, 13.25 and 13.78 μ which corresponded

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(49) K. v. Auwers, *Ber.*, **54**, 987 (1921).

(50) J. Colonge and P. Garnier, *Bull. soc. chim. France*, [5] **15**, 436 (1948).

(51) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

(52) M. T. Bogert and D. Davidson, THIS JOURNAL, **56**, 185 (1934).

(53) Synthesized by Mr. L. Schaap of this Laboratory in connection with another investigation.

(54) American Petroleum Institute Research Project 44, Catalog of Selected Infrared Absorption Spectrograms.

(55) W. J. Potts, Jr., *Anal. Chem.*, **27**, 1027 (1955).

(56) A. Zaki and H. Fahim, *J. Chem. Soc.*, 307 (1942).

(57) H. S. Martin and Co., Evanston, Ill.

to those of an authentic sample (b.p. 189–190°, $n^{20}D$ 1.4902).

2-Phenylpentane was isolated in a cut boiling at 192.4–193.3°, $n^{20}D$ 1.4893, the infrared spectrum of which was identical to that of an authentic sample (b.p. 192–192.6°, $n^{20}D$ 1.4882).

2,3-Diphenylbutane crystallized from cuts boiling at 100–110° at 1.5 mm. Recrystallization from aqueous ethanol yielded white crystals, m.p. 126–126.5° (lit.[58] m.p. 126–127°). The infrared spectrum (carbon disulfide solvent) had characteristic bands at 12.93 and 13.22 μ as reported in the literature.[55]

Experiment 15 (Ethylbenzene–Isobutylene).—Isobutylene dimers were found in a cut boiling at 95–114°, $n^{20}D$ 1.4217. Chromatographic removal of arenes and alkenes followed by distillation yielded the major product, 1,1,3-trimethylcyclopentane, b.p. 104.0–104.2°, $n^{20}D$ 1.4101 (lit.[59] b.p. 104.9°, $n^{20}D$ 1.4112). The infrared spectrum exhibited the characteristic bands of the authentic cyclane (A.P.I. 525).[54]

2-Methyl-4-phenylpentane was identified in a cut boiling at 200–205°, $n^{20}D$ 1.4869, the infrared spectrum of which was essentially identical to that of the synthetic sample IV.

Isohexylbenzene was purified by redistillation of a product cut; it boiled at 216.2–216.9°, $n^{20}D$ 1.4867. Its infrared spectrum was identical to that of the synthetic sample VII.

Experiments 16—18 (Cumene–Propylene).—Due to the low yields of monoadduct products, the cuts were combined (a small sample of each was saved for subsequent infrared analysis) into two charges for redistillation: b.p. 196–209°, 5.23 g.; b.p. 206–213°, 7.40 g. After 12 chromatographs of the resultant cuts, spectral identification was possible.

2-Methyl-2-phenylpentane was identified in cuts boiling at 207–211°. Chromatography yielded a cut having $n^{20}D$ 1.4901, which had an infrared spectrum practically identical to that of an authentic sample (b.p. 207–208°, $n^{20}D$ 1.4936), except for the presence of weak bands due to the possible presence of 2-methyl-1-phenylpentane.

2-Methyl-1-phenylpentane was indicated in product cuts, but its presence could not be positively established due to contamination by compounds of higher refractive index which were not readily separable by chromatography. A cut boiling at 213–226°, $n^{20}D$ 1.4967, had an infrared spectrum which strongly resembled that of an authentic sample (b.p. 218°, $n^{20}D$ 1.4875; synthesized by Mr. C. T. Chen) except for foreign bands at 13.14 and 13.38 μ, which may have been caused by higher boiling contaminants.

1,1,3-Trimethylindan was found in a cut boiling at 204.6–205.0°; chromatography yielded a purified fraction with $n^{20}D$ 1.5047. Except for the presence of a band in the 14.3 μ region due to minor amounts of hexylbenzene contaminants, the infrared spectrum was identical to that of the synthetic sample VIII.

1,1,2-Trimethylindan was detected in a cut boiling at 209–211°; chromatography afforded a purified fraction having $n^{20}D$ 1.5097. The infrared spectrum was identical to that of an authentic sample[53] (b.p. 211° cor. to 760 mm., $n^{20}D$ 1.5120) except for a 14.3 μ band due to the presence of a small amount of hexylbenzene impurities.

Experiment 19 (Cumene–Isobutylene).—The extremely low monoadduct yield precluded redistillation of these cuts; however, chromatography allowed the identification of two components, and the presence of certain expected compounds in the unidentified portion was excluded.

1,1,3,3-Tetramethylindan was found in a cut boiling at 187–210°; an enriched chromatographic fraction had $n^{20}D$ 1.4950. Aside from extraneous bands due to alkylbenzene contaminants, the infrared spectrum demonstrated the presence of the compound. Especially evident were the 7.54–7.60 μ doublet and the 13.18 μ main band, identical to those of the synthetic sample IX.

2,4-Dimethyl-1-phenylpentane was isolated in a cut boiling at 224.2–225.7°, which had $n^{20}D$ 1.4831 after chromatography. Except for a minor foreign band at 13.10 μ, its infrared spectrum was identical to that of a synthetic sample V.

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

(59) Selected Values of Properties of Hydrocarbons, American Petroleum Institute Research Project 44, Table 15a, October 31, 1952.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Potassium-catalyzed Reaction of Olefins with Arylalkanes[1]

BY LUKE SCHAAP[2a] AND HERMAN PINES[2b]

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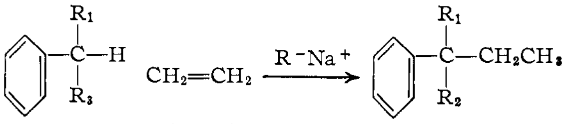
The reaction of ethylene with toluene, ethylbenzene, cumene and cyclohexylbenzene catalyzed by potassium and anthracene was studied. Besides the "normal" side chain ethylation the reaction was accompanied by a cyclization resulting in the formation of indans. The reaction of propylene with cumene resulted in the formation of 2,3-dimethyl-2-phenylbutane, 1,1,2- and 1,1,3-trimethylindan. The presence of the last compound indicates for the first time the formation of a secondary alkylcarbanion as an intermediate in the alkylation reaction. The ethylation of the aromatic nucleus of *t*-butylbenzene catalyzed by potassium takes place under the same condition as the side chain ethylation of compounds having benzylic hydrogens. The mechanism of alkylation and cyclization is discussed.

The sodium-catalyzed ethylation of arylalkanes has been shown to produce compounds in which the benzylic hydrogens of the arylalkanes are replaced by ethyl groups.[3]



R_1 or R_2 = H or alkyl

This method has proved to be useful for the synthesis of such hydrocarbons in a pure state. A carbanion mechanism has been proposed for this reaction.[3]

Benzene and arylalkanes having no benzylic hydrogens react with ethylene only under more vigorous conditions to yield products in which the aromatic ring has been ethylated.[4]

The mode of addition of arylalkanes to substituted ethylenes has been shown to be highly selective. The compounds produced are those that

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(1) Paper X of the series of Base-catalyzed Reactions. For paper IX see H. Pines and L. Schaap, THIS JOURNAL, **79**, 2956 (1957).

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(3) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77** 554 (1955).

(4) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).